# SEMI-ANNUAL REPORT

OF

# SCHIMMEL & Co.

(FRITZSCHE BROTHERS)

MILTITZ
NEAR LEIPZIG

LONDON * NEW YORK.

OCTOBER/NOVEMBER 1902.

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# Contents.

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## List of abbreviations.

d = specific gravity at 15°, unless otherwise stated.

$d_{20^\circ}$ = specific gravity at 20°.

$d\,\frac{20^\circ}{4^\circ}$ = specific gravity at 20°, compared with water at 4°.

$\alpha_D\ 15^\circ$ = optical rotation, at 15°, in a 100 mm tube.

$[\alpha]_D$ = specific rotation.

$n_D\ 15^\circ$ = index of refraction at 15°.

n = normal.

$\frac{n}{2}\left(\frac{n}{10}\right)$ = semi-normal or deci-normal (titrated solutions).

g = gramme; cc = cubic centimeter; mm = millimeter.

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Temperatures are uniformly stated in **centigrade** degrees (°).

20630

**Miltitz** near Leipzig, October/November 1902.

The depression which has spread over Germany's trade and industry after a period of industrial growth extending over several years, and which has become of such far-reaching importance for the economic life of the whole nation, still continues, and would appear to have not even yet reached its culminating point. Although here and there signs are found which seem to justify a somewhat optimistic opinion, the leading industries are still in a state of complete depression, from which they will not recover until a general improvement in the economic conditions of the German Empire has become an established fact. To attain this end, it is in the first place necessary to come to a definite settlement of the question of the Customs' Tariffs, and to conclude stable commercial treaties with foreign countries, for as long as uncertainty exists with regard to the latter, enterprise is laid in fetters which are bound to react with paralysing effect on the whole economic life.

The chemical industry of Germany could obviously not escape entirely from the evil effects of the general crisis, but thanks to its prominent position in the world's commerce, it has suffered less from the unfavourable conditions than other branches of industry. Yet the excessive increase in the number of new establishments, and the enlargement of existing works, have prejudicially affected the state of affairs, and have led to over-production of various articles, which in the present period of general decline is doubly disagreeable. The figures of the export of raw materials and manufactured articles of Germany's chemical industry are as follows:

| | | |
|---|---|---|
| 1899 | £ | 20493450 |
| 1900 | „ | 19880850 |
| 1901 | „ | 20418300 |

Like in all other industrial branches, so in ours, the offers at disproportionately low prices are more numerous than ever, and have degenerated into a veritable "struggle for life". So long as this is conducted with honest weapons, nothing can be said against it; but when it goes beyond the limits of all reason, it is all the more to be regretted, as a proper estimation of the value of the majority of our products is beset with difficulties to the purchaser, and frequently is totally impossible.

In such case it is only possible to effect a change, by continued efforts to enlighten the public on the character of the products, and all the better elements of our branch should unite, in order that the industry, which has reached such a high position, may be kept free from morbid excrescences.

The sale of our products in Germany and Austria has been normal, but business with the United Kingdom has not yet completely recovered, even after the conclusion of peace. On the other hand, a very brisk trade has been carried on with France, which country has always shown lively interest in the scientific results obtained in the domain of essential oils and modern aromatics, and which has also for years taken an active part in the work carried on in that field. In Italy, the economic conditions are progressing, and the excellent position of the exchange renders that country a much-desired market. The state of affairs in Spain is visibly improving in consequence of a favourable balance of trade. An important change is in progress in Russia, where heavy duties are about to be imposed on chemicals, in order to strengthen the chemical industry of that country, and to promote the establishment of new works. The sale of our products in the United States of America shows a considerable increase. The welfare of that country is strongly promoted by the general progress of trade and industry. In Central America, Mexico is especially prominent by a continuation of the favourable conditions of the home affairs, whilst trade with Venezuela and Colombia has been completely paralysed by the disorganised political situation.

In most of the South American countries, the conditions are also unfavourable, particularly in Brazil, where a general commercial demoralisation has developed, of such intensity as has never been seen before, which, conjointly with uncertain fluctuations in the exchange, and objectionable official regulations, threatens ruin to all commercial intercourse. The defects of the Brazilian Tariff, and the absurd requirements with regard to the customs' declarations, render trade with Brazil as troublesome as risky, for the slightest error in formalities may cause enormous losses. The consequence of this will be that independent firms will break off business transactions with Brazil.

In the Argentine Republic, trade has suffered heavy losses from numerous cases of bankruptcy. It may, however, be hoped that the favourable balance of trade of that country, in conjunction with the rich yield of the last harvest, will soon bring about an improvement in the state of affairs.

The prospects in Chile are far from favourable, as the purchasing power there has been injuriously affected by a bad harvest, and by heavy falls in the exchange.

The trade with Japan, which early in the year was very brisk, has since become rather dull, — a fact which may perhaps be due to the after-effects of the Chinese war, and the reduced purchasing power of China for Japanese products.

India and Australia sent regular orders for requirements of a normal character.

The total exports of essential oils from Germany were as follows:

| | | | | | |
|---|---|---|---|---|---|
| In | 1898, | 287 100 kilos, | value | 2 871 000 | Marks |
| „ | 1899, | 351 000 „ | „ | 3 862 000 | „ |
| „ | 1900, | 380 000 „ | „ | 4 634 000 | „ |
| „ | 1901, | 388 000 „ | „ | 4 658 000 | „ |

The total imports, on the other hand, were:

| | | | | | |
|---|---|---|---|---|---|
| In | 1899, | 416 000 kilos, | value | 5 938 000 | Marks |
| „ | 1900, | 421 000 „ | „ | 5 631 000 | „ |
| „ | 1901, | 417 000 „ | „ | 5 192 000 | „ |

The value of the export of German perfumed and toilet-soaps in 1901 again shows an increase. The latter is made up as follows:

| | kilos | | value |
|---|---|---|---|
| Soap in tablets, including scented soap . . . . . . . | 3 877 600 | Marks | 5 429 000 |
| Fatty oils, scented . . . . . | 14 600 | „ | 168 000 |
| Scents, not containing alcohol | 10 200 | „ | 10 000 |
| Liquid perfumes containing alcohol or ethers, including hair-washes, dentifrices and mouth-washes . . . . | 1 467 900 | „ | 8 073 000 |
| All other perfumes, not otherwise enumerated . . . . . | 530 400 | „ | 1 989 000 |
| Soap and perfumes, insufficiently specified . . . . . . | 2 300 | „ | 9 000 |
| Total in 1901 | kilos 5 903 000 | value Marks | 15 678 000, |
| against in 1900 | | „ | 15 048 000 |
| „ 1899 | | „ | 15 415 000 |
| „ 1898 | | „ | 12 972 000 |
| „ 1897 | | „ | 11 714 000 |
| „ 1896 | | „ | 12 549 000 |

In the spring, the values of almost all our articles were still going down, but during the last few months a decided change has come over the scene, chiefly owing to the universally abnormal weather-conditions, and at the present moment the prices of quite a number of important articles are briskly moving upwards, — a fact which has not been observed for a long time.

In the following pages we refer, as usual, in a detailed manner, not only to our own work in our laboratories, but also to all other publications which have appeared since our last Report, and it would be a matter of gratification to us if this might give a further strong impetus to the interest taken in our branch of industry.

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**Almond Oil, pressed from apricot kernels.** The prices of apricot kernels underwent a sudden change in May last, when it became known that the apricot harvest in Syria would show a great deficiency, and the movement would have acquired very considerable dimensions, if there had not been large parcels from California on the market which removed the scarcity which had arisen.

The demands of the Syrian peasants are at present still so high, that this article will have to be discarded until their quotations have somewhat fallen into line with the American values. Our prices are based upon the latter; they may without hesitation be taken advantage of to lay in large supplies.

**Almond Oil, pressed from sweet almonds.** Early in August, first quality Bari almonds reached the phenomenal price of 230 Marks; they drew all the other sorts along into the current, so much so that even the less valuable Mogador almonds advanced to an unprecedented figure. Of this sort, only 396 tons, value 531 500 Marks, were exported in 1891, against 2988 tons, value 4780 800 Marks in 1900.

Unfortunately this sort cannot be used for our purposes on account of the heavy admixture of bitter almonds. We work up only the best Bari or Sicilian fruit.

The Hamburg statistics of this important article are as follows:

| | | Imports in 1901 | | | Stocks at end of 1901 | |
|---|---|---|---|---|---|---|
| Italian | about | 3240 500 | kilos | about | 152 100 | kilos |
| Moroccan | ,, | 863 600 | ,, | ,, | 137 500 | ,, |
| French | ,, | 407 800 | ,, | ,, | 80 800 | ,, |
| Spanish | ,, | 155 900 | ,, | ,, | | |
| Persian, etc. | ,, | 28 000 | ,, | ,, | — | ,, |
| Portuguese | ,, | 16 900 | ,, | ,, | 18 400 | ,, |
| Total in 1901 | about | 4712 700 | kilos | about | 388 800 | kilos |
| against in 1900 | ,, | 4645 000 | ,, | ,, | 274 000 | ,, |
| 1899 | ,, | 4200 000 | ,, | ,, | 192 500 | ,, |
| 1898 | ,, | 4611 000 | ,, | ,, | 223 500 | ,, |

Our quotations of oil of sweet almonds, answering the requirements of the German Pharmacopœia, 4th edition, are still based on favourable purchases made before the great rise, and can therefore only be considered as firm to a limited extent.

---

**Oil of Ambrette seeds.** Advantage has been taken of the catastrophe in Martinique to raise the prices of ambrette seed, but the movement has again calmed down, and only an unimportant increase has remained. Java supplied a substitute in sufficient quantity.

At ordinary temperature, oil of ambrette seeds is solid; the body which causes the solidification is most probably palmitic acid. This fatty acid has in practice frequently proved inconvenient, and it has occurred to us to remove it from oil of ambrette seeds (analogous to orris oil), and to introduce the oil into commerce in the liquid state.

Liquid oil of ambrette seeds (which we have added to our price-lists) does not congeal at low temperature, and is about six times as strong as the ordinary oil. Its physical constants are as follows: —

Specific gravity 0,909;
Optical rotation $+ 1^\circ 10'$;
Acid number 2,4; ester number 180,5.

The oil makes a clear solution already in 5—6 volumes 80 per cent. alcohol.

Samples for further testing this new product will be supplied on application.

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**Angelica Oil.** The price of this oil is at present still high, and a reliable quality is scarce. Our angelica plantations, however, have thriven so excellently this year, that we anticipate a yield four times as large as that of last year, and that we hope again to be able to carry on the distillation of the oil under favourable conditions.

**Anise Oil.** The anise harvest in Russia is said to have suffered in some districts through continuous rainfall, but the external appearance of this year's seed is very satisfactory, and the seed is distinguished not only by purity, but also by a bright colour. On the whole the yield is reported as good, and material for distillation is available in abundance.

At the first anise market this year at Krasnoje, the supply amounted to 1390000 kilos, and was sold at from 1,40 to 1,50 roubles per pood, equal to about 14/9 per cwt. This price would mean a slight increase over that of last year.

There is an exceptionally large supply this year of Roumelian anise, which in quality far surpasses the Russian seed. If it is possible to supply this article at a corresponding price, a competitor will have arisen which should not be underrated.

The best quality anise is produced in Spain; in 1900, 864876 kilos of this were exported from that country. Alicante anise is also much esteemed; of this quality, 285897 kilos were exported in 1901.

The production of anise oil, and particularly of anethol, represents now as before one of the specialities of our firm. In our new factories, we have provided plant for this purpose which enables us to satisfy in every respect the highest requirements.

We would state here, that the idea of producing and introducing into commerce pure anethol on a large scale, has first been realised and rendered an accomplished fact by our firm, and for this reason we are fully justified in calling our anethol "the original product".

Our anethol possesses the characteristics of the greatest purity which it is possible to attain: —

Congealing point: + 21 to 22°,
Melting point: + 22,5 to 22,7°.

Although we ourselves also work up considerable quantities of Russian anise oil into anethol, it would be wholly incorrect to call this kind of anethol the best in existence, as is done in a most provoking manner by a Russian competitor. There are some kinds of anise and raw materials for anethol, which should be preferred to the Russian seed. The consumers may be quite satisfied that there is a large selection of material, for if we were exclusively dependent on the Russian production, the value of the article would undoubtedly be considerably higher.

In our April Report of this year, we already referred to the fact that an anethol is offered in commerce at a higher price, which is praised as being richer than any other anethol. We had an opportunity of testing such a product, but its physical constants as ascertained did not by any means point to special purity.

We also came in possession of a circular in Spanish, mentioning, as a criterion of the purity of anethol, a congealing point of 22 to 23°; all preparations melting at a lower temperature are declared to contain elæoptene, and to be useless for the manufacture of anisette liquor. If, in accordance with this, a selection were to be made of the various commercial anethols, not a single one would be found to possess the necessary qualification, for not one of them would show a congealing point of 22 to 23°, not even (as we have ascertained) the one produced by the firm who issued this circular!

We have always found the congealing point of freshly prepared anethol at more than 21°, up to 22°, but the melting point, on the other hand, at from 22,5° to 22,7°. Although really the melting and congealing points should lie at the same degree of temperature, the congealing point will generally be found a little lower than the melting point, as a slight delay in the occurrence of the crystallisation, or a reduction of the temperature below the solidifying point carried a little too far, must of necessity lead to errors in observation. On these grounds we may designate the condition "that anethol shall solidify at 22° to 23°", as inconclusive. We guarantee that our anethol is absolutely pure, and that it cannot be surpassed by any other make, neither in its physical constants, nor in its fine aroma and richness.

In our Report of April 1896, page 8, we discussed a work by Bouchardat and Tardy¹) on the composition of Russian anise oil. In this work, fenchone and anisic ketone were mentioned as new bodies. The presence of the former, and the fact that the oil was dextrogyre, appeared to us to prove beyond doubt that the oil was adulterated with fennel oil. For this reason we questioned the presence of fenchone and anisic ketone in anise oil.

In consequence of our indications, Tardy²) has again taken up the examination of Russian anise oil, and in this case of a material of which the purity had been guaranteed. The optical rotation was —3° 24′. This examination proved that fenchone is not present in anise oil. Our statements as to the rotatory power³) are also confirmed. The anisic ketone was again detected in this oil, and described as follows: a mobile liquid, of the boiling point 263°; $d_0 = 1,095$; melting point of the semicarbazone 182°. The odour of the ketone reminds slightly of oil of bitter almonds. It combines with sodium bisulphite, and oxidises on exposure to the air into acetic and anisic acids. The same products are formed upon oxidation with potassium permanganate. For this reason Tardy gives the ketone the formula $C_6H_4(OCH_3)CH_2COCH_3$.

The view which we expressed⁴), that anisic ketone may possibly be identic with Wallach's ethyl-anisyl ketone⁵), is refuted by the author. The ketone of Wallach, produced by Tardy for purposes of comparison, does not combine with sodium bisulphite. On the other hand, the properties of paramethoxyphenyl acetone, obtained by Béhal and Tiffeneau⁶), agree with those of anisic ketone; the oximes of both melt at 72°. Further, the ketone $C_6H_4(OCH_3)CH_2COCH_3$, obtained from anethol by Toennies⁷) has, like anisic ketone, the boiling point 264°.

A. Klages⁸) reports on syntheses of anethol and homologous unsaturated phenol ethers. According to Friedel-Crafts' method,

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1) Compt. rend. **122** (1896), 198.

2) Thèse pour l'obtention du diplôme de Docteur de l'Université de Paris, page 11 (1902).

3) Report April **1897**, 6.

4) Report April **1896**, 9.

5) Berliner Berichte **28** (1895), 2714.

6) Bull. Soc. chim. III. **25** (1901), 275.

7) Berliner Berichte **20** (1887), 2984.

8) Berliner Berichte **35** (1902), 2262.

phenol alkyl ethers were condensed, like anisol, phenetol, etc., with chlorides of fatty acids into p-alkoxy ketones; by reduction with sodium and alcohol, the corresponding secondary alcohols could be produced, which yielded with hydrochloric acid gas, at 0°, the corresponding chlorides, with carbanil solid urethanes, and upon acetylation acetates. If the latter were boiled with pyridine, intermediary pyridylium addition-products were formed, which subsequently split up into pyridine acetate and unsaturated phenol ethers.

In this manner there was obtained from anisol with propionyl chloride, the ketone $CH_3O \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot CH_3$ of the boiling point 148° at 14 mm, and from the latter the alcohol $CH_3O \cdot C_6H_4 \cdot CH(OH) \cdot CH_2 \cdot CH_3$ of the boiling point 141 to 142°, at 16 mm. The corresponding phenyl urethane melted at 74°, the acetate boiled at 156°, at 20 mm. When the latter was heated with alcoholic potassa, a strong odour of anise occurred, and after 10 hours' boiling with pyridine and dissolving in dilute acids, synthetic anethol was obtained from it, whose odour, melting point and boiling point corresponded with those of the natural compound. By the same method were produced: propenyl-para-ethoxy benzene (the name "Anaethol" selected for this body cannot be considered a very happy choice), propenyl-para-normal butoxy and isobutoxy benzene, together with the corresponding intermediary products.

**Oil of Asarum arifolium.** The leaves, and even more so the roots, of the American plant *Asarum arifolium,* contain an essential oil with a pleasant aromatic odour reminding of sassafras oil. It is obtained in a yield of from 7 to 7,5 per cent in the steam-distillation of the parts of the plant. Its chemical composition has recently been investigated by E. R. Miller[1]). According to the author the oil is colourless, heavier than water, and has a bitter taste. Under the influence of light and air it gradually acquires a reddish-yellow colour. Like sassafras oil, it dissolves with an intense red colour in concentrated sulphuric acid. Concentrated nitric acid attacks it violently, with formation of a red liquid and a resin. With bromine it reacts strongly. For three samples of the oil the author gives the following constants: Specific gravity 1,0585, 1,0609, 1,0613; optical rotation — 3°, — 2° 55′, — 3° 7′; refractive index (at 20°) 1,531875, 1,531460 and 1,531065. In most of the usual solvents the oil dissolves readily; with carbon disulphide, acetic ether, petroleum ether, and turpentine oil it forms cloudy mixtures. At 22 mm pressure it distils between 55° and 179°.

The principal constituent of the oil is safrol. The presence of this body was proved by the boiling point 230 to 231°, elementary

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[1]) Archiv d. Pharm. **240** (1902), 371.

analysis, and oxidation into $\alpha$-homopiperonylic acid of the melting point 127 to 128° and piperonylic acid of the melting point 227 to 228°. The oil also contains l-pinene, as proved by the nitrosochloride of the melting point 103°, and the latter's piperidine derivative, eugenol (benzoyl compound of the melting point 69 to 70°); a small quantity of a second phenol which produces a green colour-reaction with ferric chloride; further methyl eugenol, methyl isoeugenol, and asarone. Methyl eugenol was identified by veratric acid occurring on oxidation, and the tribromide of the melting point 78 to 79°; methyl isoeugenol by the dibromide melting at 99 to 101°. Asarone was detected in a fraction of the boiling point 165 to 179°, at 23 mm pressure, by the melting point (62 to 63°) and analysis.

**Bay Oil.** In consequence of insufficient supply of good quality leaves, genuine oil has recently been very scarce. When sounding the Hamburg market, we discovered some most peculiar qualities, concerning which we give the following particulars.

As was proved by the examination, and is shown by the analyses reproduced below, it was in every case a question of a low-grade oil which, moreover, had been adulterated. We give in the first instance the analytical results, which we have arranged in tabulated form for the purpose of greater clearness, and to which we have added for comparison the properties of a normal oil: —

| | $d_{15}$ | $\alpha_D$ | Phenols % | Solubility |
|---|---|---|---|---|
| I. | 0,8705 | — 2° 3′ | 23 | The solution in absolute alcohol, which was at first clear, becomes cloudy when more alcohol is added. |
| II. | 0,8787 | — 2° 18′ | about 24 | The solution in absolute alcohol, which was at first clear, becomes cloudy when more alcohol is added. |
| III. | 0,873 | — 2° 14′ | about 24 | |
| IV. | 0,8704 | — 2° 5′ | 20 | |
| V. | 0,8753 | — 2° 23′ | 23,5 | |
| VI. | 0,8619 | — 2° 14′ | 18 | |
| Normal Bay oil | 0,9795 | — 0° 40′ | 68 | Makes a clear solution only with 90 per cent alcohol; when much diluted, becomes cloudy. |

The low specific gravities already characterise all the oils as of inferior quality, but the small phenol-content does this still more. We have here apparently to do with adulteration with bay-oil terpenes, which are obtained in abundant quantities as by-products in the manufacture of the extra-strong oil. As is well known, the same observations have already been made previously in the case of lemon oil. But whereas here the detection of such adulteration is mostly very difficult, in bay oil these additions are readily detected, as they cause a pronounced alteration in the specific gravity and the phenol-content.

All the oils mentioned above had, however, also been adulterated with petroleum, which was discovered on the closer examination of the portions of the oil which had not been absorbed by soda liquor. By suitable, repeated treatment of these portions with concentrated sulphuric acid, and subsequent steam distillation, a bright yellow oil was finally obtained, which was proved to be petroleum, both by the odour and taste, as also by its other physical constants. This last-named adulteration consisted of perhaps about 5 per cent of the oil.

The facts here described give another striking proof of the unprecedented audacity with which the adulteration of essential oils is carried on.

**Cajeput Oil.** A consignment imported by us direct from Macassar per s. s. „Bielefeld“ comes slightly more advantageous than a previous shipment, but the heavy expenses, added to the unavoidable loss through breakage, leave but seldom a profit on Cajeput oil.

The consumption of this remedy against toothache (which antidote at one time was so much in demand), is constantly declining.

**Calamus Oil.** We have already on a previous occasion[1]) reported on some constituents of calamus oil, which Thoms and Beckstroem had detected in it. Beckstroem has investigated this matter further, and has published the results thereby obtained in a thesis[2]). The body of the melting point 168° discovered in calamus oil, which has hitherto been called calamus camphor, has now been named „calameone“ by the author, since he found in the course of his examination that this body is neither an alcohol nor a ketone, but, in view of its constitution, can be compared with cineol. Calameone is oxidised by permanganate of potassium, at ordinary temperature, into a monobasic acid $C_{15}H_{24}O_4 + H_2O$, calameonic acid, containing one molecule water of crystallisation, and melting at 153°. When heated to its melting point, this acid becomes anhydrous, and then melts at 138°. When calameone is treated with bromine, compounds are formed which have the formulæ $C_{15}H_{21}Br$, $C_{15}H_{20}Br_2$, and $C_{15}H_{18}Br_4$. With hydrochloric acid, calameone yields a product of addition melting at 119°. As already mentioned in our last Report[3]), a hydrocarbon $C_{15}H_{22}$ is formed when calameone is heated with a

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[1]) Report October **1901**, 10. Report April **1902**, 9.

[2]) R. Beckstroem, Ueber die Bestandtheile des Calmus-Oeles. Thesis, Berlin, 1902.

[3]) loc. cit.

50 per cent solution of sulphuric acid; this hydrocarbon the author has named „calamene“. When treated with bromine it yields a compound $C_{15}H_{21}Br$, and upon oxidation with potassium permanganate, an acid of the melting point 196° (in addition to acetic and oxalic acids). The compound $C_{15}H_{24}O$, which was thought to represent a uniform body, has subsequently been found to be a hydrocarbon containing asarone. With regard to the aromatic body to which calamus oil owes its specific odour, Beckstroem believes that, as it also occurs on oxidation of asarone into asarylic aldehyde, it represents an intermediate product of this oxidation-process.

**Camphor Oil.** The production of both kinds, the light and the heavy oil, has now again been freely carried on for several months.

In consequence of a change in the process of manufacture, the properties of both oils now differ somewhat from those of the previous products. The specific gravities are now lower, that of the so-called light camphor oil being about 0,900, and that of the heavy oil about 0,930. The former has a yellow, and the latter a green colour.

In addition to these two, we now also manufacture a third product, viscid and with a beautiful blue colour, which has proved very useful in painting on china, especially on smooth surfaces, and which, according to experts, is capable of replacing oil of cloves.

This oil, with a boiling temperature of about 280 to 300° C., has at 15° a specific gravity of about 0,95 to 0,96; it deflects the plane of polarised light to the right (in one case we found $+32^\circ 55'$), and appears to consist chiefly of a body of an alcoholic character, for after treatment with acetic acid anhydride, a fairly large saponification number is obtained. We have found by experiment that, in spite of its deep-blue colour, it does not stain soap; for this reason it can be employed as a fixing and binding agent for the more common soap-perfumes. Our production amounts to several thousand kilos per annum.

With regard to the camphor monopoly, we have received the following information from Kobe: —

> "It is announced officially, that the Chinese Government, at the instigation and request of the Japanese authorities, has decided to open a camphor office in Foochow, and to place the manufacture and sale of camphor under Japanese control, but not in such manner that rights of monopoly in the camphor business are conceded to the Japanese Government. It is, however, understood, that, as a set-off for its contribution towards the expenses of the monopoly, a portion of the profit on the production will be allowed to the Japanese Government. It is said that a definite arrangement on these lines has not as yet been concluded.
>
> The Japanese have, however, in any case succeeded in so far, that, when the Chinese competition ceases, they retain the power of controlling the camphor trade, and this may lead, if not to a rise in prices, at least to maintaining the values at their present level."

The report of the invention of a process for manufacturing artificial camphor has produced a panic in Japan. The „Osaka Mainichi“ newspaper published on May 15th the following article on this subject (translated from the Japanese into English): —

### A fearful rival of camphor.

> The camphor monopoly bill did not pass in the last congress, but fearing that the bill will again be brought into the next congress, the manufacturers are selling and manufacturing as much as they possibly can. This time there is a fearful rival, a great Chemical Co. in Germany having found a way to make artificial camphor out of turpentine oil, the price being 50 Yen against our camphor at 60 Yen.
>
> The German Chemical Co. has sent the specification to the Formosa Government, and the question now is whether to buy the patent, or to compete with German artificial camphor, reducing our price to 35 Yen or so. If the German process is to be adopted, the monopoly bill will not be laid before the next congress. Mr. Golós, a high official, is said to be making a trip to Europe, in order to visit the Chemical Co. and to investigate the matter.

As far as we know, artificial camphor has not yet made its appearance on the market. If its manufacture at a price which meets competition should succeed, the camphor monopoly might become completely a question of the past.

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Mr. Nakazo Sugiyama, of the Board of Health at Yokohama, has read a paper before the Japanese Pharmaceutical Society of Tokio on “The manufacture of safrol from camphor oil”, which has been published in the “Journal of the Pharmaceutical Society of Japan” No. 242, April 1902.

As this paper also contains interesting information on the production of camphor from camphor oil, and as we have succeeded in obtaining a translation of it from the original Japanese text, we reproduce below an abstract of its contents, especially as the paper would probably not find its way into the technical press on account of the difficulty of the translation.

„Distinction is made between four kinds of camphor, viz., Joko camphor, Tehuko camphor, mountain camphor, and refined camphor. Joko camphor is Tehuko camphor well dried; mountain camphor is the name given to the article which is obtained from the source of production. Refined camphor is the product manufactured in the districts of Osaka and Kobe by separation from the crude camphor oil. The camphor exported to Europe and America is chiefly mountain camphor; in addition to this, refined camphor is also exported.

Camphor oil is classified as crude oil, white oil, and red oil. The character of these oils is explained in the following: —

## Crude Camphor oil.

Crude camphor oil is made by submitting to distillation chips of camphor wood mixed with water. After removal, by mechanical means, of the camphor which crystallises out on cooling, it represents a transparent, bright-yellow to brownish-yellow, liquid oil, which has a penetrating odour. The specific gravity varies according to the origin and the age of the trees. Products from the provinces Izu and Kii, and from the older trees, generally have a higher specific gravity, whilst oils from Kiyushu, Riyu-Kiu, Zuschima and Tai-Wau, or from younger trees, show a lower specific gravity. As a rule the spec. gravity fluctuates between 0,95 and 0,995.

As far as I know, refined camphor, white camphor oil, and red camphor oil, are only separated from the crude camphor oil in the districts of Osaka and Kobe. I take this opportunity to express my best thanks to Mr. Wakichi Ono of Osaka, for having kindly placed at my disposal the accompanying report on the manufacture of camphor (Provincial Exhibition at Kochi), as also for the material for examination.

### Accompanying report (Wakichi Ono of Osaka).

The manufacture of camphor oil dates back far into past times. In my home, Tossa (province Kochi-Keu), the manufacture was commenced somewhere about the 2nd year of the Kausei; with the growing demand, camphor has become the principal product of the country. The oil oozing from the camphor tree was used by the inhabitants of the plantations for lightening purposes, — other uses of the oil have not been discovered. Since 1874 camphor oil has been sold on the market at a small profit. In January 1876 it occurred to me, as camphor oil resembles in many respects coal oil (probably paraffin oil), to improve the oil, by modifications in the manufacturing process, to such an extent, that it could be sold at the same price as coal oil.

When I accidentally discovered that a solid product separates out from camphor oil at ordinary temperature, I put 1 kiu (= 1,3 lbs.) oil in several porcelain dishes, and had these placed, after sunset, on an exposed, level surface. Next morning, before sunrise, the solid product which had separated out was removed from the oil by means of a filtering cloth; to my surprise this solid product was found to be camphor.

By the same method I then obtained 20 kiu (about 26 lbs.) camphor from 1 koku (about 40 gallons) camphor oil.

After having made this astonishing discovery, I hoped, by improvements and modifications of the apparatus, to obtain a good yield of camphor, and thus convert this hitherto useless oil into a valuable product, and even to make camphor oil a regular article of export.

Until 1878 I tested various improvements, and finally I made the following arrangement.

On the stove was placed a vessel somewhat like a tea-kettle with a capacity of about 7 scho (12,6 litres). A cooling-tub was placed alongside, with a kind of spiral tube made of copper entering the tub at the top and projecting at the bottom, which could be opened as desired by means of a valve. The tub was then filled with cold water and the kettle charged with about 4 scho (7,2 litres) oil; it was then tightly closed with a wooden cover (4 lun thick) which was provided with a cap, and the latter connected with the spiral tube. The stove was now fired, and the oil passed over into the cap and was drawn off by the spiral tube in various receptacles. In this manner 8 fractions were obtained, which were submitted to the cold of the night, as before. Of the 8 fractions, the 3rd to the 6th congealed, whilst No. 1, 2, 7 and 8 (of a blue colour) did not solidify. The camphor, which had crystallised out in the four receptacles, was filtered off through a cloth. From 1 koku (about 40 gallons) camphor oil, the yield was about 60 kiu (about 78 lbs.) pure camphor.

Of this residue of the oil, which had a pale blue colour, I recovered in this manner about 5 to and 5 scho (about 20 gallons). I expected by careful fractionating to obtain from this oil a further 30—40 kiu (39 to 52 lbs.), but notwithstanding all trouble, my expectations could not be realised.

In this manner I continued to work until October 1880. At that time I initiated interested parties from the vicinity in my process. The increased production caused a fall in the price; the distillation from the smaller kettles became irrational, and I therefore constructed in May of the following year a kettle of 2 to and 5 scho (about 40 litres) capacity, distilled from it 2 to (35 litres) oil, and divided the distillate into 10 fractions. The first and last 4 fractions yielded no congealing product, but fractions 3—8, i. e. 6 receptacles, solidified completely. In February 1882 I calculated the yield from 1 koku (about 40 gallons) oil at more than 90 kiu (= 117 lbs.).

The white portion of the residue of the oil was in great demand in the provinces on account of the similarity to coal oil. As there was no demand for the blue-coloured portion, endeavours were made to find a use for it, and it was found to be suitable as an insecticide for the trees during summer.

As in January 1883, on account of the great heat, it was feared that fires might occur, I had a partition constructed between the stove and the kettle.

In December of the same year a modification was made, by which the six kettles, which had hitherto been working for 24 hours, were increased to ten. In this way the time required for working up one koku oil, up to then 5 days, was reduced to 3 days. The oils passing over were collected in 4 fractions, of which the first was called "white oil", the second "congealing product", the third "limit oil", and the fourth "final oil".

The yield from 1 koku (40 gallons) camphor oil was now 120 kiu (156 lbs.), but this yield varied according to the character of the camphor oil.

The residue of the oil (the mixture of blue and white oils) now called "red oil", has now also become an article of export. The efforts made from 1876 up to the present day have finally been crowned with success. With the rise in the prices the production of oil increased; in my province (Tossa) the sales from the plantation-district amount to 1000 koku (about 40 000 gallons) annually, from which the yield is about 11 000 kiu (14 300 lbs.) of congealing product, and more than 400 kiu (520 lbs.) residue (red oil).

The following table shows the increase from 1878 to the present day in the proportion of camphor obtained from crude camphor oil:

| 1876 | 1878 | 1882 | 1883 | present day |
|---|---|---|---|---|
| 6,4 % | 19,2 % | 28,8 % | 38,4 % | 50—53 %. |

## White Camphor oil.

White camphor oil is obtained from the crude camphor oil by fractional distillation, after separation of the camphor; it represents a colourless-transparent, mobile essential oil, whose odour, like that of camphor, is penetrating. Specific gravity about 0,87 to 0,91. When cooled to — 20°, no separation takes place; when heated it is volatile, and boils from about 150° to 195°; it consists of pinene, phellandrene, cineol and dipentene. As it somewhat resembles turpentine oil, it is frequently used in practice instead of the latter. As this oil still contains a small quantity of camphor, it is possible to obtain a small amount of the latter by most careful distillation. The quantity of oil taken for the fractional distillation was in every case 1500 grams.

| Fraction | | 175—180° | 180—185° | 185—190° | 190—195° | 195—200° | over 200° | Loss |
|---|---|---|---|---|---|---|---|---|
| Fract. oil in % | I | 26,25 | 37,50 | 12,25 | 4,25 | 2,00 | 4,25 | 3,50 |
| | II | 37,75 | 30,50 | 13,50 | 4,50 | 3,50 | 3,75 | 6,00 |
| | III | 25,75 | 41,25 | 19,25 | 4,75 | 2,75 | 3,75 | 2,59 |
| | IV | 36,25 | 33,50 | 11,00 | 4,50 | 4,25 | 6,50 | 4,00 |
| | V | 38,25 | 32,50 | 11,00 | 6,75 | 2,00 | 5,56 | 4,00 |
| | VI | 27,50 | 44,00 | 11,25 | 5,75 | 4,00 | 5,25 | 2,25 |

The portions boiling over 200° (see table), become almost solid on cooling. 2500 grams white oil from another source gave the following results on fractional distillation: —

| Fraction | 170—175° | 175—180° | 180—185° | 185—190° | 190—195° | over 195° | Loss |
|---|---|---|---|---|---|---|---|
| Fract. oil in % | 16,50 | 40,67 | 19,50 | 8,83 | 3,83 | 8,00 | 2,67 |
| | 5,50 | 46,50 | 18,67 | 7,00 | 3,50 | 7,50 | 11,33 |

After these eight fractional distillations of white camphor oil, it still contains from 3,75 to 8 per cent camphor which, from an economical point of view, would appear to demand extracting by means of improved apparatus.

## Red Camphor oil.

Red camphor oil is obtained from the crude camphor oil by means of fractional distillation, after white camphor oil and then camphor have been removed The portions boiling higher than camphor and white oil are collected; they represent a transparent, brown to dark-brown, mobile oil, which is volatile, and has a faint penetrating odour like camphor. Specific gravity about 1 to 1,035. It boils at 225° to 270°, and consists principally of safrol; it also contains eugenol, and further a very small quantity of camphor.

## Method of producing safrol.

In order to obtain safrol from red camphor oil, it is submitted to fractional distillation, and the portions in the neighbourhood of the boiling point of safrol, which have high specific gravities, are collected. Their temperature is then considerably reduced, until rhombic transparent crystals separate out, which in a strongly cooled room are collected on a filter for the purpose of separating them from the mother liquor.

These safrol crystals are liquefied in shallow dishes by means of heat, and re-crystallised in the cold; this is repeated several times.

The crude camphor oil used for my experiment had the specific gravity, at 15° C, of 1,0165; of 100 parts oil, 4,08 parts distilled over up to 225°; 22,53 parts between 225° and 230°, 23,72 parts between 230° and 235°, and 14,83 parts between 235° and 240°.

The fractions 225° to 230°, 230° to 235°, and 235° to 240°, were placed in three different dishes, cooled with ice, and then placed in a freezing mixture. When the crystals separate out, they are filtered off in a cold room and repeatedly re-crystallised. 11250 cc red camphor oil yielded 2340,1 grams (about 21 per cent). The examination gave the following results: —

Colourless, rhombic crystals, or a colourless transparent liquid, specific gravity 1,107° at 15° C. Boils at 230° to 235°; when cooled to — 20°, white aggregates of crystals are formed which do not yet melt at + 12°. Dissolves very readily in 2 to 5 drops alcohol, chloroform or ethyl ether. In sulphuric acid it dissolves with a violet-red, in nitric acid with a deep red colour.

The results of the examinations of safrol preparations made by me up to the present, are as follows: —

| Nature | Colour | Spec. grav. | Fraction boiling betwen 230—235° in % | Congealing point | Melting point |
|---|---|---|---|---|---|
| Imported product | almost colourless | 1,0985 (28°) | 89,00 | — | — |
| " " | " " | 1,1040 (15°) | 87,14 | — | — |
| Camphor monopoly | " " | 1,1050 (15°) | 95,00 | — 20° | + 10° |
| " " | colourless | 1,1048 (15°) | — | — | — |
| Schimmel & Co. | " | 1,1065 (15°) | 96,80 | —20° | had not yet melted at + 12° |
| Prepared by myself | " | 1,1060 (15°) | 96,20 | — | |
| " " " | " | 1,1070 (15°) | — | — | |

For these examinations I had only 10 grams of No. I and II at my disposal, which was not sufficient for a more detailed test.

According to Schimmel & Co.'s Report, safrol is a colourless to faint-yellowish liquid, having the specific gravity 1,108 (15°); boiling point 233°, at 760 mm. When cooled, it solidifies into a crystalline mass, which does not yet melt at a temperature of + 11°. My examinations confirm these statements."

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Little is as yet known of the constituents of camphor oil which are soluble in alkalies. During the distillation process, aldehydes and acids collect in the aqueous first fraction, which, however, it has not yet been possible to identify further. In the higher boiling fractions eugenol[1]) is present in a comparatively small quantity.

When the high-boiling acid portions were further worked up, carvacrol was subsequently isolated, in addition to eugenol. It showed the boiling point 86 to 88° (2 mm) and was identified by the odour, as also by the phenyl urethane melting at 136°. It would appear that the crude fraction of the boiling point 94 to 99° (3 mm) contains further a second phenol, in addition to carvacrol, as moreover a urethane was obtained which melted between 85 and 95°.

Of the portions soluble in alkalies, about 3 per cent can be dissolved in dilute soda solution; they consisted of a mixture of aliphatic acids among which caprylic acid predominated. It was identified by its congealing point, + 15° C., and its boiling point, 113 to 114° (4 mm), as also by the calcium and silver salts, which gave the following analytical figures:

### Calcium salt.

0,3111 g of the air-dry substance yielded, at 110°, 0,0150 g $H_2O$, and left behind after heating 0,0516 g $CaO$.

0,5827 g treated likewise, yielded 0,0288 g $H_2O$ and 0,0956 g $CaO$.

| | Found: | | Calculated for |
|---|---|---|---|
| | I | II | $(C_8H_{15}O_2)_2Ca + H_2O$: |
| $H_2O$ | 4,82 | 4,94 | 5,23 per cent |
| Ca | 11,85 | 11,72 | 11,63 ,, ,, |

### Silver salt.

0,3160 g after heating yielded 0,1364 g Ag.
0,3155 g ,, ,, ,, 0,1365 g ,,

| | Found: | | Calculated for |
|---|---|---|---|
| | I | II | $C_8H_{15}O_2Ag$: |
| Ag | 43,16 | 43,26 | 43,03 per cent. |

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[1]) Bericht April 1886, 5.

By means of its readily-soluble calcium salt, a liquid acid of the boiling point 114 to 115° (4 mm) could be separated from the crude acids, of which the silver salt on analysis gave the following values:

0,2802 g yielded 0,4206 g $CO_2$, 0,1486 g $H_2O$ and 0,1152 g Ag;
0,2544 g „ 0,3810 g $CO_2$, 0,1342 g $H_2O$ „ 0,1045 g Ag.

0,2571 g after heating yielded 0,1052 g Ag,
0,2221 g „ „ „ 0,0911 g Ag,
0,2399 g „ „ „ 0,0980 g Ag.

| | Found: | | | | | Calculated for |
|---|---|---|---|---|---|---|
| | I | II | III | IV | V | $C_9H_{15}O_2Ag$: |
| C | 40,94 | 40,85 | — | — | — | 41,06 per cent |
| H | 5,89 | 5,86 | — | — | — | 5,70 „ „ |
| Ag | 41,11 | 41,08 | 40,92 | 41,10 | 40,86 | 41,06 „ „ |

It is, therefore, a question of an acid $C_9H_{16}O_2$, presumably belonging to the oleic acid series.

In view of the great importance of the camphor production, it would probably not be lacking in interest to obtain some light on the formation of this body in the camphor tree. A work which refers to this matter, and which deals with the history of the development of the organs (in the first place the wood, and secondly the leaves) which come especially under consideration in the production of camphor, has been supplied by A. Tschirch and Homi Shirasawa[1]). The researches in this case were made partly with the living, and partly with dead material. According to this examination, camphor is the product of conversion of an essential oil which is formed in special oil cells. These oil cells are present in every part of the tree; they are formed already in the early stages during the development of the organs, but at first do not contain any essential oil. The latter is, on the contrary, only formed gradually, and then has a yellow colour which it retains for a considerable time. Subsequently, and that in many cases only years after the formation of the secretion, the yellow oil becomes colourless; it is then much more volatile than in the first stage. It has now also acquired the property of crystallising; consequently, it often happens that irregular bright masses of crystals which consist of camphor are separated out in the cells. The very volatile, colourless oil, formed in the oil cells, now clearly penetrates the entire body of the wood, and its vapour therefore enters also into the cavities and fissures. Here the conditions are particularly favourable for crystallisation, and it follows that an abundant separation of crystals

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[1]) Archiv d. Pharm. **240** (1902), 257.

of camphor is found chiefly in the fissures of the wood. Such separation has not, however, taken place at that particular spot, but, on the contrary, the crystals occur there at a secondary stage, for the formation of the camphor itself only takes place in the oil cells.

The number of oil cells depends on climatic conditions and on the site; specimens of the camphor tree reared in the hothouse of the botanical garden at Berne contained, for example, considerably fewer oil cells than those which originated from Java. This was specially striking in the leaf-stalks which in the camphor tree, like in the other lauraceæ, are the organs richest in oil.

**Oil of Camphorosma Monspeliaca.** Of real botanical interest is a study by Cassan[1]) on *Camphorosma Monspeliaca* (a member of N. O. Chenopodiaceæ), a shrub found in the South of France, and known for its alleged camphor-like odour. The essential oil was obtained from the plant by steam distillation and ether extraction in a yield of about 0,2 per cent; it showed the following properties: colour greenish-yellow, odour suggesting bitter almonds, specific gravity at $17^\circ C = 0{,}970$, index of refraction $n_D\ 15^\circ = 1{,}3724$; the rotation could not be determined owing to the dark colour. The oil congealed at $+4^\circ$. A series of colour-reactions made with the oil gave no clue as to its constituents. It differed from the oil of the closely-related *Chenopodium anthelminticum* (which has the same specific gravity), by its pleasant odour. When distilled with aqueous potash liquor, the plant yielded a volatile base, which on examination of the platinum salt and the picrate was recognised as propylamine.

**Cananga Oil.** The over-production of this oil appears to continue, for great efforts are made to stimulate the demand. In purchasing crude cananga oil, it is advisable to use care, as large parcels have now been lying for several years in Holland and at Antwerp, of which the quality may possibly be deteriorating. Cananga oil does not keep very well, and for this reason over-production should be avoided.

**Caraway Oil.** According to reports from our buying agents, the area under cultivation with caraway in Holland is this year about one fourth smaller than in 1901. It is made up as follows:

| | | | |
|---|---|---|---|
| in North Holland . . . . . . | about | 3000 | acres |
| „ Zeeland . . . . . . . . . . . | „ | 1750 | „ |
| „ Brabant . . . . . . . . . . . | „ | 1750 | „ |
| „ South Holland . . . . . . | „ | 125 | „ |
| „ Friesland and Groningen | „ | 375 | „ |
| | Total about | 7000 | acres. |

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[1]) Etude sur le *Camphorosma Monspeliaca.* Thesis, Montpellier 1901.

The bad condition of the plants rendered it necessary in the spring to plough up several fields. The cold weather prevailing during the flowering season impaired the development, and when in addition to this the harvest time was characterised by uninterrupted rainfall, much damage was done to the quality of the seed. The average crop is estimated at barely 8 bales per acre, and the total yield for the whole of Holland in round figures at 50000 bales, whilst the quality is medium throughout. The stocks remaining from previous years are difficult to estimate, but they must be fairly heavy. Prices are low, and may harden if the trade becomes a little more brisk.

Offers have already come in from Norway, but shipments from that country do not as a rule commence before November.

In East-Prussia, the crop appears to be insignificant.

We have been able to obtain some consignments of German caraway at favourable prices. These lots were found to be exceptionally fine, with a comparatively high oil-content, which proved that with suitable cultivation, seed of intrinsic value can also be obtained in Germany.

The quotations of caraway oil and carvol may probably remain low this season. We supply carvene in quantities at a very moderate price.

**Cassia Oil, Chinese.** Since the date of our last Report, the prices in China have advanced about 15 to 20 per cent, in consequence of heavy purchases made to fill contracts. High-grade oils are remaining scarce and in an upward tendency. The cause of this remarkable depression remains hidden, and it can only be assumed that here also it is a question of over-production.

With regard to the qualities delivered of the various kinds, nothing new can be said. Slight differences between statements and facts are often noticeable, but on the whole the high-grade oils, as far as our importations are concerned, were of faultless composition. The bulk of the production consists of the medium qualities with an aldehyde-content between 65 and 75 per cent, whilst oils of 80 to 85 per cent represent about one fourth part of the exported quantity. According to the most recent reports, there was an absolute lack at Hongkong of the cheaper sorts, of 50 to 60 and 60 to 65 per cent.

The figures of the exports of cassia and star-anise oils from China show a considerable drop. The shipments from Canton were: —

From 1st January to end of July 1902
to the United Kingdom 291 piculs, against 665 piculs in 1901,
„ „ Continent 753 „ „ 907 „ „ 1901.

The exports during the same period in 1900 were
to the United Kingdom . . . . 1040 piculs,
„ „ Continent . . . . . . . . . 1176 „

that is to say, more than double the quantity of 1902.

**Cassia Oil "Schimmel & Co.".** Under the depressed market-conditions our beautiful artificial product is unable to compete direct with the natural oil, as the cost of production cannot be reduced beyond a certain limit. It remains a special article, for which clients have been found who use it on account of its superior qualities, principally as a substitute for Ceylon cinnamon oil, and for the sake of its bright colour, which is of importance for various preparations.

**Cedarwood Oil from the Atlas cedar.** The new distillate (described in detail in our April Report), which is now manufactured on a large scale and introduced into commerce under the name „Libanol Boisse" by the manufacturer, the chemist Paul Boisse, has excited lively interest, and appears to be called to play an important part in medicine. The demand is very brisk.

Mr. Boisse has recently sent us various directions for the use of this oil, which we publish here without any guarantee on our part.

1. In capsules.

0,25 g libanol.

2. Cod liver oil with libanol.

| | |
|---|---|
| Libanol | 40 to 50 g |
| Cod liver oil | up to 1 l. |

Libanol has the property of completely covering the taste of cod-liver oil, and rendering it more digestible.

3. Ointment for burns and scalds.

| | |
|---|---|
| Libanol | 1 g |
| Vaseline | 4 g. |

4. Libanol beverage.

| | |
|---|---|
| Libanol | 2 to 3 g |
| Emulsion of almonds | 150 g. |

5. Libanol beverage.

| | |
|---|---|
| Libanol | 2 to 3 g |
| Syrup of orange flowers | 30 g |
| Milk | 120 g. |

6. Inhalation.

| | |
|---|---|
| Formol 40 % | aa. |
| Libanol | |

7. Injection in urethritis.

| | |
|---|---|
| Libanol | 1 g |
| Sterilised vaseline oil | 4 g. |

8. Embrocation for rheumatism.

Libanol q. s. (as methyl salicylate).

9. Embrocation for rheumatism.

| | |
|---|---|
| Libanol | 30 g |
| Eucalyptus oil (glob.) | 20 g |
| Turpentine oil | 20 g |
| Alcohol | 30 g. |

10. As a gargle.

| | |
|---|---|
| Libanol | 1 g |
| Vaseline oil | 9 g. |

11. Ointment for skin diseases.

| | |
|---|---|
| Libanol | 4 g |
| Vaseline | 30 g. |

The prescriptions Nr. 3 and 10 can also be used, applied on pads of cotton wool, for the treatment of metritis.

We have undertaken the sole rights of sale of "Libanol Boisse" for Germany, Austria-Hungary, Russia, the United Kingdom, the United States of America, Italy, Spain, Sweden and Norway. Mr. Boisse states that his factory is now arranged in such manner, that several thousand kilos can conveniently be produced, and that there is now no longer any fear of an interruption in the supply, such as unfortunately occurred a few months ago.

According to a note in the "Chemist and Druggist"[1], the essential oil of the Atlas cedar has been further examined by P. Boisse. The most important result of his examination is that the oil contains about 16 per cent of a sesquiterpenic alcohol, which agrees very well with the statement (16,6 %) made by us on a previous occasion[2].

**Oil of Cherry Laurel.** The manufacturers have lately shown themselves very accommodating, and are thereby enabled to dispose of a large part of the accumulated stocks. On the whole, the consumption of this oil, which used to be so much in demand, has considerably decreased. We supply the oil also free from hydrocyanic acid.

**Cinnamon Oil, Ceylon.** According to information from the German Consulate at Colombo, Germany is now unquestionably the largest market for cinnamon, having outstripped the United Kingdom for the first time. The production has practically remained the same, but Germany's share as a consumer has grown from year to year.

The total exports were

| | | |
|---|---|---|
| Cinnamon quills | 2764851 | lbs. |
| „ chips | 1521149 | „ |

The shipments to the various countries were made up as follows:

| | Cinnamon quills | | Cinnamon chips | |
|---|---|---|---|---|
| Germany . . . . . . . . . . . . | 869932 | lbs. | 619941 | lbs. |
| United Kingdom . . . . . . . . | 812280 | „ | 238658 | „ |
| America . . . . . . . . . . . . . | 358300 | „ | 27837 | „ |
| Spain . . . . . . . . . . . . . . | 310162 | „ | 86500 | „ |
| Italy . . . . . . . . . . . . . . . | 178700 | „ | 153104 | „ |
| Belgium (partly for Germany) | 109200 | „ | 179855 | „ |

The value of fine cinnamon chips for oil distillation is slightly lower. Our quotations for the finest, heavy, sweet cinnamon oil have been correspondingly reduced.

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[1] Vol. **61** (1902), 236.

[2] Report April **1901**, 59.

**Oil of Cinnamon Leaves.** The oil has already frequently been the subject of chemical examinations. Up to now, eugenol[1]), cinnamic aldehyde[2]), safrol, benzaldehyde, and benzoic acid[3]) have been found in it. It differs from the oil of cinnamon bark (Ceylon cinnamon oil) by its high content of eugenol (70 to 90 per cent) and its exceptionally low content of cinnamic aldehyde (0,1 per cent).

In connection with our examination of Ceylon cinnamon oil, we have also occupied ourselves, but not thoroughly, with the oil of cinnamon leaves. The oil worked up by us had the following constants: Specific gravity 1,0479; optical rotation — 0° 10′; saponification number 40,2. 10 kilos of the oil were shaken with soda liquor (about 2 per cent) in order to remove the bulk of the eugenol. The dried oil (1,4 kilo) which now only contained a small quantity of eugenol, was next distilled in vacuo. It passed over between 34° (25 mm pressure) and 110° (12 mm). The portions boiling up to 71°, at 9 mm pressure, are probably chiefly terpenes and benzaldehyde. The next fractions, boiling up to 90°, were lævogyre, had a linalol-like odour, and yielded citral on oxidation with chromic acid mixture. The citral purified with the bisulphite compound distilled at 227 to 232°, and when heated with pyruvic acid and $\beta$-naphthylamine, yielded citryl-$\beta$-naphthocinchoninic acid of the melting point 198°. This proves the presence of linalol also in oil of cinnamon leaves. At a higher temperature than the fractions containing linalol, considerable quantities of safrol passed over. The oil did not appear to contain cinnamic aldehyde, — or if at all, only in infinitesimal quantity.

**Citronella Oil, Ceylon.** Although the exporters in Ceylon consistently declare that the value of this article cannot go down any further, the fact that within the last few months the quotations have again grown weaker throws a peculiar light on the reliability of such statements. But like everything on this earth has a limit, so it may, humanly speaking, be assumed, that citronella oil has now also reached its lowest quotation; and we would recommend ample cover if only for this reason, that at the present value, which is equally unremunerative for producers and traders, the manufacture might at last be restricted. In such a case, the interested parties would no doubt take full advantage of the existing conditions. We ourselves have purchased large parcels at the present prices, and we pay special attention to this article, as we also use large quantities for the manufacture of geraniol by our patent process (German patent No. 76435).

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[1]) Stenhouse, Liebigs Annalen **95** (1855), 103.

[2]) Report April **1892**, 45, and October **1892**, 47.

[3]) J. Weber, Archiv d. Pharm. **230** (1892), 232.

The following statistics bear out our favourable opinion: —

Average quotations of citronella oil.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| on | 1st | October | 1887, | in bond, | delivered Hamburg, | 3,90 | Marks per kilo |
| „ | 1st | „ | 1888 | „ „ | „ „ | 2,90 | „ „ „ |
| „ | 1st | „ | 1889 | „ „ | „ „ | 2,60 | „ „ „ |
| „ | 1st | „ | 1890 | „ „ | „ „ | 2,90 | „ „ „ |
| „ | 1st | „ | 1891 | „ „ | „ „ | 2,30 | „ „ „ |
| „ | 1st | „ | 1892 | „ „ | „ „ | 2,20 | „ „ „ |
| „ | 1st | „ | 1893 | „ „ | „ „ | 2,70 | „ „ „ |
| „ | 1st | „ | 1894 | „ „ | „ „ | 2,30 | „ „ „ |
| „ | 1st | „ | 1895 | „ „ | „ „ | 3,20 | „ „ „ |
| „ | 1st | „ | 1896 | „ „ | „ „ | 2,70 | „ „ „ |
| „ | 1st | „ | 1897 | „ „ | „ „ | 2,40 | „ „ „ |
| „ | 1st | „ | 1898 | „ „ | „ „ | 2,50 | „ „ „ |
| „ | 1st | „ | 1899 | „ „ | „ „ | 2,30 | „ „ „ |
| „ | 1st | „ | 1900 | „ „ | „ „ | 2,10 | „ „ „ |
| „ | 1st | „ | 1901 | „ „ | „ „ | 2,10 | „ „ „ |
| „ | 1st | „ | 1902 | „ „ | „ „ | 1,80 | „ „ „ |

The exports of citronella oil from Ceylon were as follows: —

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | from | 1st | Jan. | 1902 | to | 11th | August | 1902, | 756680 lbs. |
| against, | „ | 1st | „ | 1901 | „ | 11th | „ | 1901, | 730721 „ |
| | „ | 1st | „ | 1900 | „ | 11th | „ | 1900, | 880922 „ |
| | „ | 1st | „ | 1899 | „ | 11th | „ | 1899, | 773721 „ |

The fact that superior qualities of essential oils are fully appreciated in perfumery and in the manufacture of soaps, is confirmed by Java citronella oil, of which the consumption has recently grown enormously. The factory, of which we presented a picture to our readers in our last Report, has proved thoroughly reliable and capable of meeting the demand, and has been able to satisfy promptly the increased requirements.

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**Clove Oil.** The report issued by the Hamburg Chamber of Commerce says with reference to this important spice: —

> The imports were considerably smaller than in the previous year, and amounted to
>
> | | | | | | |
> |---|---|---|---|---|---|
> | | about | 19300 | bales | | |
> | against | „ | 27000 | „ | in | 1900, |
> | „ | „ | 24500 | „ | „ | 1899, |
> | „ | „ | 13000 | „ | „ | 1898. |
>
> In spite of the small stocks carried forward from the previous season, a complete lack of interest was shown during the first and in fact the greater part of last year, and the values could not until the last few months again reach the level of the quotations at which the year opened.

In the first months, the Dutch market caused some animation in the article, but this was only of short duration; the values which had been driven from 40,50 Marks per 50 kilos to 42 Marks, again fell to the old level, in consequence of indirect and increased supplies. Only towards the middle of the year a little more life was noticeable, as at that time the offers from Holland were below the prices quoted for direct delivery. In order to meet the demand, about 1800 bales were sold from Holland to this country at a price of from 38 to 35 Marks delivered cif. But in the following months the market became more and more favourable for the purchaser, and in October the value here had declined to 35 Marks.

Reports on the new harvest are not very satisfactory, as information from Zanzibar mentions but a small yield. In spite of this, there is little disposition towards speculative enterprise, as the reports are still accepted with all reserve. If the statements come true, there would be no prospects of low prices for some considerable time to come. Owing to these circumstances the prices have during the last two months advanced 15 per cent, and the market closes with a quotation of 40,50 Marks per 50 kilos, with much reduced stocks. Amboina cloves were only imported indirectly, and fetched better prices in the last half-year. The values improved from 60 to 65 Marks per 50 kilos.

Stock of Zanzibar and Amboina cloves: —

about 1600 bales
against ,, 3400 ,, in 1900,
,, ,, 6100 ,, ,, 1899,
,, ,, 4400 ,, ,, 1898.

The imports of clove-stems were: —

about 416000 kilos
against ,, 730500 ,, in 1900,
,, ,, 933000 ,, ,, 1899,
,, ,, 342000 ,, ,, 1898.

The value of this article usually depends upon the mother-spice, the clove. The depressed quotations recovered slightly during the course of the year, as the offers from Zanzibar were always readily accepted by the manufacturers. The value at the end of the year was quoted at 14 Marks per 50 kilos, with very small stocks.

According to Dutch statistics, the stocks of Zanzibar cloves were as follows: —

| on 1st September | 1902 | 1901 | 1900 | 1899 | 1898 | |
|---|---|---|---|---|---|---|
| in Holland | 51456 | 62960 | 74842 | 79373 | | |
| ,, London | 16034 | 16310 | 21557 | 33516 | 62617 | |
| ,, New York | 11000 | 13900 | 14700 | 10700 | 30232 | |
| | 78490 | 93170 | 111099 | 129589 | | bales. |

In consequence of the animating effect of these statistics, and the lack of confidence in the results of the harvest, the prices of cloves have recently advanced a little, and it is not impossible that they will remain at the present level, but a calmer view will be taken of the situation if the fact is taken into consideration, that the total stock of about 80000 bales represents a quantity of about 5000 tons, that is to say, a six months' supply, and that this does not include the stocks at Bombay, the most important clove market of the world.

## To Oil of cloves.

| No. | Name and origin | Spec. Grav. 15° | Opt. rotation | Index of refraction 20° | Phenol-content (determined with a 5 % sol. of *Na O H*) | Solubility | Remarks |
|---|---|---|---|---|---|---|---|
| 1. | Ol. caryoph. ang. | 1,066 | — 0° 36′ | 1,53477 | 98,75 % | Soluble in 2,5 to 3 vol. & more 60 % alcohol | |
| 2. | Ol. caryoph. ang. | 1,052 | — 0° 40′ | 1,53262 | 92 % | „ „ 1 to 1,5 „ „ „ 70 % „ | |
| 3. | Ol. caryoph. arom. opt. | 1,0525 | — 0° 36′ | 1,53287 | 90,5 % | „ „ 1 to 1,5 „ „ „ 70 % „ | |
| 4. | Ol. caryoph. arom. | 1,0287 | — 1° 12′ | 1,52766 | 74,5 % | „ „ 0,5 „ „ „ 70 % „ | Inferior quality |
| 5. | Ol. caryoph. arom. opt. | 1,0523 | — 0° 31′ | 1,53295 | 91,5 % | „ „ 1 to 1,5 „ „ „ 70 % „ | |
| 6. | Ol. caryoph. arom. | 1,0291 | — 1° 16′ | 1,52775 | 73 % | „ „ 0,5 „ „ „ 80 % „ | „ |
| 7. | Oil of cloves B. P. | 1,0501 | — 0° 40′ | 1,53146 | 88,2 % | „ „ 1 to 1,5 „ „ „ 70 % „ | |
| 8. | Ol. caryoph. opt. | 1,048 | — 0° 12′ | 1,53138 | 87,5 % | „ „ 1 to 1,5 „ „ „ 70 % „ | |
| 9. | Ol. caryoph. 2. quality | 1,0337 | — 1° 39′ | 1,52733 | 77 % | „ „ 0,5 „ „ „ 80 % „ | „ |
| 10. | Oil of cloves, Zanzibar | 1,0444 | — 0° 48′ | 1,53020 | 84,5 % | Soluble in 1 to 1,5 vol. 70 % alcohol; with more than 5 vol. cloudiness, which is only very slight with 10 vol. Soluble in 0,5 vol. and more 80 % alcohol | „ |
| 11. | Oil of cloves, stems | 1,0202 | — 1° 36′ | 1,52381 | 80 % | Soluble in 0,5 vol. 80 % alcohol; with more than 2 vol. cloudiness, which has again disappeared with about 9 vol. | „ |

When the English market of clove oil was recently sounded, the examination of eleven oils from nine different sources gave the results enumerated in the table on page 30.

These samples are kept in safe custody by us.

It will be seen from this table that the article is in no better condition in England than anywhere else, and that only experts can estimate offers of clove oil at their correct value. It is here of course also a case of the cheapest oils being the worst.

**Coffee Oil.** E. Erdmann[1]) communicates an examination of the composition of the essential oil present in roasted coffee beans. The author obtained, by distilling 150 kilos ground coffee beans with steam under pressure, and extracting the distillate with ether, a yield of 83,5 g, equal to 0,0557 per cent, of a brown oil with a strong odour of coffee, which had the specific gravity 1,0844 at 16°. The oil boiled at ordinary pressure between 150 to 230°, with decomposition. The chemical examination of the oil showed, that, apart from traces of acetic acid, it consists up to 42 per cent of valeric acid (methyl ethyl acetic acid). After removing the acids with soda liquor, the bulk of the residue of the coffee oil distilled over at 169 to 171°. This fraction was found to be furfur alcohol with a small quantity of furfurol. From the higher boiling portions, from which the phenols had been removed, a small quantity, 0,89 g, of an oil could be isolated, which possessed the coffee odour in a high degree. This oil distilled at 13 mm at 93°, and contained 9,71 per cent nitrogen. The fraction containing the characteristic aromatic substance of roasted coffee will be the subject of a special examination. The author was still able to prove that this body is very sensitive towards mineral acids, and with the latter, as products of decomposition, forms substances with a pyridine-like odour.

In connection with this examination some data are given on the properties of furfur alcohol. For the detection of this alcohol, its diphenyl carbamic acid ester is recommended, which is formed from the alcohol by heating it with diphenyl urea chloride and pyridine. The ester forms needles of a faint yellow colour, of the melting point 98°. The pharmacological examination of furfur alcohol showed, that it must be considered a poison, which in men, in doses of 0,6 to 1 g, causes respiratory frequency, and in rabbits, in doses of 0,5 to 0,6 g per kilo weight of the animal, has a fatal effect in consequence of paralysis of the respiratory organs.

**Oil from Manila Copal.** Tschirch and Koch[2]) have added the essential oil of Manila copal to the number of oils examined by

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[1]) Berliner Berichte **35** (1902), 1846.

[2]) Archiv d. Pharm. **240** (1902), 202.

them. The oil obtained from the soft and hard resin by steam distillation represented a water-white, mobile liquid with a pleasant odour, having the boiling point 165 to 170°, and the specific gravity 0,840 at 15° C. It could be dissolved in every proportion in absolute alcohol, ether, and chloroform. The yield from soft resin amounted to 6 per cent, from hard resin to 5 per cent.

Conjointly with Niederstadt[1]) they had previously examined the essential oil of New Zealand kauri copal. When kept for a prolonged period in a cool place, long fine crystal needles had separated out from the oil, which upon recrystallisation from dilute alcohol, showed the melting point 168°. Elementary analysis led to the formula $C_9H_{16}O_2$.

**Oil of Costus Root.** This oil, which we have not had in stock for some time, can now again be supplied in any desired quantity. Our present product, which is purified by a special process, has the well-known tallow-like odour in a much less marked degree than the previous make, — a fact to which we would call attention.

**Oil of Cryptomeria japonica.** C. Kimoto[2]) reports on the essential oil of *Cryptomeria japonica,* a tree (conifer) widely distributed in Japan. The wood owes its pleasant odour, reminding of peppermint, to an essential oil which the author obtained by steam distillation of chips of the wood. This oil contains a body $C_{30}H_{48}O$, a neutral liquid of the boiling point 264° and the specific gravity 0,935, which the author has called "sugiol", after the Japanese name of the plant. Sugiol is almost insoluble in water, but dissolves readily in alcohol, ether, and chloroform; it has the property of slowly reducing an alkaline silver solution in the dark. A crystalline acetyl or hydrazone compound of the substance does not exist.

**Elemi Oil.** In continuation of his elaborate „Untersuchungen über die Secrete" (Investigations concerning secretions), A. Tschirch, jointly with J. Koch[3]), reports on the various kinds of elemi resin. From the varieties hitherto examined, viz., Manila resin (hard and soft), Yucatan and Cameroon resins, the essential oil was produced by steam distillation; the yield was greatest (20 to 25 per cent) from soft Manila elemi, less (15 to 20 per cent) from Cameroon elemi; the two other varieties contain 7 to 10 per cent oil. The Manila oil had a bright yellow colour, and a pleasant, pronounced dill-like odour; the specific gravity was 0,955. The bulk boiled at 170 to 175°; between 175 and 210° a thick yellow oil passed over, from which,

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[1]) Thesis, Berne 1901.

[2]) Bull. Coll. Agric. (Tokio) **4**, 403; according to Chemiker-Zeitung Rep. **26** (1902), 175.

[3]) Archiv d. Pharm. **240** (1902), 293.

after being left standing for months, a small quantity of needle-like white crystals of the melting point 170° separated out. Yucatan elemi yielded an oil of the specific gravity 0,945, whose odour reminded of dill, lemon and turpentine. On distillation the bulk boiled at 175 to 180°; from the higher portions no crystals could be obtained. The oil of Cameroon elemi (spec. grav. 0,953) behaved similarly, but the odour was more unpleasant, probably in consequence of contaminations.

## Essential Oils, Sicilian and Calabrian.

The particulars for the following report have been supplied to us as usual through the courtesy of the German Consul at Messina, Mr. Eduardo Jacob. We avail ourselves with pleasure of the opportunity, to express to him in this place our sincere thanks.

As we foreshadowed in our April Report of this year, the prices of all essential oils have undergone a rise in the course of the summer, in spite of the fact that this season's harvest of bergamot and lemon oils placed at the disposal of the world's consumption a quantity of oil, such as had never been reached before.

The greater production with, naturally, low prices, has, however, led to such a strong requisition of our market by the consuming public, that the export of the first 8 months of this year already equals the total export of the year 1901 from Messina, whilst, as compared with that of the first 8 months of last year, it shows an increase of about 55 per cent, and one of nearly 28 per cent over that of the same period of 1900. This will be seen from the following table: —

| | 1902<br>kilos | 1901<br>kilos | 1900<br>kilos |
|---|---|---|---|
| January . . . . . | 132 509 | 76 642 | 97 294 |
| February . . . . | 74 056 | 65 735 | 77 294 |
| March . . . . . | 115 977 | 61 323 | 69 635 |
| April . . . . . | 83 453 | 45 244 | 62 671 |
| May . . . . . | 77 291 | 53 396 | 48 595 |
| June . . . . . | 45 059 | 48 142 | 59 429 |
| July . . . . . . | 61 247 | 35 695 | 46 034 |
| August . . . . . | 52 567 | 34 386 | 43 346 |
| | 642 159 | 420 563 | 504 298 |

**Bergamot Oil** was in April of this year quoted at an average price of 13,50 to 14 Marks, according to the ester-content; it kept at this level until the middle of May. In the second half of that month the price increased to 15 Marks, and in the first days of June it rose to 16,50 to 17 Marks, a quotation still justified by the circumstances.

The main cause of this upward movement is found in the apparently not very favourable prospects of the coming harvest; but the possibility was not excluded, that part of the badly-flowering trees might produce a second bloom, and the rising market was therefore looked upon with suspicion from many quarters. Only when the hope of a second flowering period had to be abandoned, and when it was clear that the coming harvest would give a result far behind that of the last one, the not insignificant party which had not provided cover endeavoured to secure the parcels sold in blank; this circumstance, favoured by the simultaneous intervention of local speculation, caused a mad rush upwards, which early in July brought the article within a few days to the parity of 20 Marks.

If buyers from abroad had at that price stepped in, further rises would have occurred in the course of the last two months; but as the consumers had laid in an ample supply ot bergamot oil during the last 6 months, it was possible to await events, until the excitement had calmed down again.

This has also happened, if only to a small extent, and the holders have gradually reduced their demands down to 18,50 Marks. At the same time, the stocks in hand are low, and may perhaps not exceed 3000 kilos.

The new crop will be considerably smaller than that of last year. It is not possible at this moment to give an approximately correct estimate, as the greater or smaller oil-content of the fruit is one of the main factors in the result of the quantity produced. It may, however, be stated with a fair degree of certainty, that in the majority of the producing districts, the quantity of fruit on the trees does not exceed one half of that of last year. In view of this it cannot be doubted that the prices will rise above the average of the last 8 months.

The more or less brisk demand from abroad will also have a decided effect on the course of the market.

S. Gulli[1]) has made some observations on oil of bergamot leaves. The distillation of this oil is only carried on to a limited extent; it takes place between February and April, when the trees are pruned. The yield also is only small (100 kilos leaves give only 150 grams oil), and the total annual production, according to Gulli, does not perhaps exceed 20 to 25 kilos. The pure oil has a specific gravity of about 0,870 to 0,873°, and an optical rotation of $+25°$ to $+26°$; it is soluble in an equal proportion of 90 per cent alcohol. It contains about 32 to 34 per cent ester, calculated as linalyl acetate, and, in addition to this, also methyl ester of anthranilic acid.

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[1]) The Chemist and Druggist **60** (1902), 995.

The author further states that the oil is rarely found in the pure state; the bergamot leaves are frequently distilled after turpentine oil has been added, and even more often leaves and young saplings of bitter orange are added into the still. It is also said that adulterations are extensively practised with the addition of peel essences.

The oil is, however, not only subjected to adulteration, but, according to Gulli, it is also itself used as an adulterant, chiefly for mixing with oils of petitgrain and of bitter and sweet orange flowers.

**Citron Oil.** The statements concerning the properties of citron oil published in our April Report, have led to a reply from the London Essence Company[1]), in which that firm endeavours to prove the unreliability of the figures of citron oil given by Gulli and ourselves. They also communicate the results of the examination of a citron oil obtained from us, which has given figures very different from those mentioned by us.

This we readily admit, but we would at the same time point out, that this oil obtained from us cannot possibly have been citron oil; it is clear that a mistake has been made in this case in our forwarding department, and that, led astray by the name "citron oil", lemon oil ("Citronen-Oel") has been sent off instead of citron oil ("Cedro-Oel"). But even when this possibility is admitted, the figures given for the supposed citron oil are somewhat remarkable.

S. Gulli refers to the same subject[2]) and holds out the prospect of a confirmation of his previous statements.

**Oil of lemon** has fallen in the course of April to such a low level as has not hitherto been known. If it is considered what a colossal quantity of lemon oil has been shipped abroad in the first few months of the new season, it may be imagined how large the daily deliveries must have been in Messina, in order to bring the price of the oil, in spite of the enormous export, down to the level of 1,20 lire per Sicilian pound, a level which has never been reached before.

In May and June the lemon trees were still laden with fruit, whereas usually at that time of the year the manufacturing season has long come to an end. It was an unusual sight, to see over-ripe winter lemons adorning the trees side by side with ripe spring fruit

Unfortunately it is not possible to obtain exact figures of the quantities of lemon oil produced during this season, but it may not be far off the mark to estimate the quantity produced on the island and in Southern Calabria at about 500 tons, a production which has never been known before.

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[1]) The Chemist and Druggist **61** (1902), 132.

[2]) The Chemist and Druggist **61** (1902), 248.

It is only natural that such an extraordinary decline has been the cause of exceptional losses to those who deal in this article and its by-products.

For this reason it is not surprising that the eyes of all interested parties were fixed with feverish suspense on the condition of the fresh blossoms of the lemon tree.

The first bloom commenced well, and appeared to progress satisfactorily, when a period of rainy, damp weather, interrupted for short intervals by scorching sunshine, caused great injury to the young fruit. When the second flowering period of the lemon-trees also developed under apparently unfavourable conditions, the opinion gained currency in interested quarters, that the slump might be considered past, and that the hope of higher prices was justified.

In consequence of this a certain reserve of the sellers was noticeable on the market, which followed on the heels of a strong demand from the local uncovered parties, — and in this manner the quotations increased by leaps and bounds, and had advanced in the middle of June by about 50 per cent. After reaching this point the bull-movement came to grief on the undisturbed tranquillity prevailing abroad, as the purchasers there, having only just received the large quantities of new oil, were in a position to await events for a time.

Under the circumstances the holders of lemon oil had no choice but to become gradually more accommodating, and the article consequently dropped slowly back almost to the level at which it stood before the rise, after the pressure had been increased by the favourable prospects of the new crop.

It is a fact that the coming lemon harvest will fall behind that of last year, but it may possibly come up to an average crop.

The question now is, whether the expected results of the production will suffice for the world's increasing consumption during the next season. The answer to this question might be found in this, that a continuation during the next twelve months of the prices of lemon oil at their present abnormally low level would appear hardly possible, but that large fluctuations in the quotations need not be feared, unless the bases of the present calculations are disturbed and altered by the appearance of a new and hitherto uncertain factor, i. e., by the greater or smaller oil-content of the new fruit.

The available stocks of old lemon oil at Messina may be estimated at about 40000 kilos. This year's oil of lemon is generally characterised by a low rotatory power; the average oil of the first three months of the season no doubt showed a rotatory power of 61° to 59°, but the oil of large districts was conspicuous, right from the commencement, by the low rotation of 60° to 59°. From that point the rotation diminishes with striking rapidity with the increasing ripeness of the fruit, and it reaches the lowest points when those fruits are worked up which had remained over-ripe on the trees, and also in the oil which has been pressed from the early-ripe spring fruit.

Since the beginning of April last, only oils have been produced the rotatory power of which, in the course of time, up to June, fell from 58° to 55° and even 54°; on the other hand, the citral-content of the oils increases, and the quality of the oils must be characterised as remarkably fine.

The discussion in our last Report of the work on oil of lemon by Burgess and Child, has induced the London Essence Company (in whose employ those two gentlemen are as chemists) to return to the subject[1]). Now there occurs in this communication the statement, that both citronellal and phellandrene are certainly not present in normal oils of lemon, whilst the presence of citronellol, or one of its esters, is very probable. As citronellal has been detected in lemon oil not once, but several times, and that by various observers, and as the presence of phellandrene has been observed repeatedly in our laboratories, the above statement is in the first place somewhat remarkable, the more so in face of the absence of all information as to what might have led the earlier investigators to their erroneous observations? So long, therefore, as strict proof to the contrary is not produced, or the cause of the error cannot be disclosed, — so long will citronellal and phellandrene have to be included in the constituents of lemon oil, whether the chemists of the London Essence Company have detected these bodies in the oil, or not.

Furthermore, exception is taken to our statement that, according to Burgess and Child, octyl and nonyl aldehydes have a pronounced influence on the production of the aroma of lemon oil. The fact that we refrained from literally quoting the statements by Burgess and Child, makes it already evident that we only wished to lay stress on the presence of these two aldehydes in lemon oil, but we did not in the least wish to assert that they have a special influence on the strength or fineness of the aroma of lemon oil. That the alcohols and esters also are not without importance for the aromatic effect, is a matter which we do not by any means desire to deny.

With regard to the citral-content, we see no reason why we should alter the opinion expressed by us, that, according to Burgess and Child, lemon oil contains 4 to 7 per cent citral. It is fairly probable that a somewhat smaller proportion will be found by a modified process, than if the determination were made with lemon oil itself; for the rest, the determination of the "citral"-content in

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[1]) The Chemist and Druggist **60** (1902), 812.

lemon oil suffers from this disadvantage, that it not only indicates the quantity of the citral actually present, but also that of the other bodies of an aldehyde- or ketone-like character, which, in addition to citral, are present in lemon oil. For this reason, this determination has only a relative value.

What we mentioned with regard to the index of refraction is no doubt due to a misunderstanding; we connected this statement with lemon oil itself, but not with fractionated oil. We therefore wish to correct the remarks in our April Report in so far, that we add, "that the individual fractions of lemon oil show an increasing index of refraction, and that, according to Burgess and Child, this increase can be utilised for the purpose of detecting possible additions to lemon oil". We have searched in vain in Burgess and Child's work for the statement (which is made in the rejoinder), that the refractive index of normal oil of lemon fluctuates between 1,4750 and 1,4760; the values for pure oil mentioned in table 2 of the original do not all agree with this.

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Since the publication of our April Report, while continuing our work in connection with the detection of pinene, we have only had an opportunity of examining two oils, obtained from a reliable source, which had been pressed specially for the purposes of our examination. One of these ($d_{15^\circ}$ 0,8595; $\alpha_D + 56^\circ 43'$; $n_{D20^\circ}$ 1,47587) was pressed entirely from over-ripe winter lemons; the other ($d_{15^\circ}$ 0,860; $\alpha_D + 53^\circ 3'$; $n_{D20^\circ}$ 1,47568) partly from ripe winter lemons, partly from spring lemons (bianchetti). As the samples were comparatively small, we only succeeded in obtaining a first fraction, which in both cases was still slightly dextrogyre, but in which pinene could be detected respectively by its nitrosochloride, and its nitrolbenzylamine.

We subsequently fractionated a considerable quantity of terpenes from lemon oil, in order to obtain a further knowledge of the lævogyre hydrocarbon therein contained. The gentlemen of the London Essence Company are surprised that we have been able to isolate this lævogyre body without having used a Young's twelve-beaded dephlegmator, and they show a considerable amount of interest to learn how we have done this. We do not, however, feel called upon to give them information on the apparatus used by us, which apparatus, as they can learn from the results of our work, must have decided advantages over Young's dephlegmator, even when the latter has twelve beads. For we have even succeeded in separating from this low-boiling lævogyre first fraction, further fractions, which at the boiling point of pinene show a decidedly higher lævogyration (— 13° to — 14°) than Burgess and Child have observed, — and also another fraction boiling still a little higher, which is even stronger lævogyre

(— 19°). For this reason we do not think it impossible, that l-camphene is perhaps also present in oil of lemon, in addition to l-pinene. The priority of the detection of the last-named hydrocarbon undoubtedly belongs to Messrs. Burgess and Child[1]); the presence of camphene we hope to be able to make still more probable.

Although a whole series of bodies has been detected in oil of lemon, viz., d-limonene[2]), cymene (?)[3]), phellandrene[4]), citral[5]), citronellal[6]), geranyl acetate[7]), a sesquiterpene[8]), octyl and nonyl aldehydes[9]), and also pinene[10]), it has not been possible to obtain a serviceable artificial product by mixing these various substances. This is due to the fact that still further bodies, which have an important bearing on the odour, have up to now been overlooked in the examinations of lemon oil.

Now we have recently succeeded in detecting methyl heptenone in the first runnings, and terpineol of the melting point 35° ($\Delta'$-terpene-8-ol) in the last fractions of oil of lemon. For the detection of methyl heptenone, the fraction consisting of terpenes, fatty aldehydes, and citral, was shaken for some considerable time with bisulphite solution. From the crystalline bisulphite compound separating out in abundance, the aldehydes were liberated by sodium carbonate with the application of heat, and were driven over with water vapour. The mixture of aldehydes isolated from the distillate, passed over between 174 and 215°, and that in the following fractions:

1. 174—179°; 2. 179—200°; 3. 200—215°.

Of these fractions, the first had a very pronounced odour of methyl heptenone, the second specially of octyl and nonyl aldehydes, and the third almost exclusively of citral. When it was attempted to obtain the semicarbazone of methyl heptenone from the first fraction, at first no solid derivative separated out. Only after the reaction-mixture (still strongly smelling of methyl heptenone) had been treated with water

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[1]) Mr. Parry, who uses his influence so much on behalf of the above-named gentlemen (The Chemist and Druggist 60 (1902), 866) will no doubt welcome the confirmation of this fact with special satisfaction.

[2]) Wallach, Liebigs Annalen **227** (1885), 290.

[3]) Bouchardat and Lafont, Journ. de Pharm. V, **27** (1893), 49.

[4]) Report October **1897**, 26.

[5]) Bericht, October **1888**, 17.

[6]) Doebner, Archiv d. Pharm. **232** (1894), 688. — Berliner Berichte **27** (1894), 352.

[7]) Umney and Swinton, Pharm. Journ. **61** (1898), 196 and 370.

[8]) Oliveri, Gazz. chim. ital. **21**, I (1891), 318.

[9]) v. Soden and Rojahn, Berliner Berichte **34** (1901), 2809.

[10]) Burgess and Child, Journ. Soc. chem. industr. **20** (1901), 1176; comp. Report April 1902, 33.

vapour, and the ketone isolated from the distillate once more had been brought together with semicarbazide, we obtained a solid compound melting at 135 to 136°. After recrystallisation the melting point rose to 136 to 137°. An analysis proved that the body was the semicarbazone of methyl heptenone.

0,1389 g of the subst. yielded 0,1169 g $H_2O$ and 0,3014 g $CO_2$.

| Found: | Calculated for $C_9H_{17}O_3N$: |
|---|---|
| C = 59,18 per cent | C = 59,01 per cent |
| H = 9,35 „ „ | H = 9,29 „ „ |

The last runnings (310 grams from 3 kilos lemon oil) serving for the detection of terpineol, were treated in the same manner for removing the aldehyde with bisulphite. The portion of the oil not reacting with it was washed and rectified in vacuo; it distilled at 9 mm pressure between 60 and 120°. After repeating the distillation in vacuo, we were able to isolate a fraction boiling at 86 to 100° (7 to 8 mm pressure), which had clearly the odour of terpineol, and of which the bulk at ordinary pressure passed over at 215 to 225°, and was collected in three portions:

1. 215—218°, 2. 218—221°, 3. 221—225°.

Not one of these fractions congealed in the cold upon introduction of a terpineol crystal.

| Fraction | | | | | |
|---|---|---|---|---|---|
| Fraction 218—221°: | Spec. gravity | 0,9150, | opt. rotation | | —2° 55′; |
| „ 221—225°: | „ „ | 0,9190, | „ | „ | —3° 47′. |

With phenyl isocyanate, a very small quantity of a phenyl urethane melting at about 105° was obtained from both fractions; after recrystallisation this had the melting point 110°. A phenyl urethane of this melting point, however, belongs to the terpineol melting at 35°, or $\Delta'$-terpene-8-ol. A mixture of the urethane of lemon oil terpineol with the terpineol of the melting point 35°, produced for purposes of comparison, melted at 110°. This proves the presence of this terpineol in oil of lemon.

**Oil of Orange, sweet,** could be bought in April at a low price; in the course of the summer it slowly advanced fully 10 per cent. The old stocks are completely exhausted.

The new crop of oranges will give a smaller result than last year's crop, so that under normal conditions a smaller quantity of oil than usual may be expected for the coming season.

Sellers of new oil, December delivery, are therefore holding back, and up to now only a few isolated transactions have taken place.

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**Eucalyptus Oil.** The Algerian distillers have again the upper hand in the distillate of the Globulus species, and they supply faultless quality at such a low price, that the Australian manufacturers have been compelled to withdraw their competition.

The demand has been confined within normal limits. Covered fully for a long period by a large contract, we are in a position to maintain the present low quotations.

We also supply an Australian oil of uncertain origin; this oil, which contains phellandrene, is a very good value, and is now largely employed for medicinal soaps.

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Deane and Maiden have communicated[1] some observations of a true botanical character on some species of eucalypts found in New South Wales. They have special reference to the following species: *Eucalyptus stellulata* Sieb., *Eucalyptus coriacea* A. Cunn., *Eucalyptus dives* Schauer, *Eucalyptus fastigiata* D. and M., *Eucalyptus obliqua* l'Herit., *Eucalyptus virgata* Sieb. var. altior D. and M., *Eucalyptus Muelleriana* Howitt, *Eucalyptus haemastoma* Sm., *Eucalyptus Sieberiana, fasciculosa* and *Bosistoana* F. v. M., *Eucalyptus cordata* Labill., *Eucalyptus longifolia* Link, *Eucalyptus goniocalyx* F. v. M., *Eucalyptus quadrangulata* D. and M., *Eucalyptus resinifera* var. grandiflora Benth., and var. Kirtoniana, *Eucalyptus punctata* D. C., *Eucalyptus punctata* var. grandiflora, *Eucalyptus terminalis* F. v. M., *Eucalyptus Gunnii* Hook., *Eucalyptus Gunnii* var. glauca, var. acervula, and var. ovata, *Eucalyptus viminalis* Labill., *Eucalyptus viminalis* var. pedicellaris, and var. Baeuerleni.

The authors further mention[2] a supposed bastard growth, which is said to have as parents *Eucalyptus paniculata* and *Eucalyptus hemiphloia.* In this connection they give a detailed description of a new species of eucalyptus, *Eucalyptus Boormani,* which appears to be most closely related to *Eucalyptus drepanophylla,* but is also connected with *Eucalyptus affinis* and *Eucalyptus Bosistoana.*

According to J. H. Maiden[3], *Eucalyptus obliqua* l'Hérit. occurs, under the name "Stringybark", in Tasmania and South Australia, and less widely in Victoria, in company with other stringybarks and eucalypts with fibrous bark. This is the same species of eucalyptus which Hooker at the time has wrongly described in the Flora of Tasmania as *Eucalyptus gigantea.*

The same author further reports[4] on the presence in Victoria of *Eucalyptus dives* Schauer, i. e., the species which, rightly or wrongly, is supposed to be the one which in the distillation of Australian eucalyptus oil comes under consideration. The details of this treatise,

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[1] Proc. Linn. Soc. of N. S. W. **1901**, part. I.
[2] Proc. Linn. Soc. of N. S. W. **1901**, part. II.
[3] Agricultural Gazette of N. S. W. **1901**.
[4] The Victorian Naturalist vol. XVIII (1901).

like those of a number of others[1]) by the above-named botanist, on *Eucalyptus pulverulenta* Sims., *Eucalyptus Stuartiana* F. v. M., and *Eucalyptus Gunnii* Hook. fil., have such an exclusively botanical interest, that we may confine ourselves to referring to these publications.

**Fennel Oil.** The fennel harvest in this neighbourhood has given a normal yield. The thrashing of the small-grained so-called straw-fennel generally takes place after the first night-frosts. It is stated that a larger quantity has been planted out this year than previously.

In Galicia, the result has remained far behind the expectations, and the prices asked for this year's seed, as well as for all fennel products, are about 30 per cent higher. The local manufacturers have again formed a ring, with prices fixed by agreement.

No reliable reports have as yet been received on the result of the fennel harvest in Roumania.

Tardy has examined fennel oils of different origin. On a previous occasion[2]) we have already referred to an examination made in 1897[3]) which is now republished in his "Thèse pour l'obtention du diplôme de Docteur de l'Université de Paris". In this treatise Tardy endeavours to refute a criticism of his work by Gildemeister and Hoffmann[4]), in which it was stated that the detection of cymene in an oil treated with dry hydrochloric acid gas, does not prove that this hydrocarbon has also been present in the original oil.

The arguments again brought forward in favour of the presence of cymene in fennel oil, cannot as yet be considered conclusive; the conversion of cymene into p-oxyisopropyl benzoic acid and isopropenyl benzoic acid[5]), which is easy to accomplish, would have removed all doubt.

Fennel oil, Algerian. The oil examined by Tardy[6]) had the constants $d_0 = 0{,}991$; $\alpha_D = + 62° 16'$. The composition of this oil is essentially the same as that of French fennel oil[7]). Detected were: pinene, phellandrene, (here the author obtained the nitrite of the melting point 102°, contrary to what is the case with French oil), fenchone, methyl chavicol, anethol, a sesquiterpene, and a small quantity of a body $C_{10}H_{14}O_2$, which is probably thymohydroquinone. It melts at 138 to 140°, dissolves readily in hot potash liquor, and

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[1]) Proc. Linn. Soc. of N. S. W. **1901**, part. IV.

[2]) Report October **1897**, 27.

[3]) Bull. Soc. chim. III, **17** (1897), 660.

[4]) Gildemeister and Hoffmann, The volatile oils, p. 566.

[5]) Wallach, Liebigs Annalen **264** (1891), 10.

[6]) loc. cit. p. 23.

[7]) do. p. 15. — Bull. Soc. chim. III, **17** (1897), 660.

is precipitated from this solution by acids; the crystals thus obtained melt at 184°. On oxidation with chromic acid mixture, a body is formed with the melting point 45°. From this Tardy concludes that his body is identic with thymohydroquinone. The latter melts at 145°, and on oxidation yields thymoquinone of the melting point 48°. The crystals obtained with hot potash liquor correspond with oxythymoquinone, which is formed when monobromthymoquinone is treated with potash liquor; it melts at 187°.

Fennel Oil, Galician. In this case Tardy has had to deal not with a normal oil, but with the waste oil from the manufacture of fennel oil stearoptene. It rotated 39° 52′ to the right, showed on cooling to — 18° a few ("quelques") crystals, and contained no aldehyde. There were found: 1. a dextrogyre turpentine-like hydrocarbon; 2. a dextrogyre terpene hydrocarbon, which Tardy without evidence declares to be phellandrene; 3. fenchone in large quantity; 4. methyl chavicol in small quantity, and 5. anethol.

In discussing the properties of fenchone, Tardy describes a number of compounds of fenchone with phenols; these will be referred to again under "fenchone" in the "Notes on recent scientific work".

**Galangal Oil.** From the hitherto unknown constituents of this oil, Schindelmeiser[1]) has isolated d-pinene, and identified this body by the nitrosochloride and the nitrolpiperidide. He further obtained from the fraction of the oil boiling between 230° and 240°, (which at 20° had the specific gravity 0,932, the refractive index 1,4922, and in a 100 mm tube showed a rotation of — 27° 12′), a viscid hydrochloride boiling at 145° to 150° (10 mm), which congealed upon cooling, and which, after frequent recrystallisation from alcohol and water, showed the melting point 51°. A determination of chlorine led to the formula $C_{15}H_{24} \cdot 2\,HCl$. As up to now no dihydrochloride of the above melting point has been known of any sesquiterpene, the author believes thas it is here a question of a new hydrocarbon. In the higher boiling portions (boiling point 274° to 276°) the presence of cadinene is suspected.

**Geranium Oil.** The African oil is at present still kept at a high price, and appears to have a tendency to remain at this level during the present season; on the other hand, according to reliable reports, a great deal more has been planted out this year, so that under normal conditions a large crop may be expected in 1903. In this connection there are already lower offers for contracts running over several years.

Réunion geranium oil has undergone a fairly considerable drop, caused by the accumulation of large stocks at different European ports.

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[1]) Chemiker-Zeitung **26** (1902), 308.

A few consignees appear to have lost patience, and to have given instructions to realise at any price, which afforded an opportunity of purchasing below the ruling import quotation. The present value must be considered as very moderate.

Of Spanish geranium oil of this year's distillation, a few consignments have already arrived. The quality is beyond all praise. No change has occurred in the prices.

In India the high prices obtained during the last two years have led to an increase in the production, which has taken effect already in this season in the form of low quotations. Statistics of the production do not exist, and facts upon which an estimate of the limits of the advance might be based, are not available.

It is to be hoped that the distillers will apply themselves to the production of the fine quality, the so called palmarosa oil, as there are at various ports large unsold stocks of the low grades, adulterated with oil of turpentine.

Common gingergrass oil, of which the origin and constitution are still obscure, is available in good quality. It is now also brought on the market from a new source of production on the Madras coast.

**Ginger Oil.** The value of African ginger, which is the only kind coming under consideration for the distillation of the oil, has undergone a very considerable rise, owing to lack of sufficient supplies, and this advance has affected all other kinds of ginger. The prices of oil moved upwards in a corresponding degree. At the present time it would not be possible to renew our stock of oil at the price at which it is sold.

**Hop Oil.** A very rich yield of this year's harvest of hops is said to be generally expected, and double the quantity of last year is even mentioned. On the other hand, in Austria-Hungary a drop is reported of nearly one half, i. e., about 7500 tons, as compared with 1901. A similar state of affairs is found in Belgium, France, and Russia. In the United Kingdom also the quantity is said to be less by one half than in 1901.

The total yield on the European continent and in the United Kingdom will probably be somewhat as follows: —

| | | |
|---|---|---|
| Germany . . . . . . . | 25 000 000 | kilos |
| Austria-Hungary . . . . | 10 500 000 | „ |
| Belgium . . . . . . . . | 3 000 000 | „ |
| France . . . . . . . . | 1 000 000 | „ |
| Russia . . . . . . . . | 2 500 000 | „ |
| United Kingdom . . . . | 15 000 000 | „ |
| Total: | 57 000 000 | kilos, |

a quantity which will be sufficient to meet the world's requirements.

America wants its own production for home consumption.

For pure hop oil of our own distillation, lower prices can hardly be expected.

**Hyssop Oil.** According to examinations made by Genvresse and Verrier[1]), hyssop oil contains a cineol which boils at 176°, and which yields with hydrobromic acid a crystalline compound which cannot be decomposed with water. They also found in the oil a tertiary alcohol $C_{10}H_{18}O$, of the boiling point 210°, at 740 mm, which was not identic with any of the hitherto-known alcohols.

**Jasmine Oil "Schimmel & Co.".** We have within the last twelve months made further improvements in the composition of this product, which was introduced by us into commerce as the first artificial flower oil in 1896. The content of natural constituents of the pure flower oil has especially been increased to such an extent, that our product makes the impression of being absolutely true to nature.

We believe that we can characterise it best by stating that it contains all the constituents of the natural jasmine oil obtained from jasmine flowers, and we would ask the numerous purchasers of our original product to examine it with special attention. We have made arrangements to obtain extraction-products of the jasmine flower on very advantageous terms, and we will go to the utmost limits in adding natural constituents (which from the first have been present in our oil), as this appears to us the best way of gradually approaching the natural oil so closely, that no longer any difference between the two oils can be detected.

In order to prevent all misunderstanding we beg to point out here, in our position as prior inventors, and in consequence of an agreement, that we are joint owners of the German patent No. 132425 for the production of artificial jasmine oil.

**Oil of Juniper Berries.** Reports from Hungary mention a failure of the crop and high prices for the new berries. The increase is calculated at about 30 per cent. The commercial oil of juniper berries, obtained as a by-product in the preparation of juniper brandy in Hungary, has under these circumstances found a ready sale, and there are at present no stocks of this oil in existence. As the distilling season has commenced during the last few days, the scarcity will soon come to an end, but higher prices will become the order of the day.

Of Italian berries from the neighbourhood of Parma, the first truck-loads have arrived. Since we made our purchases, the prices of

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[1]) Chemiker-Zeitung **26** (1902), 501.

this, the best of all known sorts, have also advanced 25 per cent. An increase in the quotations of the fine distillates from berries can hardly be avoided.

**Lavender Oil.** This important article has attained a remarkable position, of which the development and the final course cannot as yet be foreseen. The reports from the chief production-districts in the South of France are uniformly unfavourable, and throughout point to a very low yield. We received reliable original reports in the first instance from the Drôme department, where already in March and April the plants had been greatly damaged by frost and rain. The quotations of the oils with an ester-content of 26 to 30 per cent, which are exclusively distilled in that district, are expected to run to 16 francs, against 12 francs paid last year.

In the Hautes- and Basses-Alpes departments, as also in Vaucluse, the situation is equally unfavourable, and there also, at the last markets held at Sault (where we were represented), oils of 36 to 42 per cent ester-content were briskly purchased at a price about 25 per cent higher than that of last year. In some districts the yield is estimated at one half, in others at one third. The market at Apt, where oils containing 30 per cent ester are chiefly sold, was equally strong.

From the Gard and Hérault departments similar complaints are heard. The production there is also reported as very small, and high prices are anticipated. The distilling season, which usually lasts one to $1\,^1/_2$ month, has this year come to an end in three weeks.

In consequence of this critical state of affairs, there has been keen competition in the purchases in the principal districts, which has driven the prices up by 3 to 4 francs. Whether the fears, that the production will not be sufficient to meet the demand, are justified, remains to be seen. In any case the situation has totally changed, and the old experience is confirmed, that a slight obstacle is sufficient to cause a complete revolution in the values of such an important article.

We hope to be in a position to satisfy the normal requirements of our regular clients, without, however, being able, under the existing conditions, to accept any responsibility whatever.

E. Parry[1]) has again considered the question, already so often discussed, whether the esters in French lavender oil have such an influence on the fineness and strength of the aroma, that it is advisable to accept the ester-content as a standard of value for this oil. In conjunction with that group of French firms which does not approve

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[1]) The Chemist and Druggist **61** (1902), 168.

of this important criterion for the purity and quality of French oils, — a criterion which we have recommended on the strength of our examination of lavender oil, and of our observations made during a number of years, — Parry expresses the opinion that "so far as he has been able to judge, the ester-value of lavender oils is by no means a certain index of the quality of the oil".

The arguments adduced by Parry in support of his opinion, are partly the old ones. It may therefore suffice, if, with regard to these, we refer to our previous statements (Reports April 1898, 30, and October 1897, 31 to 35). The objection that linalyl acetate cannot be the most important body in lavender oil, because it has been identified as the bearer of the perfume in bergamot oil, and the two oils cannot be compared with one another, is all the more incomprehensible, as it is not unknown to Parry that, although linalyl acetate occurs in preponderating quantity, the oil also contains other esters, which, jointly with the linalyl acetate, produce the ester-aroma of lavender oil. The ester-content calculated for linalyl acetate is, of course, only a comparative quantity, which no more indicates the true content of linalyl acetate than the quantity of the other esters present in lavender oil. This may perhaps be a defect in the method of examination, but it is proved in practice that it suffices for estimating the value of the oil.

In addition to the substances capable of saponification, the other constituents of lavender oil are, naturally, also important for the production of the peculiar lavender-aroma; we would here refer only to coumarin1), detected by us in lavender oil, — but it is equally certain that their perfume-value is not as high as that of the esters.

If science should succeed in discovering also for these bodies a simple method of quantitative estimation, we would hail such discovery with joy; but even then the determination of ester would not lose its importance as the most essential factor in judging the value of the oil.

In order to prove the unreliability of the ester-determination as a basis for judging the odour-value of lavender oils, Parry has selected from a large number of pure oils of different origin, judging simply by the odour, those which appeared to him the best, and of these oils he has ascertained the ester-content. He finds, however, that the grouping of the oils according to their ester-value does not agree with the selection made by the nose.

If this experiment by Parry has given an apparently unfavourable result for the method of estimating the ester, we are able to refer to facts which bear out exactly the reverse.

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1) In estimating the ester-content, coumarin is only incompletely saponified by alcoholic potash liquor.

A few years ago, when our method of examination had fewer adherents than now, we received a series of samples of lavender oils from one of the largest manufacturers in France, who at that time was still an opponent of the "ester-theory". The examination proved that the price of the oils moved upwards with the ester-value found, and that the quality of the oils also agreed with the prices.

At the top of his list of oils selected by the nose, Parry places a sample from Annot, which, although containing but 26,5 per cent of esters, yet in his opinion has a finer aroma than all the other oils.

We are not for the present in a position to test the correctness of this assertion, but that it has not remained uncontradicted in well-informed circles of the trade, may be proved to Mr. Parry by the following lines, which we have received from an important manufacturer of essential oils at Cannes, who is an expert of the first rank. The part of his letter, which refers to this matter, reads as follows:

> "In the London 'Chemist and Druggist' of 26th July, I read an article by Ernest Parry on lavender oil and the ester-content. He endeavours to prove that the esters have no influence on the value of lavender oil. Among the samples analysed, mention is made of an oil from Annot with 26,5 % esters. This is completely wrong; I am certain that among 100 samples of the lavender oil distilled in this part of the country, not one will be found which contains less than 35 % ester. I know all the manufacturers of this district, as well as their essences of which I receive samples every year which show 38 to 44 %. Since more than half a century the lavender oils from Annot are those most in demand at Grasse, and they have always fetched prices 1,50 to 2 francs higher than those of ordinary qualities. This shows quite clearly, that the esters must have a certain influence on the value of the oils, for the determination of the ester-content of lavender oil has only been in vogue for the last ten years."

Parry admits the great advantage of the determination of the ester-value, in conjunction with the other methods of examination, for the purpose of detecting adulteration with oils of turpentine and spike, and other substances. In judging the perfume value, he recommends odour-tests with lavender water. He here suggests what every sensible perfumer already does as a matter of course in order to select the lavender oil best suited for his purpose. We also have always emphasised that the odour-test retains its full value alongside the method of determining the ester-content, and we quote here verbally a passage from our Report of October 1897, page 32, as follows: "it is so self-evident that every essential oil is first of all tested by us for the odour, that we consider it superfluous always to return to this subject. But what those gentlemen do not wish to see, they simply ignore".

After these explanations we must consider the "ester-question" as settled once for all.

In our April Report of this year we mentioned, on page 46, that in examining a lavender oil we detected benzoic acid as a new adulterant, which had clearly been used for the purpose of artificially increasing the ester-content. J. E. Weber[1]) of Cincinnati reports on a similar case, in which, however, salicylic acid had been employed instead of benzoic acid. Here also it appears first of all to have been a test-case, as the quantity of acid used in the adulteration only amounted to 1 per cent of the oil, from which an increase in the ester-content of 1,75 per cent is calculated.

The oil examined by the author had a good odour; it dissolved in 2,5 volumes of 70 per cent alcohol, and showed the following constants: $d_{15^\circ} = 0{,}893$; $[\alpha]_D$ —6° 42′; acid-number 4,48; ester-content 35,52 per cent.

Apart from the somewhat high acid-number, the data found did not give rise to any suspicion. But after some time a reddish discoloration was observed in the oil, which disappeared again on extracting the oil with caustic liquor or dilute hydrochloric acid. In the first case the volume decreased by about 2½ per cent; in the second, iron was detected in the acid used for extracting. To all appearances the colour had been caused by absorption of iron from the vessel containing the oil.

An alcoholic solution of the oil showed with one drop ferric chloride a dark-red colour, which does not occur if genuine lavender oil is used. When a larger quantity of the oil was extracted with soda liquor, a crystallising acid was obtained, which, after recrystallisation, melted at 156° to 157°, and was found to be salicylic acid. The acid was further identified by conversion into methyl salicylate, and also by the violet colour-reaction with ferric chloride.

The content of salicylic acid can be ascertained with great accuracy by titration with alcoholic potash liquor, phenolphthalein being used as indicator. A lavender oil to which 4,76 per cent salicylic acid had been added, showed on titration 4,73 per cent acid.

**Lemongrass Oil.** The prices of this oil fluctuated during the last few months between 4½ and 5½ d., equal to 14,50 to 17 Marks per kilo purchase price, but the article appears to be scarce in India, as large parcels were rarely offered. We hear from Cochin that the yield of the harvest has been very small, and that in consequence the merchants are holding the goods back in order to obtain higher prices.

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[1]) Chemiker-Zeitung **26** (1902), 875.

The export from July 1st 1901 to June 30th 1902 was
2322 cases of 12 bottles each, or 17415 kilos
against 1933 „ in the same period of 1900/1901,
2792 „ „ „ „ „ „ 1899/1900,
3288 „ „ „ „ „ „ 1898/1899.

The previous low quotations could not again be reached without a considerable increase in the production.

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The decline of the sugar industry in the West Indian islands appears to lead to this, that the lands and the labour set free by the reduced cultivation of sugar cane are employed for other purposes; and from a report which has reached us from a friendly quarter it would seem that it is intended to take up there the cultivation of the *Andropogon* grasses. That attempts to cultivate these grasses have already been made in those islands is proved by the fact, that the superintendent of the botanical garden in Trinidad, at a meeting in Barbados, produced, among other essential oils, also the oils of *Andropogon Nardus* var. and *Andropogon Schoenanthus*, which were subsequently examined more in detail at the Government laboratory in Antigua. The following results were obtained there

for the first oil:

$d\frac{15,5^\circ}{15,5^\circ} = 0,9084$, $\alpha_D = + 0^\circ\ 1'$; aldehyde-content 15,5 %;

saponification number 23, sapon. number after acetylation 168,5, corresponding to a total alcohol-content of about 53 per cent;

for the other oil:

$d\frac{15,5^\circ}{15,5^\circ} = 0,9315$, $\alpha_D = + 3^\circ$; aldehyde-content 48,2 %;

saponification number 31,1; sapon. number after acetylation 69,6, corresponding to 20,2 per cent $C_{10}H_{18}O$.

Whereas the first of the two oils, apart from the low dextrogyration, approximately agrees with Ceylon citronella oil (it does not dissolve in 10 volumes of 70 per cent alcohol, but already in the same volume of 80 per cent alcohol), the other oil differs in its properties in a very marked degree from palmarosa oil, with which, according to the mother plant, it should be identic. But the oil cannot be considered as lemongrass oil, because (even assuming that the aldehyde it contains is actually citral) the aldehyde-content is too low; it shows a certain amount of similarity with a lemongrass oil from the same district (compare Report April 1902, page 48), inasmuch as it dissolves with great difficulty, and only makes clear solutions with 94 per cent alcohol.

**Limette Oil.** We have just received a fresh consigment (and that of the hand-pressed sort) of the excellent product of the Montserrat Co., Ltd., which comes slightly lower in price. The quality is exceptionally good.

**Linaloe Oil.** Owing to difficult weather-conditions, our purveyors in Mexico have only been able to carry out the terms of their contracts with considerable delays, which have led to scarcity in the local stocks. In other respects, consignments at the various ports which have direct communication with Mexico were also scarce and insufficient, and the prices consequently moved upwards almost continuously.

As long as these conditions continue, a change in the situation must not be thought of.

**Oil of Sweet Marjoram.** Genvresse and Chablay¹) have isolated, from two oils of sweet marjoram of different origin, a lævogyre pinene, a new ketone $C_{10}H_{16}O$, and a body which is probably identic with pulegone. Pinene was identified by its hydrochloride and the nitrosochloride. The ketone boiled at 208 to 209°, at 740 mm, and yielded compounds with sodium bisulphite, hydroxylamine, and semicarbazide. The body, supposed to be pulegone, boiled at 220 to 225°, at 738 mm, and yield an oxime melting at 118 to 119°.

**Oil of Milfoil.** A. B. Aubert²) gives in a preliminary communication some details on milfoil oil. Specific gravity 0,9217 (at 22°); $n_{D20°}$ 1,506; 86 parts by volume of the oil passed over at 170 to 235°, at reduced pressure; the distillate showed, according to the fractions, a more or less deep blue colour. The first portions of the oil, boiling up to 190°, may possibly contain chiefly cineol³) and further some small quantity of an aldehyde. Compounds of sulphur were not detected. The principal fraction of the boiling point 210 to 220°, representing 50 parts by volume, when freshly distilled, had a blue colour, which changed into yellowish-green after 1½ year's standing in the dark. Analysis and determination of molecular weight led to the formula $C_{10}H_{20}$. This fraction had the following constants: Rotatory power (in an 100 mm tube) — 14,2°; index of refraction 1,492; boiling point 254° at 754,8 mm. The action of bromine and of hydrochloric acid yielded no characteristic products. On the other hand, the oil gave most of the reactions with terpenes. The blue distillate of milfoil oil differs, in the opinion of the author, from that of oil of chamomile.

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¹) Chemiker-Zeitung **26** (1902), 501.

²) Journ. Americ. Chem. Soc. **24** (1902), 778; according to Chem. Centralblatt 1902, II, 798.

³) The presence of cineol in oil of milfoil was demonstrated by us years ago; compare: Gildemeister and Hoffmann, "The Volatile Oils", p. 675, and also our Report October 1894, 38.

**Mustard Oil.** In a treatise[1]) entitled “Sur le dosage de l’essence de moutarde”, P. Roeser makes the proposal to modify Gadamer’s method for the determination of the sulphur-content of oil of mustard in so far, as to determine the excess of silver nitrate in an ammoniacal solution, instead of an acid solution according to Volhard’s method, as is usually done. According to this, the process should therefore be as follows: when the conversion of the thiosinamine with silver nitrate, after 24 hours’ standing, has taken place, an excess of $\frac{1}{10}$ n. solution of potassium cyanide is added to 50 cc of the clear filtrate, and the excess of potassium cyanide titrated back with $\frac{1}{10}$ n. solution of silver nitrate, in the presence of a few drops of a weak ammoniacal solution (5 per cent) of potassium iodide. Comparative determinations according to this method, and after Gadamer and Dieterich’s methods, have, according to Roeser, shown no differences that were at all considerable.

We have not yet had occasion to make use of this modification, and are therefore not as yet in a position to give an opinion about it, but it is our intention to try it when the opportunity arises.

**Neroli Oil** (Oil of orange-flowers). The part played by the natural oils is now much less important than previously, as the quality of the artificial oil has been perfected to such an extent, that the former can be completely dispensed with. In order to obtain an oil which is at all normal, it is necessary to distil the orange-flowers either for the essential oil only, or only for water, and not, as is at present done, obtain the essential oil as it were as a by-product in the distillation of the water, or vice versa. It will therefore be necessary to do what has to some extent already been done before, that is to say submit the water to cohobation until it is odourless.

Mr. Jean Gras of Cannes once more communicates to us, like last year (compare Report October 1901, 38), a series of observations collected during this year’s harvest of orange-flowers. We reproduce the interesting details in full in the table on page 53.

“The average temperature of May was much lower than in previous years. I believe that to this circumstance must be attributed:

1. the somewhat smaller yield;
2. the lower rotatory power;
3. the higher saponification number;
4. the solubility only in 80 per cent alcohol (last year the neroli oil was soluble in 75 per cent alcohol);
5. the colour of the neroli oils, which is lighter than in previous years.

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[1]) Journ. pharm. chim. VI. **15** (1902), 361.

## Distillation of Neroli Oil in 1902.

| Origin | Spec. grav. at 15° | $\alpha_D$ at 20° | Sapon. number | Yield from 1000 kilos flowers | Solubility in 80 per cent. alcohol |
|---|---|---|---|---|---|
| Own manufacture: May 12. 13. 14. | 0,8725 | + 2° 51′ | 43 | 0,85 | Soluble in 1—2 vol., becomes cloudy when more alcohol is added |
| „ „ 15. 16. | 0,8745 | + 2° 52′ | 47 | 1,00 | „ „ 1—2 „ „ „ „ „ „ „ „ |
| „ „ 17. 18. | 0,8750 | + 3° 18′ | 48 | 1,01 | „ „ 1—2 „ „ „ „ „ „ „ „ |
| „ „ 19. 20. | 0,8750 | + 3° 14′ | 48 | 1,04 | „ „ 1—2 „ and in every proportion |
| „ „ 21. 22. | 0,8729 | + 3° 54′ | 44 | 1,12 | „ „ 1—2 „ with cloudiness |
| „ „ 23. | 0,8727 | + 3° 32′ | 47 | 1,22 | „ „ 1—2 „ becomes cloudy when more alcohol is added |
| „ „ 24. | 0,8723 | + 2° 53′ | 50 | 1,15 | „ „ 1—2 „ with cloudiness |
| „ „ 25. | 0,8725 | + 2° 27′ | 47 | 1,33 | „ „ 1—2 „ becomes cloudy when more alcohol is added |
| „ „ 26. | 0,8720 | + 2° 53′ | 43 | 1,26 | „ „ 1—2 „ with cloudiness |
| „ „ 27. | 0,8727 | + 4° 16′ | 42 | 1,22 | „ „ 1—2 „ becomes cloudy when more alcohol is added |
| „ „ 28. | 0,8726 | + 4° 13′ | 44 | 1,20 | „ „ 1—2 „ and in every proportion |
| Total manufacture: | 0,8733 | + 3° 22′ | 45 | 1,118 | „ „ 1—2 „ becomes cloudy when more alcohol is added |
| Total manufacture A. le Cannet: | 0,8721 | + 5° 28′ | 36 | | Soluble in 1—2 vol. and in every proportion |
| 31. May B. le Bar: | 0,8737 | + 4° 5′ | | | „ „ 1—2 „ „ „ „ „ |
| Total manufacture C. le Cannet: | 0,8729 | + 3° 38′ | 42 | | „ „ 1—2 „ „ „ „ „ |
| „ D. le Cannet: | 0,8751 | + 3° 54′ | 38 | | „ „ 1—2 „ „ „ „ „ |
| „ E. le Cannet: | 0,8727 | + 5° 14′ | 35 | | „ „ 1—2 „ „ „ „ „ |

The neroli oils A, B, C, D and E are samples examined by me.

The neroli oil A cannot be pure, but must contain oil of bitter orange (low specific gravity and saponification number, high rotatory power).

The neroli oil B is pure; I have received it from a business friend at Grasse. It was distilled on 31st May.

The neroli oil C I consider pure.

The neroli oil D must contain neroli oil from the autumn distillation, for it is very dark (low saponification number, high rotatory power).

For neroli oil E the same remark applies as for neroli oil A.

All these oils, except sample B, had been distilled over an open fire; I believe that this causes a higher degree of solubility in alcohol, and a lower saponification number, the same as in the case of lavender oils.

Distilled oil of bitter orange is largely used for adulterating neroli oil; it is distilled over blossoms, in the month of May."

J. C. Umney and C. T. Bennett¹) report on a Chinese neroli oil. The product examined by the authors is said to be derived from *Citrus triptera (trifoliata)*, a species of citrus which thrives luxuriantly in Southern Europe, and whose fruit resembles the mandarin. A remarkable fact is that this species has a large number of thorns.

The yellowish-brown oil had a peculiar, sweet odour, showed a very faint blue fluorescence, and had the following constants: Specific gravity 0,850; optical rotation + 35°. It boiled between 165 and 220° and its ester-content amounted to 4,97 per cent (calculated as linalyl acetate); its total content of alcohol was 25,17 per cent (calculated as linalol). In the opinion of the authors the oil contains limonene, camphene, linalol, linalyl acetate, methyl anthranilate, and a paraffin hydrocarbon. The authors do not, however, state how these bodies were detected.

Although the authors believe that this oil cannot bear comparison with French neroli oil, or with the imported petitgrain oils, it will yet be found suitable for use in perfumery and in the manufacture of soaps, on account of its very pleasant odour.

In connection with our examination of petitgrain oil we have also occupied ourselves with neroli oil, and we wish to publish here the results obtained.

The material worked up had been obtained from Roure Bertrand fils of Grasse, and had the following properties: Specific gravity 0,8772;

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¹) Pharm. Journal **69** (1902), 146.

optical rotation + 3° 28′; saponification number 44,4. After having satisfied ourselves that the oil did not contain any highly volatile constituents, we fractionated at first with a moderate, later with a stronger vacuum. The first portions passed over at 52°, at a pressure of 10 to 11 mm. With these portions a pyrrol-reaction with a chip of firwood moistened with hydrochloric acid (as observed in some oils by E. and H. Erdmann)[1]) did not occur. We succeeded, however, in detecting the following bodies, some of which are interesting:

l-Pinene. The first fraction obtained consisted of 10 grams of a colourless oil, with a turpentine-like odour, of the boiling point 160 to 167°, specific gravity 0,8592, and rotatory power — 18° 38′. When it was endeavoured to obtain the nitrosochloride from the fraction which probably contained pinene, an insignificant separation of crystals only resulted after introduction of a crystal of nitrosochloride. The pure compound melted at 103°, and yielded, upon treatment with benzylamine, pinene nitrolbenzylamine of the melting point 122 to 123°.

l-Camphene. When the fraction (consisting of 10 grams) of the boiling point 168 to 170°, and the optical rotation — 12° 42′, was heated to 60° with glacial acetic and sulphuric acids, an oil was produced which had the characteristic odour of isobornyl acetate. This oil was saponified, and purified by driving over with water vapour. The oil thus rectified, which had a strong odour of isoborneol, yielded on distillation a fraction of the boiling point 210 to 215°, which partly congealed in the cold. The transparent, laminated crystals, of which the quantity was not sufficient for recrystallisation, melted at 195°, and had the unmistakable odour of isoborneol. Although we were unable to find the melting point of this body at 212°, we are convinced that camphene is a constituent of neroli oil.

Dipentene. For the detection of this terpene, fractions were used of the boiling points 175 to 176° and 179 to 182°. After treatment with sodium, repeated 4 to 5 times, the constants of the oil boiling at 175 to 179°, were as follows: Specific gravity 0,8581; optical rotation — 1° 6′. On brominating, a fairly considerable quantity of crystals was formed of the melting point 117°. They melted in the pure state at 125°, and therefore represented the tetrabromide of dipentene.

Decylic aldehyde. When 160 grams of the portion distilling between 70 and 82° at 7 to 8 mm pressure, which showed a fairly pronounced aldehyde-reaction with fuchsine and sulphurous acid, were continuously shaken for a prolonged time with a saturated solution of sodium bisulphite, an exceedingly small quantity (less than 1 gram)

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[1]) Berliner Berichte **32** (1899), 1217.

of a well-crystallised bisulphite compound separated out. When treated with a carbonate solution, these crystals developed the unmistakable odour of decylic aldehyde. Paucity of material prevented the direct demonstration of the presence of this body; in our opinion, this could only be successfully accomplished by working up very large quantities of oil. We would, however, point out that decylic aldehyde has been detected by us with certainty[1]) as a constituent of oil of sweet orange, i. e. an oil which in its origin is closely allied to neroli oil.

Phenyl acetic acid. Saponification of a portion of the fractions boiling at 82 to 97°, at 7—8 mm pressure, whose saponification number was 58, yielded an acid, which crystallised from water in well-defined small scales. In the pure state it melted at 76 to 77°, that is to say like phenyl acetic acid. The material was not in sufficient quantity to identify it further.

Benzoic acid. A small quantity of this acid was obtained on saponifying the residue of the distillation. As it was strongly contaminated with resinified products and anthranilic acid, it was purified through the barium salt. The almost colourless product thus obtained melted at 116° to 117°, and, after subliming through filtering paper, at 121°. When esterified with methyl alcohol and concentrated sulphuric acid, the unmistakable odour occurred of methyl benzoate.

It may be accepted that phenylacetic and benzoic acids are not contained in the oil as such, but in the form of esters. In view of the high boiling point of the fractions in which they were detected, it is probable that they are combined with benzyl alcohol[2]) or phenyl ethyl alcohol[3]). The latter could be detected, by oxidation into phenyl acetic acid, in a saponified fraction of the boiling point 210° to 220°.

Alcohol $C_{10}H_{18}O$. With reference to this alcohol we would mention, that only after we had obtained a derivative of it in the examination of petitgrain oil, we examined the corresponding fractions of neroli oil for the same purpose. For this reason we confine ourselves in this instance to mentioning the fractions in which the alcohol was detected, together with their constants, and also an analysis of the phenyl urethane of this alcohol.

Unsaponified as well as saponified fractions of the oil were employed for the detection. The fractions of the boiling points 76° to 78°, and 78,5° to 79°, at 7 to 8 mm pressure, which had an odour very similar to that of the corresponding fractions of petitgrain oil, were carefully distilled at ordinary pressure after repeated distillation in vacuo. The following fractions were isolated:

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[1]) Journ. f. prakt. Chem. II. **62** (1900), 524.

[2]) Esters of benzyl alcohol have been repeatedly met with in essential oils.

[3]) According to Hesse (Journ. f. prakt. Chem. II. **64** (1901), 259, phenyl acetic acid and phenyl ethyl alcohol are present in the oil of orange-flower water.

1. Boiling point 194—196°; spec. gravity 0,8704; $\alpha_D$ — 5° 48′;
2. „ „ 196—197°; „ „ 0,8711; $\alpha_D$ — 8° 30′;
3. „ „ 197—198°; „ „ 0,8701; $\alpha_D$ — 8° 12′;
4. „ „ 198—199°; „ „ 0,8699; $\alpha_D$ — 8° 15′;
5. „ „ 199—200°; „ „ 0,8714; $\alpha_D$ — 7° 51′.

All these fractions yielded with phenyl isocyanate, after standing for a long time, a phenyl urethane which melted in the pure state at 65°, and which had the same properties and behaviour as that described under petitgrain oil. The analysis gave values corresponding to the formula $C_{17} H_{23} O_2 N$, i. e. the phenyl urethane of an alcohol $C_{10} H_{17} OH$.

0,1088 g of the substance yielded 0,0820 g $H_2O$ and 0,2974 g $CO_2$.

| | Found: | Calculated for $C_{17} H_{23} O_2 N$: |
|---|---|---|
| C = | 74,55 per cent | 74,70 per cent |
| H = | 8,37 „ „ | 8,44 „ „ |

The same phenyl urethane was also obtained from higher unsaponified fractions (boiling point 88 to 93° at 7 to 8 mm, saponification number 126,3; and 93 to 97° at 7 to 8 mm, saponification number 139,1). In a saponified fraction of the boiling point 74 to 77° at 8 mm pressure, (boiling point before saponification 94 to 98°, at 7 to 8 mm pressure) the alcohol was also detected. For the rest we refer to what is said under petitgrain oil.

d-Terpineol of the melting point 35°. The high-boiling portions which come under consideration for this body, were comparatively rich in methyl anthranilate; they were first of all treated with dilute sulphuric acid for the purpose of removing this ester. The fractions thus treated distilled between 90 and 114°, at 7 mm pressure, and showed only a slight fluorescence. The portion collected between 90 and 95° was once more carefully fractionated at ordinary pressure. Between 215 and 220° an oil passed over which had a terpineol-like odour, and which on cooling first became viscid, and finally congealed when a terpineol crystal was introduced. The specific gravity of this fraction was 0,912. The pure white crystals melted above 33°. From the fraction mixed with phenyl isocyanate, which was dextrorotatory and contained terpineol, terpinyl phenyl urethane of the melting point 110° crystallised out. After recrystallisation from alcohol the melting point increased to 112°.

This proves the presence in neroli oil of d-terpineol of the melting point 35°, and that as such, and not in the form of ester.

Several years ago, A. Hesse¹) made the assertion that oil of orange flowers contains indol, without however having produced up

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¹) Berliner Berichte **32** (1899), 2612.

to the present a proof in support of this statement. We also believe, by the odour, that we have detected indol in neroli oil. Although we have observed with a brownish-red product, which had a pronounced indol-like odour, a colour-reaction with isatin and concentrated sulphuric acid, which pointed to this, we have not been able to demonstrate the presence of indol by its combination with picric acid. The oil probably contains such a small quantity of this body which has such an intense odour, that the detection of it offers great difficulties.

The foregoing examination has therefore shown, that in addition to the hitherto-known constituents, neroli oil also contains the following bodies: l-pinene, l-camphene (?), dipentine, decylic aldehyde (?), an alcohol $C_{10}H_{18}O$, probably l-linalol, phenyl ethyl alcohol (free or as ester), d-terpineol (melting point 35°), phenyl acetic and benzoic acids.

The method for the quantitative estimation of methyl anthranilate in essential oils, recommended by E. Erdmann[1]), which is based on the property of the ester of forming azo-dyestuffs, has been verified by A. Hesse and O. Zeitschel[2]). Their examination has proved that Erdmann's method is not sufficient for the quantitative estimation of this body in essential oils, but that it gives satisfactory results if the anthranilic acid ester is present substantially or in an acid solution. The last-named authors therefore believe that it is more correct to adhere to the method mentioned by themselves, and in cases where methyl anthranilate as well as methyl ester of methyl anthranilic acid are to be estimated, to combine the two methods.

**Oil of Neroli Portugal** (Sweet orange-flowers). E. Theulier[3]) has published a short work on the oil from the flowers of the sweet orange. The oil obtained by simple distillation, without cohobation, had a dark-yellow colour, and an odour not reminding of that of ordinary neroli oil. The specific gravity at 23° was 0,860, the optical rotation $+ 29° 30'$, the ester-content 6,35 per cent. With 90 per cent alcohol the oil showed a silky cloudiness; in the cold, a paraffin of the melting point 55° separated out. The oil distilled between 160° and 233°, and appeared to contain a considerable quantity of higher-boiling terpenes. Theulier succeeded in demonstrating the presence of d-camphene by means of the isoborneol melting at 212°, produced from it; of d-limonene, by the limonene tetrabromide melting at 105°; and of d-linalol by Döbner's citral-compound melting at 198,5°, which was obtained by oxidation of the fraction coming under

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[1]) Berliner Berichte **35** (1902), 24.
[2]) Berliner Berichte **35** (1902), 2355.
[3]) Bull. Soc. chim. III. **27** (1902), 278.

consideration for linalol. The portions of the oil boiling at higher temperatures than linalol were not examined.

**Neroli "Schimmel & Co.".** In our last Report, we have referred in detail to the considerations which, in a general way, are decisive in judging the value of artificial essential oils. Nevertheless our original product, in conformity with our experience, has since its introduction into commerce undergone improvements in its quality, which consisted in incorporating in it (like in jasmine oil) all those natural constituents of the orange-flower, the presence of which is desirable. The product in its action replaces, up to a certain degree, both the essential oil, and the perfume of orange-flowers obtained by maceration or extraction. These improvements are universally appreciated. At the same time, the extra-expense which has resulted from these improvements has been the cause that with our neroli "Schimmel & Co." we can take no part in the excessive cutting in the prices which has now, unfortunately, taken place in this article, and we are therefore compelled to maintain our quotations.

Careful comparisons show that our original product stands without equal.

**Oil of Opopanax.** This article is very scarce, as the supplies of the raw material rich in contents are permanently wanting. We have not succeeded in obtaining again the excellent resin to which we were formerly accustomed.

**Orris Oil.** The yield of this year's harvest of orris-root in the province Tuscany will again be abundant, as the weather-conditions have been favourable for the development of the rhizomes. The quantity of the production will depend upon this, whether only the three-year old, or also the two-year old roots are dug up? In the latter case the crop would amount to about 1000 tons; in the former, to about 800 tons. Our correspondents have ascertained that up to the present almost exclusively three-year old roots have been gathered, but the growers may change their mind, as they need not come to a decision until the middle, or in some cases even the end of October. The state of the weather is an important factor in this matter; if October is very rainy, the gathering and drying of the roots comes quickly to an end.

The quantities still in stock are estimated by some at 400000 kilos, by others at 600000 kilos, but the last-named figure is believed to be exaggerated, so as to paint the deplorable condition of the Florentine orris-root cultivation in the most glaring colours, and to obtain support for the project mentioned in the newspaper-report quoted below.

It is a fact that at the present market quotations the growers do not cover their expenses, and for this reason a reduction in the number of plants bedded out, by about 40 to 50 per cent, may be looked for. Time only can bring about a lasting improvement in the present conditions, provided that the production be brought back within reasonable limits. The producers themselves are to a great extent to blame for the present state of affairs, for it was self-evident that the competition of ionone would affect the value of orris-root.

The issue of August 24th of "L'Economista", the trade-paper published at Florence, contains a long article, as detailed as it is interesting, of which we reproduce here a free translation. The article is entitled:

### Orris-root in Tuscan agriculture.

Orris-root suddenly threatens to bring about a disturbance of the economic equilibrium, a small crisis in Tuscan agriculture, and we will, with the help of statistics, examine the questions relating to this subject, with the view of ascertaining what their practical solution might be.

The decline in the prices of orris-root, with which we are face to face, is such, that the cultivation no longer pays. We do not propose to demonstrate this, as both producers and exporters agree that the present value of Florentine orris-root, at 43,— lire per 100 kilos, is barely sufficient to pay a miserable rate of wages, without leaving the smallest profit to the owner of the land, or to the tenant. The following statistics give particulars of the movement in the prices during the last twenty years.

Price per 100 kilos of Florentine orris-root.1)

| | | | | | |
|---|---|---|---|---|---|
| 1881 | Lire | 146 | 1892 | Lire | 310 |
| 1882 | „ | 128 | 1893 | „ | 200 |
| 1883 | „ | 80 | 1894 | „ | 200 |
| 1884 | „ | 60 | 1895 | „ | 135 |
| 1885 | „ | 46 | 1896 | „ | 180 |
| 1886 | „ | 45 | 1897 | „ | 135 |
| 1887 | „ | 40 | 1898 | „ | 65 |
| 1888 | „ | 50 | 1899 | „ | 70 to 100 |
| 1889 | „ | 82 | 1900 | „ | 80 „ 100 |
| 1890 | „ | 130 | 1901 | „ | 50 „ 65 |
| 1891 | „ | 176 | 1902 | „ | 40 „ 50 |

In view of the present low quotations the question arises, whether we have before us a variable or a lasting economic fact, an operation which may come to an end to-morrow, or a manifestation of the unbending law of supply and demand.

Our opinion above everything is, that the orris-root market at present pays the penalty for the old mistake committed in 1892 by the artificial increase in the prices, when the quotations, with a dexterity never suspected, were driven up to over 320 Lire per 100 kilos. This operation for a rise was a complete success, for it was started at a time when, owing to various circumstances, the stocks in the Florentine district had dwindled down to 250 tons. The inevitable reaction has not stayed away, as we see at this moment, for from that time the cultivation of orris-root ceased to occupy a subordinate position, but

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1) The prices of 1881—1898 agree with the checked selling prices of one of the principal trading firms of the province; those of 1899—1902 have been taken from the official market reports.

became one of the leading industries, the more so, as it was such an easy cultivation in the suitable soil of loam and lime, and as the fertilisation with lupine was as simple as it was cheap. In a short time the production increased almost three-fold, advancing from 400 tons in 1892, to 1000 tons in 1901, and at present it is estimated at 1100 tons.

The following statistics referring to this matter, although not official, may be taken as conclusive.

Crops of orris-root in the province Florence: —

| | | | |
|---|---|---|---|
| 1892 | 400 tons | 1898 | 850 tons |
| 1893 | 500 ,, | 1899 | 900 ,, |
| 1894 | 600 ,, | 1900 | 950 ,, |
| 1895 | 700 ,, | 1901 | 1000 ,, |
| 1896 | 700 ,, | 1902 | 1100 ,, (estimated) |
| 1897 | 800 ,, | | |

In view of these figures, and of the fact (still to be discussed) that the demand has meanwhile not increased, it requires no further proof that a heavy fall in the prices was inevitable.

Another fact to be considered, which has injured our market, is the development of the cultivation of orris-root since 1892 in the province Verona. No doubt the root does not thrive there so well as in Tuscany, but nevertheless it succeeded, at the time of the great boom, in pushing itself ahead under its own or an assumed name, and in occupying a position which it was previously denied. The Veronese root is unsuitable for distillation purposes, for it contains little oil, and, above all, oil of lower quality than the Florentine article. In spite of this, the former has maintained its position for ordinary uses, such as for example in the drug trade; North America imports this article now regularly, and it is there preferred by many to the other kind; on the New York market *Veronese orris-root* is quoted regularly. The following figures are of interest:

Crops and prices of orris root in the province Verona: —

| | | | | | |
|---|---|---|---|---|---|
| 1891 | 280 tons, | 120 Lire | 1897 | 430 tons, | 80 Lire |
| 1892 | 290 ,, | 125 ,, | 1898 | 450 ,, | 52 ,, |
| 1893 | 300 ,, | 132 ,, | 1899 | 410 ,, | 50 ,, |
| 1894 | 280 ,, | 140 ,, | 1900 | 380 ,, | 48 ,, |
| 1895 | 300 ,, | 120 ,, | 1901 | 400 ,, | 55 ,, |
| 1896 | 360 ,, | 110 ,, | 1902 | about 450 tons | 30 ,, |

The foregoing figures leave no doubt that the abundant Veronese crops must have had an unfavourable effect on our market, and that they are partly responsible for the present critical situation.

The downward tendency of the market has been accentuated during the last twelve months by the fall in the premium of gold from about 6 per cent in July 1901, to about 1 per cent in August 1902, which equals a loss of about 5 per cent, or say 2,50 lire per 100 kilos, as the article must finally bear the loss of the premium which has gone past the exporter. To this should be added, that the continued and pronounced fall in the prices both of the Florentine and the Veronese root has caused a general want of confidence in the further course of the market, and has turned the speculators entirely away from this article.

Statistics of the stocks held abroad are impossible to obtain, owing to the fact that orris-root in foreign countries is not stored in bond, but is kept only in private warehouses. It may, however, be assumed that those stocks are not excessive; on the other hand, in our province the unsold stock of last year's crop held by growers and traders amounts in all to about 600 tons.

To these facts, which by themselves are sufficient to explain the present position of the market, should be added a further fact which may serve to grasp the situation. Chemistry, which has caused a complete revolution in the entire agriculture, has also exerted its powerful influence on the modest cultivation of orris-root. Until a few years ago, the violet aroma was only obtained from orris-root, of which 1000 kilos yield about 2 kilos concrete oil. At the present day it has largely been replaced by ionone, a ketone isomeric with irone, which is obtained by condensation of citral with acetone, and subsequent conversion of the condensation-product with concentrated sulphuric acid. Pure ionone is a colourless liquid with a strong odour of violets, which certainly does not equal pure concrete orris oil, and does not replace it synthetically. Ionone has, however, succeeded, on account of its cheapness and convenient manipulation, in frequently taking the place of Florentine orris oil, the consumption of which, contrary to that of other products of luxury, has not increased; at any rate this applies to the last five years.

If the means are considered by which this crisis may be overcome, the first thought must certainly be of reduced production; but at the same time the question arises, whether it is possible to demand such a reduction from the producers of a whole province, — whether it is, after all, any use, to make arrangements and to receive promises, which in the end are not carried out? It would rather appear to us that the equilibrium will be restored in a natural manner in the course of a few years, by the fact that the cultivation of orris-root will grow smaller owing to the absence of profit.

In face of the complete depression of the market, it seems to us that the time has come when producers and exporters, whose interests run in the same channel, should combine, — when manufacturers and traders should work together in a sensible manner. We believe that offers to buyers abroad, from producers without commercial experience, have only been made in isolated cases, but for that very reason they confuse the purchasers, whereas a well-considered, properly-conducted export trade, carried on by a few exporters, hardens the prices and puts a stop to a further decline. For this reason we most strongly recommend the proposal made by the Marchese Ricci, viz , to form a Company well provided with capital, which would distil the concrete orris oil in this country, for we must and we can fight against the foreign industry and may succeed in driving it from the field. A factory erected on the place of origin would have no expenses for carriage of the raw material, and would therefore apparently have a prospect of success. But if the new undertaking should be in the form of a company, and if it is to progress, it should only consider its own advantage which may occasionally be opposed to that of the producers, for it should take advantage of specially favourable market conditions, in order to cover itself at a low price; on the other hand, its sales are again subject to the influence of supply and demand.

We see salvation in a well-organised industry, satisfied with a small profit and fitted up with the most modern plant in such a way that it can immediately enter into competition with the important factories abroad, — otherwise it will soon come to grief.

But the manufacture alone is not enough; the product must also be sold at a profit, and skilled, careful management of the sale is therefore of great economic importance, for its duty will be to bring about and maintain the equilibrium between production and consumption; the present crisis is a consequence of the disturbance of that equilibrium.

The contemplated undertaking has been planned on a modern, sound basis, and it will show the practical and productive results which the gentlemen to be placed at its head will be able to obtain for it.

> From the study of the statistics and the objective examination of the situation, upon which we have bestowed great care, we draw one practical conclusion. Florentine orris-root is the subject of a crisis which, though not new, is surely but transitory. If the commercial value of a product sinks below the cost of production, experience teaches that the production decreases, and that the smaller yield cannot fail to raise again the commercial value of the article. The present crisis also obeys this law, and its severity can only be tempered by an honest understanding between producers and exporters. But the future of a strong undertaking may bring a happy fate to the distillation of orris-root in Tuscany, and through the latter to the national economic life, and to such we repeat the old proverb: "Every man is the architect of his own fortune".

Our quotations for both kinds of orris oil — the concrete and the liquid — are now so low, that it will pay to make contracts at once. We have secured a fair stock of splendid raw material at the lowest rates and are able to offer our products at exceptional figures.

**Patchouli Oil.** In accordance with an arrangement made with a firm at Penang, we now receive regularly direct consignments of the best patchouli-leaves which can be obtained. The purchase is difficult and requires great caution, as the danger of admixture of bad leaves is very great. For a long time this was carried on on such a large scale, that several parcels caused great disappointment.

At this moment a large consignment which is reported to be of very fine quality, is just arriving at Hamburg.

Within the last few weeks there has been a brisk demand for patchouli oil, which induced us to exercise a certain reserve in concluding business transactions. We use every effort to obtain a sufficient supply for our regular clients, but in spite of this we are bound to point out that our quotations are without engagement.

**Oil of European Pennyroyal.** Tétry[1]) has further examined and carefully fractionated this oil. The small quantity of first runnings was repeatedly distilled over sodium in order to isolate the terpenes, but the author did not succeed in obtaining the lowest boiling portions free from oxygen. Up to 173° fractions which were more or less strongly lævorotatory passed over; the last of these fractions, of the boiling point 170 to 173°, showed a specific rotation $[\alpha]_D = -52^\circ 11'$; when brominated, it yielded a bromide melting at 106 to 109°, which Tétry considers to be a mixture of the tetrabromides of l-limonene and dipentene. Treatment with amyl nitrite and hydrochloric acid produced a small quantity of a well-crystallising nitroso chloride of the melting point 135°. From the principal fraction boiling at 110 to 112° (at 20 mm pressure) menthol was produced; the separation from the pulegone was obtained by conversion of the menthol into the benzoate boiling at 190° (18 mm), whilst pulegone passed over at 107° (at

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[1]) Bull. Soc. chim. III. **27** (1902), 186.

the same pressure). By saponification of the ester a small quantity of crystallised menthol was produced in the pure state. Another method for the detection of menthol consisted of oximating the fraction containing menthol with an excess of hydroxylamine hydrochloride and oxide of zinc in alcoholic solution. Upon subsequent distillation, acetoxime of the melting point 59 to 60° passed over at 50° (20 mm pressure); Tétry assumes that this acetoxime, along with the oxime of methyl cyclohexanone, is formed by decomposition from the hydroxylamide of normal pulegone oxime. The fraction of the oximation-product boiling at 20 mm pressure at 100 to 120° contains the menthol, which could be obtained in crystalline form, in the pure state, by repeated distillation (boiling point 110° at 17 mm). The phenyl urethane produced from it melted correctly at 111 to 112°. From the portions of pennyroyal oil boiling at 90 to 110° (20 mm) menthone was isolated by von Baeyer and Henrich's[1]) method, and identified by analysis of its semicarbazone melting at 184°.

**Peppermint Oil, American.** In order to obtain a perfectly clear view of the position of this important article, our New York branch has made enquiries in the peppermint districts, of which the following is the result.

The question, whether a full normal harvest may be expected, has been unanimously answered in the negative by 17 of the most important producers of Michigan. The estimates vary from $^1/_4$ to $^1/_2$ of an average harvest. This is said to be due to the excessive rainfall which has occurred there as well as in Europe, and which has absolutely flooded the fields, and caused an abnormal growth of weeds, such as has not been observed for years. The proportion of weeds is estimated at from 10 to 25 per cent. Only a few districts make an exception to this rule.

With regard to the question as to how much lower this year's yield of oil will be than that of last year, the statements fluctuate between 20 and 75 per cent. One producer even says that the yield will be nil, and that his still will not be put in operation. The average of ten producers puts the deficiency at 40 per cent. The quality of the oil may possibly here and there leave something to be desired, owing to the enormous quantities of weed, although the high price of the oil renders it possible to allow a certain amount for weeding the fields, for which chiefly children are employed.

The distilling season commenced in some districts as early as the beginning of August, in others, according to the situation, a few weeks later.

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[1]) Berliner Berichte **28** (1895), 652.

It will be seen from the foregoing that the pessimistic reports originally circulated, which stated that the harvest would scarcely yield a quarter of the usual result, were exaggerated. On the other hand, it is confirmed, beyond a shadow of doubt, that the result of the harvest will be essentially lower than that of last year. For this reason it may be accepted that the present value of the article, which rests on a sound basis, will be maintained. But if speculative purchases should be made on a large scale, the possibility of a further advance of the prices is not excluded; the latter are no doubt high, as compared with the ruinous values of 1898, 1899 and 1900, but not by any means abnormal; they are such, that under ordinary conditions they leave a fair profit to the producers.

The following comparative summary shows the approximate average values of crude American oil during the last 13 years, and may be of assistance in judging the present state of the prices:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Value | on | 1st | October | 1890 | about | $ | 2,50 | per | lb. |
| " | " | 1st | " | 1891 | " | " | 2,70 | " | " |
| " | " | 1st | " | 1892 | " | " | 3,00 | " | " |
| " | " | 1st | " | 1893 | " | " | 2,80 | " | " |
| " | " | 1st | " | 1894 | " | " | 2,20 | " | " |
| " | " | 1st | " | 1895 | " | " | 2,00 | " | " |
| " | " | 1st | " | 1896 | " | " | 1,70 | " | " |
| " | " | 1st | " | 1897 | " | " | 1,80 | " | " |
| " | " | 1st | " | 1898 | " | " | 1,00 | " | " |
| " | " | 1st | " | 1899 | " | " | 0,80 | " | " |
| " | " | 1st | " | 1900 | " | " | 0,90 | " | " |
| " | " | 1st | " | 1901 | " | " | 1,30 | " | " |
| " | " | 1st | " | 1902 | " | " | 2,00 | " | " |

Before this Report went to press, a sudden change in the value of peppermint oil took place on the American market. Prices were driven up every day by some leading parties, and in less than two weeks attained the level, never known before, of $ 5 per lb. Quite in a secret way a syndicate had been formed, which brought under his control nine tenth of the whole crop, and which dictated the prices to the surprised dealers.

There is no doubt that under such unusual circumstances the abnormal price of $ 5.— is not and will not be paid willingly, but only in case of absolute necessity. All consumers of peppermint oil, being seriously prejudiced by such an unexpected and unjustified manœuvre of speculators, should unite in mesures against them and in the next time buy only from hand to mouth.

Every body interested in the article will do well to restrict his purchases to the utmost limit. For the present it is very difficult to say whether the actual value will be permanent or a decline take place in due time.

**Peppermint Oil, Italian.** Although the peppermint oil distilled in Italy is usually consumed in that country, and not much exported, we have come into possession of a small parcel of this oil which has been distilled in the province Piemont. This oil has a faint greenish-yellow colour, and an odour which reminds somewhat of pennyroyal. Its physical constants are as follows: Specific gravity at 15°, 0,9122, optical rotation — 16° 21′; it is soluble in about 7 volumes 70 per cent, and in 1,1 volume 80 per cent alcohol, with considerable opalescence, which in both cases becomes gradually fainter if further quantities of the solvent are added. The oil has a total content of menthol of 52,5 per cent; of this 7,89 per cent are esterified, and the remainder is present as free alcohol. In conformity with this low menthol-content, the oil does not congeal when placed in a freezing mixture. On the other hand, it shows a fairly considerable content of menthone, viz., 22 per cent.

These figures, with the exception of the menthol-content, approximately correspond to those which we have already previously given for Italian peppermint oil.

**Peppermint Oil, Japanese.** The results of the peppermint harvest in Japan are said to have been somewhat better than had originally been expected, but definite figures cannot as yet be given. The following table shows that the shipments of both sorts of liquid oil were very small in the first seven months of this year, and the stocks in Europe are correspondingly insignificant.

Export of peppermint oil from Yokohama

from 1st January to 31st July 1902: —

| | | |
|---|---|---|
| to Hongkong . . . . . | 9 245 | catties |
| „ London . . . . . . | 5 995 | „ |
| „ Hamburg . . . . . | 3 600 | „ |
| „ Havre . . . . . . . . | 1 590 | „ |
| „ Calcutta . . . . . . | 1 530 | „ |
| „ Bombay . . . . . . | 229 | „ |
| „ Shanghai . . . . . . | 30 | „ |
| „ Singapore . . . . . | 19 | „ |
| | 22 238 | catties, |
| or about | 13 330 | kilos. |

This figure falls rather considerably behind the average of the last few years.

At the present moment the condition of the Japanese market is very strong. Prices have risen about 50 per cent in consequence of a considerable shortage of crop.

**Peppermint Oil, Mitcham.** The reports from the English peppermint districts all agree, that the result of the cultivation has been middling. For the best brands, prices are asked which fluctuate between 26/- and 30/- per lb. for crude oil, or 64 and 70 marks per kilo for the rectified article, and if the producers do not become more accommodating, the selling prices will soon have to be raised considerably.

Business in this article has become as difficult as unremunerative for the honest middleman, as he has frequently to fight against dishonesty and want of common-sense — the former in the case of most of the competing products, and the latter with the merchants, who look solely to the name "Mitcham" in their purchases, and who can only be taught with difficulty that it is impossible to supply a faultless original quality at the lowest cut prices. The quotations mentioned above leave but a modest profit to the reliable producer, and no longer allow him to carry on the cultivation with the same care that was bestowed upon it when the value was rarely below 30/-, but mostly fluctuated between 33/- and 36/- per lb. In consequence of this, the excellent oils to which we were at one time used, and of which we still have a recollection, can no longer be obtained, and one has now to make the best of the existing circumstances. We only supply the best English oils in existence, and we believe that through our London branch we are in a position to utilise every advantage in the purchase of the oil.

**Peppermint Oil, Saxon.** The distillation of the large quantities of Mitcham peppermint plants, grown here in the neighbourhood of our factory, has this year given excellent results. The rainy weather has had the effect of producing a luxuriant growth of the plants. The yield of oil is satisfactory, and the quality of the manufactured article, of which large quantities are ready, is much superior to that previously made, thanks to the experience gained in the cultivation of the plants. We can with justice claim that our product has reached the highest degree of perfection, and we confidently hope that before long we shall be able to compete with the English distillate.

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Charabot and Hébert[1]) have recently published in a connected form the results of their examinations regarding the chemical changes

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[1]) Bull. Soc. chim. III. **27** (1902), 204.

in plants which had been submitted to the action of common salt. In our last Reports[1]) we have mentioned the most important results of these experiments which had already been published previously, so that we may now confine ourselves to referring to the last detailed publication.

Both investigators[2]) next examined the influence which a dressing with a solution of nitrate of sodium exerts on the peppermint plant. The results which they have thereby obtained agree with the changes caused in the plant by the fertilisation with common salt. From a definite stage in the development, the water-content of the plant treated with nitrate of sodium decreases in a greater degree than that of the normally cultivated plant; on the other hand, the increase of organic substance is larger in the former case than in the latter. The ester formation is also promoted by nitrate of sodium. Under the latter's influence the oil produced by the plant becomes permanently poorer in menthol and menthone, but richer in menthol esters, than the oil of the plants cultivated in a natural manner. Nitrate of sodium has also an accelerating effect on the growth of the plant.

**Petitgrain Oil, Paraguay.** The market still suffers from the pressure of the stocks accumulated both in the country of production and at the various continental ports; these stocks are sufficient to meet the demand for several years to come, and may possibly partly run to waste. This article does not keep, and for this reason is as unsuitable for speculation as is possible. As a matter of principle we never buy from any of the European speculators' stocks, but regularly import our requirements direct, as in this manner we are certain of always obtaining fresh essence.

A parcel which is now on the way includes samples of an extra quality petitgrain oil. Of this kind only about 2,000 kilos have been distilled, and its price comes decidedly higher. In our next Report we propose to return to the properties of this new oil.

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Up to now petitgrain oil has but rarely been examined chemically. The only fact really known, was, that it contains linalyl acetate as principal constituent, and further limonene and geraniol, the latter both in the free state and as acetic ester. The following particulars may form a contribution towards the knowledge of Paraguay petitgrain oil.

We used for the purpose of this examination a genuine Paraguay oil of the specific gravity 0,8912, optical rotation —0° 36′, and

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[1]) Report October **1901**, 57; April **1902**, 54.

[2]) Compt. rend. **134** (1902), 1228. — Bull. Soc. chim. III. **27** (1902), 914.

saponification number 135. At ordinary pressure it commenced to boil at 157°, at 20 mm pressure at 65°. The vapours of the drops first passing over gave an intense cherry-red colour to a chip of pine wood moistened with hydrochloric acid (pyrrol reaction). A red colour of the portions boiling at 157 to 166°, produced with fuchsine and sulphurous acid, indicated that the fraction contained aldehyde. With a solution of aniline hydrochloride in aniline, the fraction showed an intense furfurol reaction.

In order to remove this aldehyde, the first portions were treated with sodium until the latter no longer reacted upon them. The oil now boiling at 160 to 167° had the specific gravity 0,8503, the optical rotation — 13° 2′, and a pronounced pinene odour. It was however impossible, even after introducing a crystal of pinenenitroso chloride, to isolate from it a nitroso chloride of the melting point 103°, which would have proved the presence of pinene in this fraction.

The absence of the pinene reaction may perhaps be explained by the fact that the oil contained comparatively little pinene, in consequence of the presence of other terpenes, such as camphene, limonene, etc.

We were also unable to demonstrate with certainty the presence of l-camphene in petitgrain oil, although in the various attempts made to convert the camphene in the fractions boiling at 160 to 170°, by means of glacial acetic and sulphuric acids, into isobornyl acetate and isoborneol (melting point 212°), the unmistakable odour of both bodies could always be recognised. In any case, the camphene-content was not sufficient for supplying the proof of its presence in the oil.

For the test for dipentene, the portions of the higher terpene fractions, which came under consideration for this purpose, were freed from oxygenated compounds by repeated treatment with sodium. When the now only faintly active oil ($\alpha_D = + 2° 27'$) was brominated, it yielded a crystalline product which, after recrystallisation from acetic ether, melted at 125°, and is therefore to be considered as the tetrabromide of dipentene. Other terpenes, such as terpinene or phellandrene, could not be detected in this fraction.

The portions distilling under 7 to 8 mm pressure at 63,5 to 76°, showed in a marked degree the characteristic odour of petitgrain oil. Their low saponification number pointed to the presence of only infinitesimal quantities of ester. From the brisk action of sodium which already occurred in the cold, it could be concluded that the fractions consisted chiefly of an alcohol. We also succeeded in obtaining a derivative of this alcohol in the form of a solid urethane of the melting point 65°, after the oil had previously been separated by repeated careful fractional distillation into the following fractions:

1. Boiling point 185—193°; spec. gravity 0,8599; $\alpha_D - 2^\circ 14'$;
2. „ „ 193—195°; „ „ 0,8621; $\alpha_D - 1^\circ 38'$;
3. „ „ 195—198°; „ „ 0,8640; $\alpha_D - 3^\circ 36'$;
4. „ „ 198—200°; „ „ 0,8680; $\alpha_D - 4^\circ 8'$;
5. „ „ 200—202°; „ „ 0,8712; $\alpha_D - 3^\circ 14'$.

From every one of the above fractions the same phenyl urethane was obtained, which was done in the following manner: a mixture of 2 to 3 g of the oil with a little more than the calculated quantity of phenyl isocyanate, was left standing for 3 to 4 days at ordinary temperature, at first well-closed, subsequently with admission of air. As soon as the pungent odour of carbanil had completely disappeared, which occurred after 2 to 3 days, the crystalline mass, which still contained small quantities of oil, was boiled repeatedly with petroleum ether, which resulted in a separation of the phenyl urethane formed, from the diphenyl urea formed at the same time. We then exposed the solution of petroleum ether in a flat dish to spontaneous evaporation, when a very gradual separation of long needle-shaped crystals took place. The crystals dried on tiles showed the above-mentioned melting point after repeated recrystallisation from dilute alcohol.

Two analyses gave values which point to the phenyl urethane of an alcohol $C_{10}H_{18}O$.

1. 0,1420 g of the substance yielded 0,1081 g $H_2O$ and 0,3877 g $CO_2$.
2. 0,1350 g of the substance yielded 0,1025 g $H_2O$ and 0,3680 g $CO_2$.

| Found: 1. | Found: 2. | | Calculated for $C_{17}H_{23}O_2N$: | |
|---|---|---|---|---|
| C = 74,46 | 74,35 | per cent. | C = 74,70 | per cent. |
| H = 8,46 | 8,44 | „ „ | H = 8,44 | „ „ |

As the separation of the phenyl urethane had been much delayed by the admixture of oil, we modified the method indicated, in this way, that the reaction mixture was left standing for about a week in a well-closed vessel, and was then immediately brought in contact with water. The slight admixture of oil was next removed from the mixture of crystals by means of steam distillation. The crystalline mass, dried on tiles, was treated further in the manner already indicated. The crystallisation was now completed very rapidly. In an attempt to regenerate the corresponding alcohol from the phenyl urethane, by prolonged boiling with a 20 per cent potash liquor, we obtained a bright yellow lævorotatory oil, which had the odour and boiling point of linalol, and which yielded citral on oxidation with chromic acid mixture.

As, after this observation, there were reasons to assume that the urethane of the melting point 65° which was under consideration, was a derivative of linalol, it was endeavoured to obtain in the above manner a phenyl urethane from l-linalol. For this purpose, commercial linalol (produced from linaloe oil) was submitted to careful fractional distillation, at first under reduced, and subsequently at ordinary pressure. The principal fraction (spec. gravity 0,8715, optical rotation — 14°7′) boiling at 9 mm pressure at 81,5° to 82°, at ordinary pressure at 196° to 199°, yielded, as a matter of fact, the phenyl urethane whose melting point in this instance was found at 65° to 66°. An analysis gave figures which agree well with those calculated for a linalyl phenyl urethane.

0,1589 g of the substance yielded 0,1218 g $H_2O$ and 0,4365 $CO_2$.

| Found: | Calculated for $C_{17}H_{23}O_2N$: |
|---|---|
| C = 74,91 per cent. | = 74,70 per cent. |
| H = 8,51 „ „ | = 8,44 „ „ |

The body crystallises from dilute alcohol in well-defined prisms, from ether and petroleum ether in long needles. It dissolves readily in ether, alcohol, benzene, petroleum ether, chloroform, acetic ether, methyl alcohol, and glacial acetic acid, but is almost insoluble in water. The best medium for crystallisation is therefore dilute alcohol.

According to the observations which we have up to now made the phenyl urethane (assuming that it actually proves to be a derivative of linalol) might be found very suitable for the rapid and certain detection of this alcohol. At any rate, we have been able to isolate the phenyl urethane of the melting point 65° with facility from a portion of 1,5 grams of a fraction containing linalol. Subsequent tests with d-linalol from coriander oil (specific gravity 0,8687, optical rotation + 12° 51′) have produced the same derivative of the identical melting point. We shall not fail to follow up this interesting discovery, and therefore reserve this body for further work.

It has not yet been possible to obtain in the above manner a solid phenyl urethane from geraniol. Geraniol reacts with phenyl isocyanate with considerable evolution of heat. We mixed equal molecules of geraniol and phenyl isocyanate whilst cooling with ice, and left the mixture standing for 7 days at ordinary temperature. After 3 days a solid product began to separate out, which was clearly diphenyl urea, and which had certainly been formed by the geraniol splitting off water. As the final product of the reaction, a bright-yellow, viscid oil was obtained, which up to now has shown no tendency to crystallise. This also will be submitted to further examination.

We also succeeded in detecting d-terpineol in petitgrain oil, like in neroli oil. This body, which may not be without importance for the odour of petitgrain oil, was isolated from a fraction boiling under

8 mm pressure at 88 to 93°. When distilled at ordinary pressure, the following fractions could be distinguished:

1. First runnings — 205°, 2. 205—217°, 3. 217—221°,
4. 221—224°.

Of these fractions, the third solidified in the cold, the second and fourth only when a crystal of terpineol was introduced. The constants of the oil boiling at 217 to 221° were as follows: specific gravity 0,9286; optical rotation + 30° 56′. The melting point of the solid terpineol was found at 34°. With phenyl isocyanate it formed a phenyl urethane of the melting point 110°, which, after recrystallisation from alcohol, melted at 112°.

The presence of free d-terpineol of the melting point 35° in petitgrain oil has therefore been demonstrated.

Fractions which came under consideration for the boiling point of citronellol, were heated for a prolonged time with concentrated formic acid, for the purpose of removing the other alcohols contained in them, such as geraniol, linalol, and terpineol. The reaction-product thus obtained was a thick oil, which commenced to boil at 195°, at 8 mm pressure, and which therefore only consisted of products of polymerisation of the above mentioned alcohols.

Primary alcohols could not be isolated either by treating some of the fractions (especially the one boiling between 83 and 98° at 8 mm pressure) with phthalic anhydride.

As Passy¹) had already observed, geraniol and its acetic acid ester represent a not unimportant constituent of petitgrain oil. As, however, no proofs had yet been produced in support of this statement, we wish to add here briefly the results of our examination concerning these two bodies.

When distilling the portions boiling above 90°, at 8 mm pressure, we arrived at fractions which, according to their odour, ought to consist of fairly pure geranyl acetate. A faint but yet clearly discernible blue fluorescence, which was characteristic of all fractions passing over between 100 and 114° at reduced pressure, might perhaps be caused by an infinitesimal admixture of anthranilic acid ester. By sufficiently repeated fractionating in vacuo we succeeded in obtaining a fraction very rich in ester, whose constants are exceptionally close to those of pure geranyl acetate. The physical properties were as follows: Specific gravity 0,9178, optical rotation + 1° 6′, saponification number 266,8, the latter corresponding to a content of 93,4 per cent of geranyl acetate. The acid obtained by saponification of this fraction was converted into the silver salt, which, after recrystallis-

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¹) Bull. Soc. chim. III. **17** (1897), 519.

ation from hot water, was sufficiently pure for analysis. The determination of silver made with it gave the following figures:

0,2031 gram of the substance yielded on heating 0,1310 gram Ag.

| Found: | Calculated for $C_2H_3O_2Ag$: |
|---|---|
| Ag = 64,50 per cent. | 64,67 per cent. |

The value found therefore agrees with that calculated for silver acetate. The alcohol obtained from the saponification distilled at 11 to 12 mm pressure at 111 to 112°. Its specific gravity was 0,8842, its optical rotation $+0° 18'$. After purification by the calcium chloride compound, the specific gravity was 0,8830, the optical rotation almost 0°. The diphenyl urethane of this alcohol melted at 82°. The presence of free geraniol was also proved by the diphenyl urethane. For this purpose a fraction was used which boiled at 90 to 96°, at 6 mm pressure.

We have also by the odour established the presence of a basic body in petitgrain oil. It can be extracted from the fractions of the boiling point of linalol, by means of dilute sulphuric acid, and it appears to have a special influence on the odour of petitgrain oil.

It follows from the foregoing, that we have detected in Paraguay petitgrain oil: furfurol, l-pinene (?), l-camphene (?) dipentene, an alcohol $C_{10}H_{18}O$ (l-linalol), d-terpineol (melting point 35°), geraniol, geranyl acetate, and also traces of a basic body.

**Pine-needle Oils.** The fine distillates from the needles of *Pinus Pumilio* and *Abies pectinata* could in the spring only be obtained with difficulty in sufficient quantities, and that at higher prices, owing to the unfavourable weather prevailing in the Alps. On the other hand, the distillate from the cones of the last-named species was abundant, and could be purchased at favourable prices. The very advantageous oil of the Siberian fir, which is now distilled in Russia on a large scale and of faultless quality, has recently become very popular. It is also eminently suitable for pine-odour soaps, for which purpose it is generally diluted with a small quantity of lavender oil, so as to soften the pungent odour. This oil can be obtained in any quantity.

**Oil of Pseudocymopterus anisatus.** Brandel[1]) has produced the oil of *Pseudocymopterus anisatus* Gray (C. and R.) which grows in the wild state in the Western United States of America, in a yield of 4 grams from the whole plant.

The odour of the fruit and of the oil resembles that of anise in a marked degree; the specific gravity 0,978 (20° C) also closely agrees

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[1]) Pharm. Review **20** (1902), 213.

with that of the oils of anise, star-anise, and fennel. But in spite of this the oil does not solidify at a low temperature, a fact which is attributed to the presence of methyl chavicol.

**Rose Oil (artificial) "Schimmel & Co.".** The precarious conditions prevailing on the Bulgarian market of rose oil have led to many trials on a larger scale with our excellent article protected by the German patent No. 126736. We would especially recommend the product free from stearoptene, from which every difficulty with regard to the solubility is excluded. The perfumer can be absolutely certain that perfume-mixtures, solutions of essential oils, or extracts, which contain our artificial rose oil, will neither become cloudy in the cold, nor separate out stearoptene in the well-known flakes.

Experiments which have been made show that our oil, free from stearoptene, is soluble in every proportion in 96 per cent alcohol.

It is further dissolved in the proportion of

about 10 grams oil in 1 kilo 90 per cent alcohol
" 4 " " " 1 " 80 " " "
" 1,5 " " " 1 " 75 " " "

Our artificial rose oil has this great advantage over the natural Turkish oil, that it is always of exactly the same composition, and that a constantly uniform effect can be absolutely relied upon. We need not waste words on the considerable differences which exist in Turkish oils. The confidence in the latter is disappearing more and more, in view of the attempts incessantly made with new adulterants.

**Rose Oil, Bulgarian.** This year's distillation of roses has, according to reliable estimates, given a total yield of 3200 kilos rose oil, a result approximately the same as that of the previous year. The prices paid by Bulgarian firms fluctuate between 580 and 600 marks, from which fact a conclusion can be drawn as to the quality of the ordinary market oils offered. We are assured that the demand for rose oil is very brisk, and that the prices have an upward tendency.

The measures to be taken by the Bulgarian Government, for the purpose of consolidating the rose oil trade, are still in abeyance. The intention of the Government is to protect the small distillers from impositions by the large traders, by means of the distribution of exact instruments of precision, such as scales, thermometers, etc., so that every producer may be able to check the values of gravity and congealing point given by the buyer who, it is said, often makes use of unreliable instruments. According to a notice which reached us early in July, the Minister of Finance, in whose department the Customs are, has directed that all coppers and cases of rose oil intended for export shall be marked with the Government seal. But in order to show that the seal only guarantees the Bulgarian origin, and not the quality, the Minister has given directions for cardboard labels with the words "Essence de Rose, provenance bulgare" (Rose oil of Bulgarian origin), which are attached to the neck of every copper by means of a cord, of which the ends are attached to the cover with the Government seal. The seals have been ordered in various dimensions, according to the size of the coppers, and are printed with the above-mentioned text in the French language.

It will be seen at the first glance, that these measures are absolutely valueless, so long as the contents are not examined and guaranteed as pure. They may even be used as a cloak for the purpose of carrying on the adulteration with all the more security, and to some extent under official protection. No sensible person will on these grounds accept rose oil as "pure", but, on the contrary, will only approve it, if the contents of the copper have been examined and acknowledged, as far as the existing state of knowledge and experience admits.

It has already been published in the technical press ("The Chemist and Druggist", No. 1176 Vol. LXI), that a Mr. Chier, a gentleman from the South of France, has, jointly with native Bulgarians interested in rose oil, erected in the neighbourhood of Karlovo a factory for the distillation of rose oil by means of modern steam apparatus, and commenced working there. It was intended to distil in this factory about 450 tons of roses with 4 stills, and contracts for the roses had been made at high prices before the time of the harvest. But Mr. Chier was only able to deal with one third of this quantity, and the rest is said to have gone to waste.

The whole enterprise has ended in complete failure, and Mr. Chier is held responsible for the loss by his Bulgarian partners and the farmers who supplied the roses. The latter have not been paid for their deliveries of flowers, and have made a most unpleasant riotous scene in the factory, which necessitated the interference of the police. It is stated that both the factory and the oil found in it have been seized by the Government.

With regard to the adulteration of rose oil, our principal purveyor of that article writes to us:

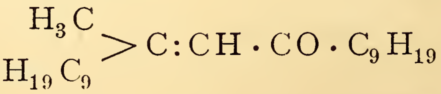
> "We think it necessary to mention to you a new adulteration of rose oil, even at the risk of wearying you.
>
> It cannot be denied that pure rose oil with a low congealing point is preferred to that which congeals at a higher temperature. Now, as the addition of geranium oil lowers the congealing point, and as the latter at + 20° C. is generally accepted as characteristic of pure oil, the persons who practise these adulterations found about a year ago means by which to remedy this evil.
>
> They add to rose oil, which has been adulterated with geranium oil, a mixture of salol and antipyrine, which has the property of bringing the congealing point to the desired height.

This method of adulteration has acquired fairly large dimensions, but as both bodies can be easily detected, the persons who practise this method will soon be compelled to look about for some other means."

**Rose Oil, German.** The rose plants of our Miltitz fields have been trimmed considerably during the spring of this year, for horticultural reasons, and their yield has consequently been only one fourth of the normal.

The gathering of the flowers was much delayed by the inclement weather, but was finally accomplished under exceptionally favourable conditions, and the result was a faultless flower-material. In consequence of orders received, a considerable portion was worked up for rose-pomade and rose-water, and only a few kilos of rose oil have been distilled, of which the bulk had also been sold in advance. For this reason we can only offer small quantities of the latter, and that without engagement.

**Oil of Rue.** C. Mannich[1]) has produced a few derivatives of the ketones present in oil of rue. Methyl nonyl ketone, which forms the principal constituent of the oil, is converted on reduction into the corresponding secondary alcohol, methyl nonyl carbinol (boiling point 120° at 14 mm pressure). Its acetyl and benzoyl derivatives boil respectively at 147—149° (42 mm) and 197,5—200° (15 mm pressure). Its oxalate melts at 34,5°, the phenyl carbamate at 36,5—37°. Sulphuric acid splits off water from the ketone, with formation of 2-undekylene $CH_3 \cdot CH : CH \cdot C_8H_{17}$ (boiling point 192—193°) and 2-undekanyl ether $[CH_3 \cdot CH(C_9H_{19})]_2O$, boiling point 198—200°. 2-Undekylene absorbs 2 atoms bromine; the dibromide boils at 145 to 146°, at 9 mm pressure. When treated with potash liquor, the bromide is converted, with liberation of 2 molecules hydrobromic, acid into 2-undekin $CH_3 \cdot C \vdots C \cdot C_8H_{17}$, an unpleasantly smelling liquid of the boiling point 199—201° (81,5° at 10 mm pressure). Methyl nonyl ketone, when treated with hydrochloric acid gas, splits off water and yields a liquid product $C_{22}H_{43}OCl$; from this results, upon distillation in vacuo, the ketone



$$\begin{matrix} H_3C \\ H_{19}C_9 \end{matrix} \!> C : CH \cdot CO \cdot C_9H_{19}$$

of the boiling point 214—216° at 10 mm pressure.

The methyl heptyl carbinol produced in a manner analogous to that of methyl nonyl carbinol, has the boiling point 193—194° (87,5° at 10 mm pressure); the 2-nonylene $CH_3 \cdot CH : CH \cdot C_6H_{13}$ obtained from it boils at 147—148°. The oximes of both ketones yield on strong reduction the corresponding amines. 2-Undekylene amine boils

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[1]) Berliner Berichte **35** (1902), 2144.

at 26 mm pressure at 113—114°; 2-nonyl amine at 11 mm pressure, at 69—70°. The examinations regarding methyl nonyl and methyl heptyl ketones are continued.

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**Sandalwood Oil, East Indian.** The prices of all the various kinds of sandalwood have hardened during recent times, chiefly owing to a report originating from Mysore, that a disease has broken out among the sandal trees which is causing great anxiety.

We reproduce a literal translation of this report exactly as it has reached us:

> We hereby beg to inform you that a severe disease has appeared among the sandal trees. It was first observed two years ago in Coorg, whilst in Mysore little was seen of it. No further notice was taken of it until it occurred in Coorg with such severity during the last six months, that all the trees in the provinces were threatened with destruction. This alarmed the Coorg Government, which therefore instructed Mr. Barber of Ooty to proceed to Fraserpett and examine the trees, in the hope that he would be able to discover a remedy to arrest the disease. On his return he reported that the matter was very serious, and that up to that time he had not been able to undertake anything against it. Eight days ago Mr. Butler of Dehra Dun was sent to the plantations by the Indian Government, also with the view of examining the trees. He is at this moment still at Fraserpett, and we will endeavour to see him on his return.
>
> With regard to Mysore, we believe that the disease has made its appearance throughout the district, but not as yet to such an extent as in Coorg. We have during the last 3 months paid special attention to this matter, and we are in a position to state that the disease is spreading rapidly. Yesterday evening we noticed in one hedge 6 trees, standing at distances of 20 yards, of which 5 were dead, whilst the sixth also appeared already to be attacked.

If this information should be confirmed, the next Government auctions in India would in any case be very animated, and the price-cutting in sandalwood oil would come to a sudden end.

According to information received from India, the following quantities will be offered for sale at this year's auctions: —

| | | | | | |
|---|---|---|---|---|---|
| 24th | November | in | Hunsur . . . | 450 | tons |
| 27th | „ | „ | Seringapatam . | 200 | „ |
| 1st | December | „ | Bangalore . . | 78 | „ |
| 4th | „ | „ | Hassan . . . | 200 | „ |
| 8th | „ | „ | Chikmagalur . | 250 | „ |
| 12th | „ | „ | Shimoga . . . | 450 | „ |
| 16th | „ | „ | Sagar . . . . | 250 | „ |
| 20th | „ | „ | Tirtahalli . . | 180 | „ |

Total in 1902, 2058 tons,
against in 1901, 2215 „

The quantity is somewhat scanty, probably for the purpose of preventing a further drop in the value. No further details have yet been received as to the various sorts of which they are composed.

In our last Report we mentioned on page 63 that "the methods which are nowadays employed for testing the quality of sandalwood oil, have been devised by us". We notice that E. Parry[1]) takes umbrage at this remark, in which he sees an attempt to belittle his services in the examination of sandalwood oil, which surprises him all the more, as we had hitherto not denied him our acknowledgments in this matter. We admit that our above-mentioned words may possibly seem to imply that we attach no value to the method[2]) of quantitative estimation of santalol first communicated by Parry, but this is not by any means the case. On the contrary, we consider the determination of santalol the most important help in the analysis and in judging the value of sandalwood oil, and we fully appreciate Parry's work on this subject. Now, while we fully recognise Mr. Parry's merits with regard to this important method, we believe that there can be no impertinence on our part in reminding him, that the process of determining the alcoholic constituents of essential oils by acetylation and subsequent quantitative saponification of the acetylised oil, was first of all proposed by us as a universal method for essential oils, and elucidated by various examples[3]). The application of this method to sandalwood oil lay on the very path which we had indicated.

For this reason we believe that we have a claim to the santalol-determination, and all the more so, as the quantitative acetylation of sandalwood oil by means of acetic anhydride instead of acetic acid, which we indicated shortly after Parry's communication, has, as far as we know, been more generally adopted as representing a more convenient working method.

**Sandalwood Oil, West Indian.** In his first treatise[4]) on West Indian sandalwood oil, E. Deussen mentions that, on introducing hydrochloric acid gas into the dextrogyrate oil ($\alpha_D + 27^\circ 18'$) diluted with ether, he obtained a lævogyre cadinene hydrochloride ($[\alpha]_D^{9,5^\circ} = -36,65^\circ$ in chloroform). In the author's opinion, the dextrogyre cadinene present in West Indian sandalwood oil is in this case inverted to lævogyre cadinene by the action of the hydrochloric acid. In the

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[1]) The Chemist and Druggist **60** (1902), 866.

[2]) Pharm Journ. (London), **55** (1895), 118. The conversion into santalyl acetate by heating with acetic acid to 150°, has been adopted by Parry from Chapoteaut (Bull. Soc. chim. II. **37** (1882), 303.

[3]) Report October **1894**, 62.

[4]) Archiv d. Pharm. **238** (1900), 149.

further course of his examination[1]), E. Deussen attempted to produce the dextrogyre cadinene in the pure state from West Indian sandalwood oil by repeated fractional distillation over sodium. The hydrocarbon thus obtained had the composition $C_{15}H_{24}$, and showed the following constants: boiling point 260° to 261°, at atmospheric pressure; $d_{15^\circ} = 0{,}9247$; $\alpha_D = + 50^\circ$; $n_D = 1{,}5108$. With hydrochloric acid it formed a hydrochloride melting at 118°.

He further obtained a hydrocarbon of the formula $C_{15}H_{24}$ which had a lower dextrorotatory power; it showed a great tendency to become resinified, and yielded no solid hydrochloride. This hydrocarbon agrees in its properties with galipene.

The lævogyre cadinene hydrochloride obtained from West Indian sandalwood oil yielded, by splitting off the hydrochloric acid, lævogyre cadinene of the boiling point 264° to 266° (only the bulb of the thermometer in the steam); $\alpha_D = - 89^\circ$ to $108^\circ$.

**Spearmint Oil.** The prices of this American speciality have gradually advanced more than 100 per cent, in sympathy with those of peppermint oil, and it is feared that the quantities produced, jointly with some stocks left over from the previous season, will not be sufficient to meet a normal demand. In the further course of business the quotations may possibly go still higher.

**Star-anise Oil.** Since our last Report, the prices of this important article have been materially unchanged. The oil of Chinese origin reached its lowest level at 4/2 per lb.; that from Tonquin at 12 francs per kilo, — but even those figures were not able to create considerable demand for it, a fact which clearly shows to what extent the trade has lost interest in an article which, at one time, was one of the pet objects of speculators.

We prefer, now as formerly, the Tonquin oil, on account of its higher anethol-content; the trade, however, following ancient habits, continues to admire the Chinese product, and frequently gives preference to brands which have been proved to have been positively adulterated.

A detailed examination of star-anise oil has recently been published by Tardy[2]). His material was an oil from which the greater part of the anethol had been removed, and which showed a lævogyration of 3° 15′. In addition to the already known bodies[3]) pinene, phel-

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[1]) Archiv d. Pharm. **240** (1902), 288.

[2]) Thèse pour l'obtention du diplôme de Docteur de l'Université de Paris, p. 22 (1902).

[3]) Report April **1893**, 62; October **1895**, 7.

landrene, methyl chavicol, hydroquinone ethyl ether, anisic aldehyde and anisic acid, the author detected as new constituents, anisic ketone, a sesquiterpene with a rotatory power of — 5°, and a body of the melting point 212°, which is perhaps identic with the body[1]) melting at 213° discovered in fennel oil. According to Tardy, star-anise oil also contains terpineol, but of this he submits no evidence, beyond the boiling point 216 to 218°; a definite proof of his assertions is therefore still in abeyance.

Tardy was not able to confirm the presence of safrol which Oswald[2]) had considered very probable.

The oil from the leaves and fruit of *Illicium religiosum*, which is designated as Japanese star-anise oil, differs widely from Chinese star-anise oil. On a previous occasion[3]) we have already given some information on this point. Eykman[4]) has examined this oil more thoroughly, and has detected in it a terpene, eugenol, and safrol. Tardy gives some particulars on the composition of the oil from the fruit. He extracted the dried and pulverised fruit successively with petroleum ether, alcohol, and water.

The extracts obtained with alcohol and water were solid amorphous masses, but with petroleum ether an oil was produced, which, after purification by destillation in vacuo, turned the polarised light 1° 50′ to the left. By extracting the oil with potash liquor, eugenol could be isolated, in addition to a small quantity of fatty acids; it could be converted into vanillin, which was clearly recognised by its odour. From the low boiling fractions of the oil not absorbed by potash liquor, the author obtained two hydrochlorides.

The fraction of 170 to 177° consisted chiefly of cineol. It was converted into the bromide and regenerated from the latter; a small quantity could then be obtained in the solid state.

The fraction of 220 to 230° yielded on oxidation a small quantity of anisic acid, from which the author draws the conclusion, that the presence of anethol, or at least of methyl chavicol, might not by entirely denied. Oxidation of the fraction 230 to 235° yielded piperonylic acid of the melting point 228°, which points to the presence of safrol. The higher fractions contained chiefly sesquiterpenes.

The residue, which was considerable, yielded on saponification palmitic acid of the melting point 62°.

**Vetiver Oil.** The consumption of this oil shows a large increase in recent times, probably due to the constantly growing taste for intense

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[1]) Report October **1897**, 28.

[2]) Archiv d. Pharm. **229** (1891), 95.

[3]) Bericht September **1885**, 29; Report October **1893**, 50.

[4]) Rec. trav. chim. des P. B. **4** (1885), 32. — Berliner Berichte **18** (1885), Ref. 281.

and durable perfumes. Such, in the true sense of the word, is our distillate, especially if it is compared, with regard to its richness, with the imported commercial oils from Réunion and the East Indies.

Genvresse and Langlois[1]) discovered in vetiver oil a sesquiterpene of the boiling point 262 to 263°, at 740 mm, which did not completely agree with any of the hitherto-known sesquiterpenes. The oil also contained an ester of the boiling point 160° at 10 mm, which on saponification yielded an alcohol of the formula $C_{15}H_{26}O$, and an acid $C_{15}H_{24}O_4$.

**Wintergreen Oil.** Higher prices for genuine oil are reported from America. In consequence of important contracts we still supply the oil, until further notice, at a moderate price.

Cosma[2]) recommends artificial oil of wintergreen for internal administration in rheumatism and various kinds of neuralgia. The results obtained with it are said to be much superior to those obtained with sodium salicylate. The daily dose may be up to 8 grams. Up to now the ester was used almost exclusively as an embrocation.

**Wormwood Oil.** In a few weeks' time we expect to have again an excellent assortment of this oil, and also a stock of the American distillate, but the prices will be comparatively high. The fine French wormwood oil of this year's distillation, also produced from the cultivated herb, is already on the way. Algiers also supplies a product well worthy of attention.

In spite of the fact that in France the use of wormwood oil for articles of consumption is now prohibited, fairly large quantities are still consumed in other countries. The prohibition is exclusively directed against the increasing use of absinth, but no objections have as yet been raised against the employment of very small doses of the oil, such as for example in the preparation of wormwood-wine.

**Ylang-Ylang Oil (artificial) "Schimmel & Co".** The increased demand for fine natural oils has also greatly promoted the use of our beautiful artificial product, whose quality constantly finds the greatest appreciation.

This case proves once more, that both the natural and the artificial oil are qualified to exist alongside one another, without the one affecting the consumption of the other. The creation of cheap and

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[1]) Chemiker-Zeitung **26** (1902), 501.

[2]) Münch. Med. Wochenschrift **1902**, No. 26; according to Pharm. Zeitung **47** (1902), 542.

yet aromatic artificial flower oils has rendered it possible for the perfumer to use the perfumes of luxury, such as ylang-ylang, also for less expensive products, and no one will certainly maintain that this has had an injurious effect on the perfumery industry.

The "Sartorius" distillate is the example upon which we have based our ylang-ylang oil "Schimmel & Co.". We make bold to say, without presumption, that a certain degree of expert knowledge is required to distinguish the one from the other.

**Ylang-Ylang, "Sartorius" I.** The consumption of the finest ylang-ylang oils has increased to such a considerable extent, that the yield of flowers in Manila proved to be inadequate, and led to a rise in the prices. For this reason, an increase in the quotations of the oil could not be avoided. The competition in the purchase of the flowers was so keen among the different distillers, that the latter had often to forego every profit, if they did not wish to demand prices for their oil which were almost incredible.

In view of this critical state, our friends in Manila have made a scheme for increasing the production, which within the next few months may become an accomplished fact, provided they succeed in remaining victors in the struggle for the flower-material.

Our friends hope that an increase of 50 marks per kilo will be found sufficient, and they have promised us most faithfully to return to the old selling price as soon as the situation in Manila allows this at all. Above all they will endeavour, by using the most extreme care in the selection of the flowers, and with the help of improved distilling plant, to produce in the future as in the past a quality which stands unparalleled.

On the occasion of the recent visit of one of the partners of the Manila firm, we have thoroughly discussed the situation with him, and we have received his assurance that every endeavour will be made to meet the increased demand. A consignment which at this moment is being landed at Marseilles, has again been sold in advance. Firm prices cannot be quoted at present.

## Novelties.

**Oil of Bystropogon origanifolius.** We received as a novelty from Mr. L. Rigal, Arona Cristianos, Teneriffe, an oil which had been obtained from *Bystropogon origanifolius* L' Hérit. (Labiatae), a shrub often met with in the Canary Islands, and whose odour was very similar to that of oil of pennyroyal. This oil has a bright yellow colour, and shows the following constants: Specific gravity 0,9248

(15°); optical rotation + 2° 57′; acid number 0; saponification number 11,1, after acetylation 53,83; index of refraction $n_D$ 1,48229; soluble in $2^1/_2$ volumes 70 per cent, and in 0,7 volume 80 per cent alcohol. The oil distilled between 162 and 234°.

From the 75 g oil obtained, $4^1/_2$ g of a fraction boiling at 162 to 182° were isolated, whose high rotatory power (in a 20 mm tube = — 10° 34′) pointed to limonene. As a matter of fact it yielded on brominating a crystalline product, of which the melting point, after repeated recrystallisation, was found at 104°. This proves the presence of limonene. The principal fraction of the oil, boiling at 219 to 223°, which amounted to 30 g, had a pronounced odour of pulegone; its specific gravity was 0,9279, the optical rotation + 20° 21′. From the physical properties of this fraction it was concluded that it contained pulegone. The oxime obtained from it by Wallach's method melted within 85 to 119°, which pointed to a mixture of two oximes. After repeated recrystallisation from dilute alcohol a body was obtained melting at 114 to 116°.

But the absolutely certain proof of the presence of pulegone was found in the oxime containing water, which melted at 157°; this was obtained by Beckmann and Pleissner's method from the fraction of the boiling point 223 to 234°.

Finally we succeeded in detecting menthone (by its semicarbazone melting at 180 to 181°) in a fraction boiling at 205 to 215°.

The oil consists chiefly of pulegone and menthone; the content of limonene is but small.

**Oil of Mandarin leaves.** In our Report of April last we mentioned an oil designated as "petitgrain mandarinier", originating from the South of France, which had clearly been distilled from the leaves and the twigs carrying unripe fruit, of the mandarin tree. We are indebted to the kindness of Mr. Pablo Journet of Carcagente, for a sample of a similar oil, distilled only from the leaves of the mandarin tree. This gentleman obtained from 300 to 350 kilos selected leaves about 1 kilo oil, which during the distillation separated into two portions, one sinking in water, and the other of less specific gravity.

The sample sent to us was an average sample of the whole distillate. The oil has a yellowish colour, with a strong blue fluorescence, and refracts the light very strongly; its odour is somewhat like that of neroli, yet differing from the latter in a marked degree. Its specific gravity was found to be 1,0142, at 15°, and the rotatory power + 7°46′. It dissolves in 6 to 6,5 volumes 80 per cent alcohol, and consequently does not show any material difference in its physical properties from the oil designated as petitgrain mandarinier. Like the latter, it is very faintly acid, and has a very considerable ester-content (ester number 216,23), which, however, is still higher than that of petitgrain mandarinier. We are not yet in a position to supply further details on the character of this ester.

In accordance with the foregoing, oil of mandarin leaves appears to have a composition which is entirely different from that of oil of bergamot leaves, concerning which we give some information elsewhere.

## Notes of recent scientific work concerning terpenes and terpene derivatives.

In the province of literature we have to record the publication, which has just taken place, of an enlarged edition of Heusler's work on terpenes, which at the time was so favourably received in interested circles. This new edition has been prepared by Professor Pond of Philadelphia, who has become known as Wallach's collaborator; it is a translation of the original German work into English, which in suitable places has been enlarged, occasionally to a very considerable extent, by additions which have become necessary since Heusler's work first appeared. The English (and American) literature has received a valuable addition by the publication of this enlarged edition, for, apart from a few short abstracts which had been given in works on essential oils, a treatise in the English language, dealing with the whole question of terpenes, had always been wanting. But as the book gives information on the results obtained during the last few years, it will also be useful to German chemists who have full command over the English language.

We believe that we may abstain from a detailed discussion of the work, as this will no doubt appear from a qualified hand in another place.

A long lecture on "The Industry of Perfumes" has been held before the Société chimique de Paris by J. Dupont[1]). After a short criticism of Klimont's experiments to adopt "aromatophorous" groups in aromatic bodies, based upon Witt's example in the case of pigments, the lecturer turned to the nitrogenous bearers of perfumes which have in recent times claimed a constantly growing amount of attention, especially the indol derivatives and ptomaines produced by animals and plants during the vital process, or after death. Of the three sharply defined branches of the technical science of aromatics, viz., the manufacture of natural floral odours, the synthetic production of

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[1]) Bull. Soc. chim. III. **27** (1902), supplement to No. 15.

artificial aromatic bodies, and the perfumery industry utilising the products of both, the lecturer discussed the first two in detail.

The oldest, most largely used, and most improved method of obtaining flower-oils, is the method of steam-distillation, which produces not only valuable oils, such as the oils of orange-flowers, roses, and lavender, but also aromatic waters. Chemical analysis of the numerous oils obtained by this process has brought to the light a large number of components, of which, in spite of the activity of scientific investigation of the present day, we have as yet no full and complete knowledge. By methods of examination of an increasingly detailed and exact character, it has in recent times been possible to isolate from many oils certain constituents which occur only in most subordinate quantities, yet have an exceptionally important effect on the odour, — and to estimate the part played by them in the composition of the perfume. Such, for example, are nonylic aldehyde and other constituents in rose oil, or methyl anthranilate in neroli oil. Another process is the so-called enfleurage, based on the property which natural odours have, of becoming incorporated in fats. The enfleurage process is used especially for flowers, such as the jasmine and tuberose, whose aroma is sensitive to high temperatures. The flowers are placed in vaseline or melted fat, or wrapped in cloth prepared with fat, and fresh quantities of flowers are constantly brought into contact with the fat until the latter is saturated. When clarified by filtration, the fat, laden with perfume, represents a most important article of commerce. By treatment with dilute alcohol (which does not dissolve the fat), the perfume can be extracted from these flower pomades, and is thus offered to the perfumer in a convenient form. The most recent method is the one of extracting the aroma from the material by means of volatile solvents, such as ether, or more generally petroleum ether. On evaporating the latter, usually in vacuo, waxy residues remain behind, from which, as in the case of pomades, the pure flower oil can be isolated in the most concentrated form without fatty secondary odours.

The published statistics throw light on the great development of this industry in the departments of Southern France. In the competition with foreign products, the lecturer sees a great impediment in the high duty on alcohol, which frequently exceeds the value of the article itself, and he strongly advocates the complete or partial abolishment of this duty.

For our present knowledge of the chemical composition of perfumes and essential oils, so Dupont continues, we are indebted to the unexampled development of organic chemistry within the last decades. And whereas the first investigations in this domain were preferably carried on by French chemists, in recent times German chemists have taken a leading part. It is a matter of importance in political economy, that the production of most perfumes by synthetical or artifical means has rendered it possible to effect a very considerable reduction in the prices of the aromatics which up to that time had been looked upon as a privilege of the wealthy classes; and further that, in spite of the fact that the artificial article in many cases (as with vanillin or coumarin) is richer than the natural product, yet both move onwards, each following its own path. The cultivation of vanilla has not been curtailed by the discovery of vanillin, although in the case of dye stuffs restriction has followed the competition-struggle between the natural and the artificial product; and of coumarin, fresh sources are again and again discovered in nature, which are successfully turned to account. But scientific research became supremely important when it was a question of detecting foreign admixtures in, or adulterations of, the products of the perfume industry.

The lecturer further discusses in detail the synthetic production of the most important perfumes, which we can here only mention briefly. He describes for example the production of artificial musk by Baur, by nitrating certain homologues of benzene; that of ionone, obtained in 1893 by Tiemann by converting the condensation product of citral with acetone by means of dilute sulphuric acid; further, the production of vanillin, also by Tiemann, first from the cambial sap of conifers, subsequently from eugenol, and later still from isoeugenol; that of heliotropin or piperonal, by oxidation from safrol or isosafrol; and finally that of coumarin, by condensation of salicylic aldehyde with sodium acetate and acetic anhydride, and of many other aromatics which are important for purposes of perfumery.

It will be seen that Dupont's lecture deals almost exclusively with known facts; at the same time we believe that, in reproducing the main points of his paper, we may have communicated matter which will not be entirely devoid of interest to at least some of our readers.

C. Mann[1]) has communicated a method for the quantitative estimation of essential oils in spices, or in any other drug whose content of essential oil has to be determined. His method is as follows: the body to be examined is pulverised as required, mixed with small pieces of pumice stone, and exhausted in the usual manner by steam distillation. To the aqueous distillate, conveniently cooled to about + 10°, 25 per cent of its weight of pure common salt are added, and then the solution is extracted for half an hour with a measured quantity rhigolene, i. e. very volatile petroleum ether of the boiling point of about 20 to 35°. The extraction-liquid, increased

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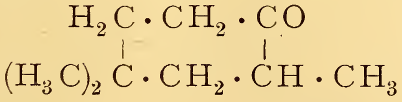
[1]) Archiv d. Pharm. **240** (1902), 149.

by the absorbed essential oil, is carefully measured in a graduated tube and made up to the original quantity; an aliquot part of it is next placed in a weighed glass, the solvent evaporated by means of a current of air passing over it, and the weight of the residue ascertained, from which the content of essential oil in the drug can be calculated forthwith.

Mann emphasizes especially as particular advantages of his method (which is said to be also suitable for the quantitative estimation of essential oils in liqueurs, soaps, and perfumes), that with the use of rhigolene it is not necessary to dry the extract (a process which gives rise to inaccuracies), because the rhigolene, when shaken with water, does not absorb any of the latter. Further errors are prevented by the use of a definite quantity extraction-liquid, and by taking an aliquot part of the solution of essential oil for the determination; finally, the exact moment when the whole of the rhigolene is evaporated can be fixed with great precision, and errors in weighing caused by the presence of some remaining solvent, can thus be entirely obviated.

## Hydrocarbons.

Cyclogeraniolene. The similarity in the physical properties between pulegene and Tiemann's cyclogeraniolene, as also the similarity between the ketonic acids formed from both hydrocarbons on oxidation, led Wallach to the conclusion that a thorough comparison of the two compounds was necessary, by which the absolute difference between the two bodies was established[1]). Tiemann's assertion that, when cyclogeraniolene was produced from acyclic hydrocarbon, chiefly $\alpha$-cyclogeraniolene was formed, could be confirmed; the same investigator was also able to demonstrate, that the $\alpha$-compound yields a nitrosochloride and a nitrosate characterised by the property of only dissolving with great difficulty. When boiled with alcoholic potash liquor, these compounds yield trimethyl cyclohexenonoxime $C_9H_{14}NOH$, which, on being decomposed with acids, yields the unsaturated trimethyl cyclohexenone $C_9H_{14}O$. This ketone passes over by reduction into saturated trimethyl cyclohexanol, which can be converted by oxidation into trimethyl cyclohexanone



$$\begin{array}{l} \qquad\quad H_2C\cdot CH_2\cdot CO \\ \qquad\qquad | \qquad\qquad\; | \\ (H_3C)_2C\cdot CH_2\cdot CH\cdot CH_3 \end{array}$$

That this body actually represents a derivative of $\alpha$-cyclogeraniolene, is proved by the fact, that on oxidation it first of all yields a ketonic acid with the same content of carbon, but next $\beta$, $\beta$-dimethyl adipic acid.

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[1]) Liebigs Annalen **324** (1902), 97.

Wallach states in another treatise[1]) that $\alpha$-cyclogeraniolene is identic with the trimethyl cyclohexene which can be obtained from dihydroisophorol by the action of phosphorus pentoxide.

Pinene. By boiling one part arsenic acid with four parts pinene, Genvresse[2]) had on a previous occasion obtained considerable quantities of lævogyre terpinene. But if 1 part crystallised $AsO_4H_3$ was made to react with 40 parts oil of turpentine[3]), the actual odour of turpentine no doubt disappeared, but the pinene itself remained unchanged. The characteristic odour of turpentine oil must therefore be due to a contamination which is removed or destroyed by small quantities $AsO_4H_3$.

From pinene hydrochloride and benzene, Konowaloff[4]) obtained by Friedel-Crafts' reaction a saturated hydrocarbon, phenyl dihydropinene, boiling point 286° to 291° at 745 mm; $d\frac{20^\circ}{0^\circ}$: 0,9594; $n_{D\,20^\circ}$: 1,52691.

If pinene nitrosochloride is heated with an equivalent quantity potassium cyanide in the presence of strong alcohol, there is formed (as Tilden and Burrows[5]) have observed), a pinene nitrosocyanide $C_{10}H_{16} \cdot NO \cdot CN$ of the melting point 170°, whose constitution is, however, still doubtful. This cyanide does not change if it is boiled for hours with alcoholic potash solution; on the other hand it is completely decomposed when it is heated with dilute sulphuric or hydrochloric acids. By treatment with methyl iodide and alcoholic potash solution it is converted into a compound $C_{10}H_{15} \cdot CH_3 \cdot NO \cdot CN$ melting at 67°. When this is reduced with sodium, a small quantity of ammonia is generated, and an almost quantitative yield of pinylamine is obtained, but acid reducing agents produce hardly any change. Concentrated sulphuric acid appears to have at 100° an isomerising or polymerising action, for a product is then obtained which corresponds to the formula $C_{10}H_{16} \cdot NO \cdot CN$, and melts at 220°; this product will be submitted to further examination. Warm nitric acid appears to oxidise the nitroso group, and to have at the same time a nitrating action; at least, the compound which is formed during this reaction and which melts at 105°, has the composition $C_{10}H_{15}(NO_2)_2CN$.

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[1]) Liebigs Annalen **324** (1902), 102.

[2]) Compt. rend. **134** (1902), 360; compare Report April **1902**, 85.

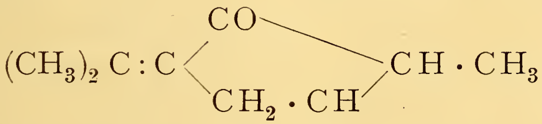
[3]) Ann. chim. phys. VII. **26** (1902), 31; after Chem. Centralbl. **1902**. I, 1296.

[4]) Journ. d. russ. phys.-chem. Ges. **34** (1902), 31; after Chem. Centralbl. **1902**. I, 1296.

[5]) Proc. of the chem. Soc. **18** (1902), 161.

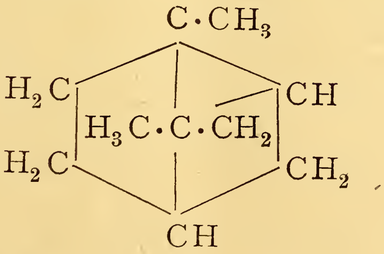
Camphene. F. W. Semmler[1]) has made a communication on the question of camphene and camphor. In recent times it has generally been accepted that camphene is unsaturated, and its molecular refraction is taken as representing the most important proof in support of this contention. Several chemical reactions, such as, for example, the phenomena observed during oxidation, can very well be explained by the unsaturated camphene; but the explanation is equally satisfactory, if the presence of a tri-ring in camphene is accepted, for a combination of rings, such as takes place under this hypothesis, might be the cause of a behaviour of camphene which is similar to that which occurs in the presence of a double linkage.

The author next discusses the formation and constitution of tricyclene, bornylchloride, bromocamphene dibromide, and camphene trichloride, and finally mentions that, contrary to Kerp's statement, camphorphorone $C_9H_{14}O$ can by reduced to an alcohol $C_9H_{18}O$, which, when oxidised, yields a ketone $C_9H_{16}O$, from which on further oxidation two isopropyl ketonic acids $C_9H_{16}O_3$ are formed. For this reason the formula



previously given by Semmler for this ketone, may by accepted as correct.

F. D. Dodge has also made the constitution of camphene the subject of a communication[2]). From the fact that camphene, like pinene, reacts with glacial acetic acid in the presence of sulphuric acid, and that in the last-named hydrocarbon the double linkage remains unattacked, but the tetra-ring opens, Dodge concludes that in camphene no double linkage exists at all, but that there also a tetra-ring is present. On the strength of this conclusion, and having regard to the close relations between camphene and isoborneol and camphor, the author proposes for camphene the following formula:



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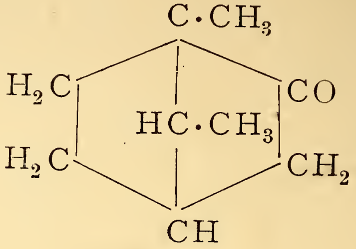
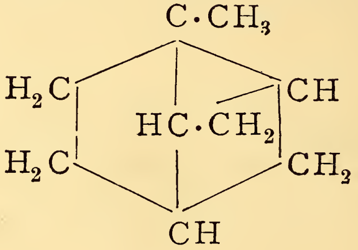
[1]) Berliner Berichte **35** (1902), 1016.

[2]) Journ. Americ. chem. Soc. **24** (1902), 649; after Chem. Centralblatt **1902**. II, 591.

In his opinion the formation of the various oxidation-products of camphene, viz., camphoric acid and apocamphoric acid, camphenilone, etc., can be quite well explained by this formula. Especially the formula of camphenilone, which would therefore be as follows:



would give expression to the fact that this body is a low homologue of camphor. The reactions which lead to the formation of the hydrocarbon $C_9H_{14}$ from camphenilone:



correspond to those which occur during the conversion of camphor into camphene. If this supposition is correct, camphenilone should in an anologous manner be capable of conversion into a further low homologue of camphor.

Kondakow¹) deals in a long treatise with the syntheses in the hydroaromatic series, which occur under the action of zinc chloride. Many years ago he found already that ethylene hydrocarbons with a tertiary carbon atom in the double linkage, in the presence of zinc chloride absorb organic acids, and therewith yield esters of tertiary alcohols; tertiary alkyl haloids are also absorbed under the same conditions, forming haloid anhydrides of tertiary alcohols of a fairly complicated composition. This result induced the author to apply this reaction also to hydroaromatic unsaturated hydrocarbons, and that not only to those which contain the double linkage in the nucleus, but also those which contain it in the side-chain, on the supposition that zinc chloride could be used for the identification of

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¹) Journ. f. prakt. Chem. II. **65** (1902), 201.

tertiary carbon atoms in double linkages. His experiments now show, that mentho- and carvomenthene, which both contain the double linkage in the nucleus, do not react with zinc chloride and acetic acid; menthyl chloride can also only be added very slowly to menthomenthene. Tetrahydrotoluene behaves in exactly the same manner as the menthenes. But the conditions are different with camphene and fenchene, on whose history and constitutions Kondakow expresses himself in detail; here the isomerides of the two hydrocarbons which contain the double linkage in the side-chain, are those which give rise to the formation of esters of tertiary alcohols.

It follows that in some degree Kondakow's supposition, as at first expressed, has been confirmed, but with this reservation, that a double linkage with a tertiary carbon atom can only then be detected in hydroaromatic compounds by this method (i. e. by absorption of organic acids in the presence of zinc chloride), when it is present in the side-chain, and not when it occurs in the nucleus.

We would here mention that Ertschikowsky[1]) has already years ago employed zinc chloride as a substitute for sulphuric acid in Bertram's hydration-method.

In a treatise entitled "Zur Geschichte der Fenchene", O. Wallach[2]) opposes Kondakow's statement on the development of the ideas regarding the constitution of fenchene, a statement which does not agree on all points with the actual facts. He shows there that Kondakow's reproach, that he (Wallach) had only formed an opinion on the constitution of these hydrocarbons by appropriating the views expressed by Kondakow, is perfectly untenable, and only proves the awkwardness of the situation which results when one chemist invades the sphere of action of another, without awaiting the completion of the particular subject by the earlier investigator.

Sabinene. In continuation of his researches concerning sabinene, the hydrocarbon characteristic of oil of savin, F. W. Semmler has made a further study of the sabinene ketone $C_9H_{14}O$ which is formed in the oxidation of sabinene with potassium permanganate[3]). In conformity with its saturated character, this ketone undergoes very little change if it is attempted to oxidise it further with potassium permanganate; on the other hand, it is readily split up into a dibasic acid $C_9H_{14}O_4$, if it is submitted to the action of an alkaline solution of bromine. As this acid

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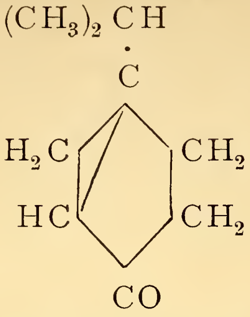
[1]) Journ. der russ. phys.-chem. Ges. **28**, 132; compare Bull. Soc. chim. III. **16**

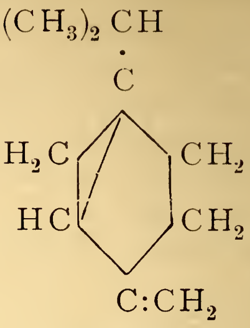
[2]) Journ. f. prakt. Chemie II. **65** (1902), 586.

[3]) Berliner Berichte **35** (1902), 2045.

is identic with tanacetone dicarbonic acid, Semmler concludes that the following formulæ must belong to the sabinene ketone and sabinene:



Sabinene ketone



Sabinene

It is a remarkable fact that if the semicarbazone of sabinene ketone is heated with dilute sulphuric acid, the ketone is not regenerated, but an unsaturated hydrocarbon $C_9H_{14}$ of the boiling point 165 to 166° and specific gravity 0,836 at 20° is formed, to which the author attributes a penta-ring with two double linkages, and that with the limonene-type of the hexa-ring.

It appears that in reducing sabinene ketone, not only the alcohol $C_9H_{16}O$, but also the saturated alcohol $C_9H_{18}O$ is formed, so that the effect of the tri-ring which is near to the ketone group, appears to be analogous to that due to the presence of a double linkage.

## Alcohols.

Thujyl alcohol. While engaged in the study of the isomerisation of secondary into tertiary hydroaromatic alcohols, Kondakow[1]) observed that isomerisation also takes place with thujyl alcohol when it is converted into the chloride by means of phosphorus pentachloride or hydrochloric acid. If thujyl alcohol is converted, by means of phosphorus pentachloride, into thujyl chloride, the latter shows neither a constant boiling point, nor a uniform composition, and it is moreover not as indifferent as might be assumed after Semmler's statements. This is due to the fact, demonstrated by Kondakow, that the crude chloride is not a uniform compound, but on the contrary a mixture of two chlorides, which probably consists chiefly of a tertiary compound. When treated with moist silver oxide, it yields a probably tertiary alcohol with a mouldy odour; treatment with alcoholic potash solution produces (if only with difficulty) a mixture of at least two hydrocarbons, which are closely allied in their properties,

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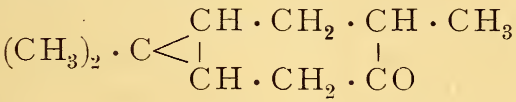
[1]) Chemiker-Zeitung **26** (1902), 720.

on the one hand to Tschugaeff's dicyclic thujene, and to sabinene, on the other to the monocyclic tanacetene of Semmler, and to Wallach's thujene.

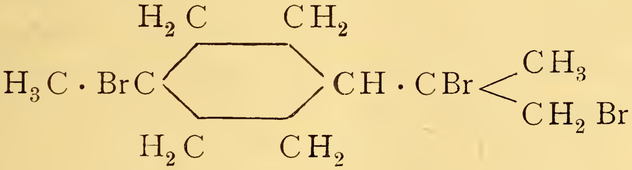
If, however, thujyl alcohol is submitted to the action of hydrochloric or hydrobromic acids in a concentrated aqueous or acetic solution, very little tertiary thujyl chloride (or bromide) is formed, but on the contrary chiefly the corresponding secondary compound.

The author has also studied the action of hydrochloric acid on the two thujyl chlorides, and made a more detailed examination of the dichlorides which are thereby formed. He concludes from this, that the facts established by him cannot be deduced from the formulæ which have up to now been given to thujone; he therefore proposes the following new formula for this ketone:



$$(CH_3)_2 \cdot C < \begin{array}{l} CH \cdot CH_2 \cdot CH \cdot CH_3 \\ | \qquad\qquad\quad\ | \\ CH \cdot CH_2 \cdot CO \end{array}$$

Terpineol. O. Wallach 1) reports on the degradation-products of terpineol 2) of the melting point 32°. If the terpineol is mixed in a solution of glacial acetic acid with one molecule bromine, and a solution of hydrobromic acid in glacial acetic acid is added, a tribromide is formed, to which the formula



must belong. This tribromide has an odour reminding of the hydrohalogen addition-products of dipentene, to which it is closely allied; if it is submitted to the action of bromine, it also yields dipentene tetrabromide.

If the glycerol $C_{10}H_{20}O_3$ formed from terpineol by hydration, is oxidised with a solution of chromic acid in dilute sulphuric acid, or if the hydroxyketone $C_9H_{16}O_2$ is heated with dilute sulphuric acid, a ketone $C_9H_{14}O$ is obtained; the simplest manner of preparing this same product is by oxidation of the terpineol direct with chromic acid. This ketone must be considered a tetrahydro-p-methyltolyl ketone, as is proved by its convertibility by concentrated sulphuric acid into p-methyltolyl ketone. When reduced in an ethereal or alcoholic solution

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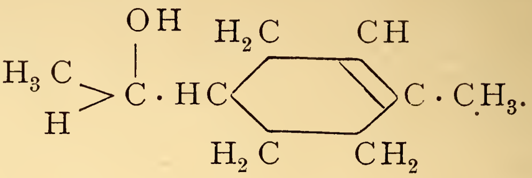
1) Liebigs Annalen **324** (1902), 79.

2) Compare our Report of April **1901**, 75; Berliner Berichte **35** (1902), 2147.

with sodium, the tetrahydro ketone absorbs only two atoms hydrogen, and is converted into an alcohol $C_9H_{16}O$. The latter is specially interesting for this reason, that it represents a low homologue of the terpineol melting at 35°, as is proved by the formula



Borneol. Minguin and Grégoire de Bollemont¹) have examined a series of esters of lævo-borneol (Ngai camphor) prepared by means of fatty and halogenated fatty acids, for their optical rotatory power. For equimolecular alcoholic solutions ($^1/_4$ gram-molecule in 1000 cc absolute alcohol) of homologous esters of the fatty acids series, the same rotation, $\alpha_D$ = about 4,30° in a 200 mm tube, was observed in almost every case; for the halogenated esters examined, the rotation also was uniformly 4,80°. This confirms that the proposition of the constancy of the molecular rotatory power, laid down by Tschugaeff for the esters of menthol, also applies to the homologous bornyl esters of fatty acids; but in both cases the esters of formic acid must be eliminated from the series.

A work by Minguin on isomeric borneols and their esters, which appears in the same publication, deals with the crystallographic²) properties of these bodies. The succinic esters of d- and l-borneol are dimorphous; they crystallise from petroleum ether in hexagonal tablets, from methyl alcohol in rhombic prisms. Both crystal-forms are remarkable on account of the occurrence of certain zones which have also been observed with the crystals of the condensation-products from camphor and aromatic aldehydes, and also with camphor itself. If, further, a mixture of d-borneol and l-isoborneol is converted into the succinate, and crystallised from methyl alcohol, petroleum ether, or otherwise, it always yields hexagonal tablets, and never the rhombic prisms. The isobornyl esters are therefore isomorphous, but not isodimorphous with the corresponding bornyl esters. The same thing occurs, if the mixture of d-bornyl and l-isobornyl succinates is crystallised from methyl alcohol or petroleum ether. The crystals of racemic bornyl succinates could not be measured on account of their minuteness and opacity, but under a magnifying glass their totally different character from the active forms could be observed, such as

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¹) Bull. Soc. chim. III. **27** (1902), 593.

²) Bull. Soc. chim. III. **27** (1902), 683.

was generally to be expected with racemic bodies. Analogous occurrences were observed in the case of the acid phthalates of different borneols; the molecular compounds from chloral, or bromal, and the isomeric borneols, are also isomorphous.

Menthol. On the strength of numerous tests made with the benzoate, oxalate, carbonate, succinate, and acetate, of menthyl, and also with menthyl benzyl ether and diphenyl menthyl urethane, Tschugaeff considers it an established fact, that these derivatives of menthol with an ester-like character are extremely difficult to decompose by distillation, and further that, when decomposition actually takes place, occurrences of isomerisation are then not at all excluded.

On the other hand, the xanthogenates of terpene alcohols are distinguished by a very peculiar and characteristic behaviour, and in this respect they appear to have no analogy whatever with any other compound. The dixanthogenides of the general formula $C_nH_{2m+1}OCS \cdot SS\ CSOC_nH_{2m+1}$ decompose as readily as the corresponding xanthogenates. The xanthogenic amides and thiourethanes, which only contain the group ROCS as residue of xanthogenic acid $ROCS \cdot S$, rank in every respect with the xanthogenic compounds mentioned above (as Tschugaeff has recently found[1]); in their case, however, the decomposition occurs at a somewhat higher temperature. Tschugaeff, following the method indicated by Debus, produced by means of the action of alcoholic ammonia on the methyl esters of the corresponding xanthogenic acids, a number of these xanthogenic amides, viz., menthyl xanthogenic amide, the two optically active bornyl xanthogenic amides, and the racemic isomers, fenchyl xanthogenic amide, and dihydrocarvyl xanthogenic amide. The reaction takes place according to the equation:

$$ROCSSCH_3 + 2NH_3 = ROCSNH_2 + NH_4SCH_3.$$

Only the behaviour of menthyl xanthogenic amide was, however, examined more in detail. If this body is heated in a fractionating flask, decomposition with evolution of gas commences already a few degrees over 200°; at about 220° it becomes very brisk, and it is then soon completed. Ammonia and carbon oxysulphide thereby occur as gaseous reaction-products, whilst in the receiver menthene can be condensed, which, after one distillation over metallic sodium, shows the following properties: Boiling point 167—168; specific gravity $\frac{20^\circ}{4^\circ}$ 0,8121; $n_D$ 1,45202, and $[\alpha]_D + 113^\circ 28'$. It is therefore very similar to the distillate from menthyl xanthogenate.

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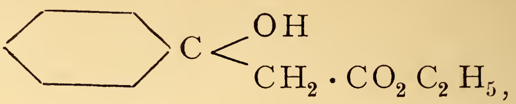
[1]) Berliner Berichte **35** (1902), 1016.

## Aldehydes.

Citral. Condensation of cyclic ketones with zinc and iodacetic ester, and subsequent hydrolysis, produces oxyesters of the formula



which are converted into unsaturated esters by splitting off water. When applying this reaction to citral, Tétry¹) obtained, besides a lactone $C_{14}H_{20}O_3$ of the boiling point 160° at 10 mm, citralidene acetic ester as a pleasantly smelling oil of the boiling point 129° at 9 mm. On saponifying the ester with alcoholic potash solution, citralidene acetic acid was obtained as a colourless mobile oil of the boiling point 175°, at 18 mm.

## Ketones.

According to observations made by Wallach²), alkylated cyclohexenones which contain a double linkage in the ring, can, like the saturated cyclic ketones of various ring-systems, be condensed with brominated fatty esters by means of zinc. He examined more particularly methyl and dimethyl cyclohexenones, and also methyl ethyl and isopropyl cyclohexenones. But the oxyesters $R'': C(OH)CH_2 \cdot CO_2R$ which occur first of all when using saturated ketones, cannot be isolated when unsaturated ketones are employed; — on the contrary, the compounds which contain one molecule water less, are those always met with. Probably, the double linkage formed by the elimination of water, immediately transfers itself to the nucleus, so that the acids formed on saponification must be considered as dihydroaromatic acids. Under suitable conditions the latter lose carbon dioxide with formation of hydrogenated benzene hydrocarbons, which can be converted into benzene derivatives; and the facility with which hydrogen is split off appears to increase with the growing molecular weight, and also to be rendered more easy by the entry of certain atom-groups, such as, for example, isopropyl.

In conformity with these experiences is the behaviour of carvone, already communicated on a previous occasion; just as little as from this body, can an oxyester be obtained from carvenone, whose ethylene-linkage is situated in the nucleus. On the other hand, dihydrocarvone with a saturated ring is capable of forming a stable oxyester.

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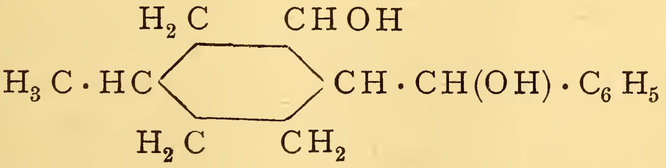
¹) Bull. Soc. chim. III. **27** (1902), 601.

²) Liebigs Annalen **323** (1902), 135.

In connection with the foregoing, menthone, tetrahydrocarvone and pentanone, were also submitted to condensation, and the compounds then formed were examined in detail.

Methyl hexanone. For a long time it had been accepted as a fact that the acid $C_7H_{12}O_4$, formed on oxidation of both menthone and pulegone, and also of the latter's product of decomposition, β-methyl hexanone, was β-methyl adipic acid, until Markownikow[1]) expressed a doubt on this point, and stated that he had obtained α-methyl adipic acid from β-methyl hexanone, using nitric acid as oxidizing-agent. This statement has since been checked by Bouveault and Tétry[2]), but they found that Markownikow had fallen into an error, and that, even when the oxidation is carried out with nitric acid, only β-methyl adipic acid is formed from β-methyl hexanone.
This result has recently been confirmed by N. Speranski's[3]) work, who compared the acids $C_7H_{12}O_4$ from menthone, pulegone, and β-methyl hexanone, produced from these bodies by means of the calcium salt, the corresponding methyl pentanones, and condensed the latter with benzaldehyde. In every case the same dibenzylidene methyl pentanone of the melting point 150° was obtained. α-Methyl pentanone, on the contrary, yields a monobenzylidene compound melting at 123—124°. This shows that on oxidation of menthone, pulegone, and β-methyl hexanone, the same acid, β-methyl adipic acid, is formed.

Condensation of β-methyl hexanone with bezaldehyde in the presence of sodium ethylate, yields not only benzylidene- and dibenzylidene methyl hexanones, but, as L. Tétry[4]) has established, also a further body, which is formed by fixation of one molecule water to the double linkage of benzylidene methyl hexanone, and reducing the carbonyl-group; it must therefore be designated as oxybenzyl methyl cyclohexanol:



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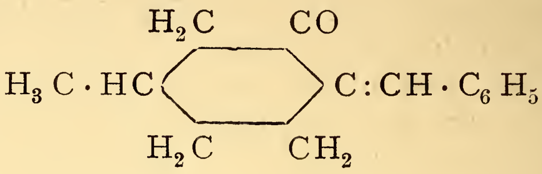
[1]) Berliner Berichte **33** (1900), 1908.
[2]) Bull. Soc. chim. III. **25** (1901), 441.
[3]) Journ. der russ. phys.-chem. Ges. **34** (1902), 10; after Chem. Centralbl. **1902**. I, 1221.
[4]) Bull. Soc. chim. III. **27** (1902), 302.

and yields as such a diacetate, which on saponification reproduces the original glycol of the melting point 152° to 153°.

Monobenzylidene methyl hexanone is decomposed on oxidation with potassium permanganate into benzoic acid and β-methyl adipic acid, and the following formula might therefore belong to it:



On reduction with sodium amalgam the monobenzylidene compound yields benzyl methyl hexanone, the dibenzylidene compound, however, dibenzyl methyl cyclohexanone; the first is obtained as a colourless oil, the latter in colourless needle-shaped crystals of the melting point 100°. Benzyl methyl hexanone still reacts with hydroxylamine, but the dibenzyl compound does so no longer.

Fenchone. Like camphor, fenchone is also capable of forming molecular compounds, especially with phenols. A number of such compounds, which are mostly formed with energetic reaction and evolution of heat, have been examined in detail by E. Tardy[1]). When molecular quantities of phenol and fenchone, previously heated to 60°, are mixed, the temperature increases to 70°, and the resulting non-crystallising reaction-product has a higher rotatory power than fenchone itself. The compound formed, however, dissociates, very readily under the influence of solvents. α-Naphthol fenchone, produced by mixing the component parts at ordinary temperature, yields, upon recrystallisation from an excess of fenchone, needle-shaped crystals of the melting point 51°; the compound obtained in the same manner from β-naphthol yields broad prisms melting at 57°. Both compounds decompose readily, and if they are exposed to the atmosphere, fenchone volatilises, whilst the phenols remain. Thymol, guaiacol, eugenol and resorcinol also clearly form with fenchone double-compounds which, however, do not crystallise; resorcinol even appears to unite with one, and also with two molecules fenchone. Equal quantities of chloral and fenchone yield a syrupy liquid, congealing in crystalline form, from which crystals of the melting point 25° to 30° can be obtained.

Fenchone, however, has also the property of dissolving nitrocellulose. One part nitrocellulose and two parts fenchone give a gelatinous mass,

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[1]) Thesis, Paris 1902. — Bull. Soc. chim. III. **27** (1902), 603.

which is completely soluble in ether; and with an alcoholic solution containing 10 per cent of this ketone, gun cotton forms a kind of collodium.

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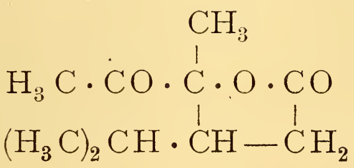
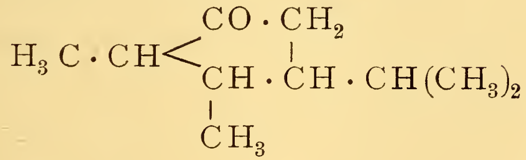
Thujone. Wallach's 55th treatise¹) gives a number of interesting particulars on compounds of the thujone series. It is a well-known fact that thujone $C_{10}H_{10}O$, when boiled with dilute sulphuric acid, is converted into an isomeric ketone $C_{10}H_{16}O$, isothujone, which again can be converted by reduction into a ketone $C_{10}H_{18}O$, thujamenthone, which is isomeric with menthone and tetrahydrocarvone. Wallach first reports on the products formed on oxidation of isothujone, the ketolactone $C_{10}H_{16}O_3$ discovered by Semmler (which this investigator, however, erroneously declared to be identic with the ketolactone $C_{10}H_{16}O_3$ formed from thujamenthone), a ketonic acid $C_9H_{16}O_3$, and an isopropyl lævulinic acid. From the fact that the latter can be converted into isopropyl succinic acid, and that isothujone can be condensed with benzaldehyde into a monobenzylidene compound pointing to the presence of a $-CO\cdot CH_2$-group, Wallach concludes that the formula



$$\begin{array}{rcccc} & CH_3 & & & \\ & | & & & \\ H_3C\cdot CO\cdot & C & \cdot O\cdot & CO \\ & | & & | \\ (H_3C)_2CH\cdot & CH & - & CH_2 \end{array}$$

which Semmler has laid down for the keto lactone $C_{10}H_{16}O_3$, is correct.

The author further shows that the formula



$$\begin{array}{rccccl} & CO & \cdot & CH_2 & & \\ H_3C\cdot CH< & & & | & & \\ & CH & \cdot & CH & \cdot & CH(CH_3)_2 \\ & | & & & & \\ & CH_3 & & & & \end{array}$$

accepted for isothujone, is not opposed to the behaviour of thujamenthone. The treatise ends with a discussion of the relationship in which thujone stands to tanacetone.

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Pulegone. Some time ago Wallach has already demonstrated, that on treating pulegone dibromide with sodium alcoholate, pulegenic acid is formed; but L. Bouveault and L. Tétry²) have recently discovered that this acid is not the only reaction-product which is

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¹) Liebigs Annalen **323** (1902), 333.
²) Bull. Soc. chim. III. **27** (1902), 307.

thereby obtained. Especially a solid lactone of the melting point 79 to 80°, isomeric with pulegenic acid, is formed by that reaction, but this lactone is in no way identic with the lactone formed by isomerisation of pulegenic acid itself. Other neutral secondary products formed in the production of pulegenic acid, are menthol (in small quantity), pulegone, and an unsaturated compound of the composition $C_{10}H_{16}O_2$, which appears to have neither an alcoholic, nor a ketone-like character.

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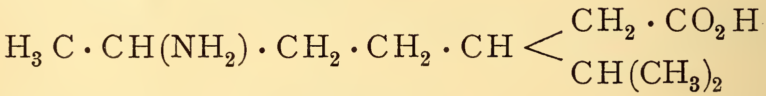
Tetrahydrocarvone. In the isomerisation of tetrahydrocarvoxime with sulphuric acid, there is formed, as Wallach showed some time ago, a compound $C_{10}H_{19}ON$ melting at 104°, which can be readily split up into an amidoacid $C_{10}H_{21}O_2N$ of the melting point 201 to 202°. Wallach[1]) has recently succeeded in clearing up the constitution of this compound, which he did in the following manner: If, namely, the amidoacid is treated with nitrous acid, an oxyacid is formed, which is converted by loss of water, partly into an unsaturated acid (decylenic acid) and partly into a lactone, both corresponding to the composition $C_{10}H_{18}O_2$. If the oxyacid is oxidised, a ketonic acid of the same carbon-content is obtained, and this ketonic acid is identic with the one which A. v. Baeyer obtained in splitting up tetrahydrocarvone. On further oxidation this ketonic acid yields an isopropyl glutaric acid.

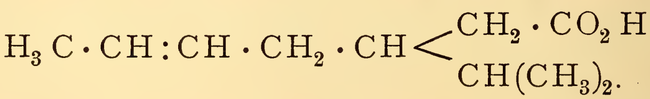
Only an acid of the formula



$$H_3C \cdot CH(NH_2) \cdot CH_2 \cdot CH_2 \cdot CH<\begin{matrix} CH_2 \cdot CO_2H \\ CH(CH_3)_2 \end{matrix}$$

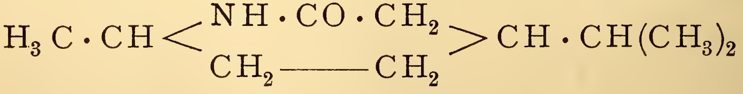
can give such products of degradation.

The position of the ethylene-linkage in decylenic acid was ascertained in a corresponding manner; to the latter belongs the formula:



$$H_3C \cdot CH:CH \cdot CH_2 \cdot CH<\begin{matrix} CH_2 \cdot CO_2H \\ CH(CH_3)_2. \end{matrix}$$

If, however, the amidoacid has the above-mentioned formula of a $\beta$-isopropyl-$\varepsilon$-amidoheptylic acid, it follows that for the isoxime (melting at 104°) of tetrahydrocarvone, only the following is possible:



$$H_3C \cdot CH<\begin{matrix} NH \cdot CO \cdot CH_2 \\ CH_2 \text{———} CH_2 \end{matrix}>CH \cdot CH(CH_3)_2$$

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Menthone. Leser[2]) has successfully accomplished a synthesis of menthone. By introducing the isopropyl group into acetyl-4-methyl-

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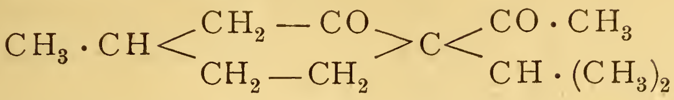
[1]) Liebigs Annalen **323** (1902), 323.

[2]) Compt. rend. **134** (1902), 1115.

1-cyclohexanone-3, by means of potassium ethylate and isopropyl iodide, he arrived at 4-acetyl menthone,



$$CH_3\cdot CH<\begin{matrix}CH_2-CO\\CH_2-CH_2\end{matrix}>C<\begin{matrix}CO\cdot CH_3\\CH\cdot(CH_3)_2\end{matrix}$$

an oil of the boiling point 133—135° (13 mm), specific gravity 0,967 (15° C.), $n_D = 1{,}45737$. By eliminating the acetyl group with alcoholic potash solution, a ketone with a menthone-like odour resulted; boiling point 207 to 208° at atmospheric pressure. The menthone semicarbazone produced from it melted at 179 to 180° (according to Wallach at 184°), the menthoximic acid, obtained by v. Baeyer and Manasse's method, at 98 to 99° (according to v. Baeyer and Oehler1) at 103°); both compounds also gave corresponding analytical figures. As methyl cyclohexanone, and the acetyl compound obtainable from it by condensation with acetic ester, can be produced synthetically, it follows that the complete synthesis of menthone is an accomplished fact.

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Methyl heptenone. When methyl heptenone is oxidised by means of permanganate, it is decomposed into acetone and lævulinic acid. The conclusion which Tieman and Semmler have drawn from this behaviour, namely that methyl heptenone must therefore contain the double linkage in $\gamma$-$\delta$-position towards the carbonyl group, is not entirely free from objection, inasmuch as it had not hitherto been possible to isolate the glycol which should be formed in the first place on oxidation of this ketone. C. Harries2) has now however succeeded in producing this body, and that in two ways. If methyl heptenone is treated with potassium permanganate in a solution of acetone, that is to say under conditions, under which the potassium hydroxide formed is not expected to effect a change, only about 20 per cent of the ketone were invariably attacked, and the corresponding glycol is not formed, but a further oxidation into a hydroxyketone $C_8H_{14}O_3$ takes place immediately. But if an aqueous solution of permanganate is employed, methyl heptenone is readily converted into a very well crystallising glycol $C_8H_{16}O_3$ of the melting point 66—67°. As this glycol, on further oxidation with permanganate or chromic and glacial acetic acids, yields the same hydroxyketone $C_8H_{14}O_3$ already mentioned, the latter may also be considered a primary oxidation-product of methyl heptenone. The hydroxyketone is converted readily into a pyrrol derivative by heating with ammonia and acetic acid, and is thereby identified as a $\gamma$-diketone. When boiled with dilute sulphuric acid, the glycol is converted, with

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1) Berliner Berichte **29** (1896), 27.

2) Berliner Berichte **35** (1902), 179.

loss of water, into the asymmetric α, α-dimethylacetonyl acetone which Tiemann and Semmler had already obtained in the degradation of β-tanacetogene dicarbonic acid. These results can only be explained if methyl heptenone possesses the constitutional formula which Tiemann and Semmler assigned to it:

$$(CH_3)_2\,C:CH\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$$

$$\downarrow$$

$$(CH_3)_2\,C(OH)\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$$

Glycol

$$\swarrow \qquad \searrow$$

$$(CH_3)_2\,C(OH)\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3 \qquad (CH_3)_2CH\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$$

Hydroxyketone — Asymm. α, α-dimethylacetonyl acetone

**Citral.** The value of this article depends upon that of lemongrass oil. In view of the upward tendency of the latter, a reduction in the prices was out of the question.

We would call attention to the fact that our citral, as distinguished from many other commercial products, is specially pure, and has a specific gravity of 0,895. It differs in no way from the citral of lemon oil, which in the perfectly pure state has exactly the same character. The so-called terpeneless lemon oil, however, has a different aroma; this oil no doubt consists chiefly of lemon oil citral, but also contains other bodies, viz., citronellal, linalol, linalyl acetate, geraniol, geranyl acetate, octyl and nonyl aldehydes, methyl heptenone, and terpineol.

**Coumarin.** After the price of this article had been forced down in an unheard-of manner by the competition, several manufacturers have combined to prevent a further drop, and they have succeeded in arresting the fall in the prices. The quotations will now no longer show the large differences of previous times.

There are pronounced differences in the qualities of the products met with in commerce, differences which are due to the degree of perfection of the technical installations. Our plant, which on our removal to Miltitz has been completely re-arranged and improved, will now soon be in full operation.

**Eucalyptol** (cineol). We would here once more point out, that a pure eucalyptol must be optically inactive; rotatory power always points to contamination. Our product melts at — 1°.

The uses of eucalyptol have in the course of time been greatly extended, and that not only for medicinal purposes, but also on account of its excellent qualities as an article of toilet, for the care of the teeth, and as a disinfectant of the cavity of the mouth.

Medicinally it is employed in tuberculosis, gangrene of the lung, pneumonia, asthma, catarrhal affections of the urinary organs, externally as a disinfectant in dressing wounds, and further as an embrocation in rheumatism, neuralgia, etc. According to Duquesnel, the disagreeable odour and taste of cod-liver oil are covered by the addition of eucalyptol (2 drops to 150 grams ol. morrhuæ).

This information may be useful, as we constantly receive enquiries for a practical remedy for this purpose.

Eucalyptol injections also are said to have answered very well in malaria. According to a publication by Dr. Peter Buro, of Kubin, it is injected in the form of a mixture with fatty oil. Dose 0,33 gram.

**Geraniol from citronella oil** (German Patent No. 76435). We now carry on the manufacture of this product on a large scale, and supply it in every quantity and at a reduced price, which should be an inducement to give this beautiful article a thorough trial. The knowledge of the fact that it represents the principal constituent of natural rose oil, may lead to the adoption of this product on a larger scale than hitherto, especially as it can now be obtained in any desired quantity and at a lower rate than heretofore.

For trials with this object in view, we shall be pleased to assist with a liberal supply of samples.

**Mignonette (Reseda) geraniol.** We have this year again produced a sufficient quantity of this article, to meet in full the demand from our regular clients. The material was of the highest quality, and it was so abundant, that the proportion of 500 kilos flowers to 1 kilo geraniol could be exactly adhered to.

The use we make of geraniol as the basis for the aroma of mignonette, is fully justified, as geraniol is present in a large number of flower oils, and probably also in mignonette oil. In any case it should be preferred to fat as the bearer of the aroma. Mignonette geraniol is prepared without foreign additions for the purpose of fixing the odour, such as are employed in pomade. Every user of our product has confirmed that it stands unequalled as a basis for mignonette preparations, and that with our product by adding fine aromatic perfumes such as ionone orris oil, etc., preparations of the highest degree of perfection can be produced.

We would recommend our mignonette geraniol for thorough trial to everyone who has not yet employed it.

Of mignonette pomade, which was completely out of stock, we have this year also manufactured a parcel.

**Heliotropin.** This preparation has been singled out as a special favourite for competition. The prices are cut down without intermission, and the end is not yet in view.

We do not, of course, wish to be driven from our position, and we assure our clients that we will meet all honest competition. By producing safrol ourselves on the largest scale, and by means of a modern installation, we hold an exceptionally favourable position for the manufacture of this product.

**Menthol, recrystallised.** Although the unusually brisk demand for this preparation, which existed in the spring, has somewhat fallen off in the course of the summer, it has had the effect of clearing the stocks to such an extent, that the value since that time has been constantly going up and reached by and by an unusual high level.

The shipments of crude menthol from Japan were exceptionally small. They amounted to the following: —

from 1st January to 31st July 1902:

| | | |
|---|---|---|
| to Hongkong | 7711 | catties |
| „ London | 4095 | „ |
| „ Havre | 3106 | „ |
| „ Hamburg | 2025 | „ |
| „ Seattle | 1800 | „ |
| „ New York | 1125 | „ |
| „ Antwerp | 947 | „ |
| „ Bombay | 841 | „ |
| „ Milan | 675 | „ |
| „ Rangoon | 94 | „ |
| „ Marseilles | 30 | „ |
| „ Melbourne | 30 | „ |
| „ Bangkok | 22 | „ |
| Total | 22501 | catties, |
| or about | 13500 | kilos. |

against a quantity of about 25000 kilos in the second half of 1901, which no doubt exceeded the demand, but which has been compensated for by the smaller imports of the last 7 months.

From these, as from previously communicated figures, it will be seen that the total annual consumption of menthol amounts to 35000 to 40000 kilos.

Shipments from Japan have practically ceased during the last few months, as old stocks are sold out, and this year's product is not ready for shipment until October. Our first consignments of the latter are just now coming in. The value of the article is high but still normal. The highest price, 140 marks per kilo, was paid in 1881; it gradually fell to 90 marks, but rose again in 1883 to 130 marks.

The lowest quotations, 15 to 22 marks, were caused in 1887 to 1898 by enormous over-production, against which the Japanese Government at last intervened. From that time the value has fluctuated between 25 and 37 marks, but we do not think that in the near future it will come down again to such figures.

Menthol was first introduced by us into commerce on a large scale in the year 1881, and for several years we held almost a monopoly. It is one of the specialities of our factory, and in our new buildings arrangements have been made for the rational manufacture of a first rate product.

**Safrol.** By means of the plant erected at our new Miltitz works, we are now in a position to reduce the cost of production to the lowest limits, and to supply a faultless article at an exceptionally low price.

We repeat here that we are prepared to meet the competition of the Japanese product under all circumstances.

For the particulars communicated by Mr. Nakazo Sugiyama on the production of safrol from camphor oil, we refer to page 20.

**Terpineol.** No alterations in the value of this article can be recorded, in spite of the fact that the higher prices of oil of turpentine would justify an increase.

**Thymol, cryst.** Since our last Report the prices have gone further back, due not so much to a reduction in the price of the raw material, as to keen competition with continuous over-production. How long this state of affairs will last, is impossible to say.

Ajowan seed has recently been quoted higher in India.

**Vanillin.** The fall in the quotations of this article appears to know no bounds. The only one who fares best under these conditions, is the consumer. In how far these competing products, sold at the very lowest prices, answer the just demands as regards quality, must be left to the judgment of individuals. In our opinion, the necessary care can under such circumstances no longer be given to the manufacture of this preparation, and we recommend caution both in the purchase and the use, as an imperfect quality, or adulteration of the vanillin, may be the cause of great loss to the purchaser.

**Schimmel & Co.**

J. J. Weber, Leipzig.

apr/may 1903

Head Offices of Schimmel & Co. and Imperial Post and Telegraph Office at Miltitz.

# SEMI-ANNUAL REPORT

OF

# SCHIMMEL & Co.

(FRITZSCHE BROTHERS)

MILTITZ
NEAR LEIPZIG

LONDON ◆ NEW YORK.

APRIL/MAY 1903.

# Contents.

## List of abbreviations.

d = specific gravity at 15°, unless otherwise stated.

$d_{20^\circ}$ = specific gravity at 20°.

$d\frac{20^\circ}{4^\circ}$ = specific gravity at 20°, compared with water at 4°.

$\alpha_{D_{15^\circ}}$ = optical rotation, at 15°, in a 100 mm tube.

$[\alpha]_D$ = specific rotation.

$n_{D_{15^\circ}}$ = index of refraction at 15°.

n = normal.

$\frac{n}{2}\left(\frac{n}{10}\right)$ = semi-normal or deci-normal (titrated solutions).

g = gramme; cc = cubic centimeter; mm = millimeter.

Temperatures are uniformly stated in **centigrade** degrees (°).

**Miltitz** near Leipzig, April/May 1903.

Since the date of our last Report (October 1902) no decided change has come over the general economic situation in Germany. At the same time, it cannot be denied that in numerous branches of Industry features of a somewhat more favourable character are apparent, which manifest themselves in good dividends of the leading financial institutions and of a large number of important firms in other branches of Trade and Industry.

In spite of all competition and other difficult internal conditions, the Chemical Industry still continues its upward movement. Although at this moment it is not yet possible to bring forward statistic proofs in the form of comparative figures of the turnover and exports in support of this statement, we have yet valuable and reliable data in the statistics of the Manufacturers' Union of the Chemical Industry, according to which the number of chemical Works has increased in 1902 by 183, and that of the qualified workmen therein employed by 3487.

By way of comparison we give the figures of the last four years, as follows: —

| | Number of works | Number of qualified workmen |
|---|---|---|
| 1899 . . . . | 6589 | 135350 |
| 1900 . . . . | 6911 | 143119 |
| 1901 . . . . | 7169 | 153001 |
| **1902** . . . . | **7352** | **156488.** |

The foregoing figures show clearly that the German Chemical Industry has passed intact through the economic crisis of the last few years. Further, there are no grounds for fearing that it will be outstripped by competition from abroad, so long as the German Universities possess such eminent representatives of Chemical Science.

The Industry of essential oils and artificial perfumes has to place 1902 on record as one of its best commercial years. But yet it looks anxiously into the future, as the new German Tariff does not provide the relief which had been desired, and which is necessary for maintaining the trade in seed-oils.

In accordance with the Tariff now passed, the import duty on the so-called spice-seeds, such as anise, coriander, and fennel, has been raised from 3 to 4 marks per 100 kilos; on the other hand, they may be admitted free under supervision on an official permit. But it is not stated whether what we at the time in our memorial had represented as absolutely necessary, has also received due consideration, viz., —

> that the destruction of the seeds which have been distilled duty-free, as is usual with spices, under no circumstances can be considered practicable, as the residues are usefully employed as a valuable food for cattle; and that it is exactly this utilisation of the residues which renders the distillation at all possible, for in the competing countries, such as Holland, Russia, and Galicia, the profitable utilisation of the residue is a matter of very great advantage to the manufacturer of essential oils.

If this source of revenue is closed to the German manufacturer, his position will be even more unfavourable than hitherto, and the distillation of seed-oils will then become an impossibility.

As it can hardly be considered possible that agrarian influences have extended as far as this subject, we are really at a loss to understand why these just and carefully substantiated wishes for the prosperity and credit of the whole industrial branch, have not been taken into consideration, and we hope that it may yet be possible to grant the necessary concession by special decree.

The new Russian Tariff of January 13, 1903, has made unimportant changes as far as our industry is concerned. The import-duty on essential oils has remained the same (formerly 24 roubles + 10 per cent., now 26,40 roubles per pood); but on the other hand, the following increases, very disagreeable for the perfumery-trade, have been made: —

| | | | |
|---|---|---|---|
| Aromatic waters without alcohol | from 4,77 | to 7,95 | roubles per pood. |
| Cosmetics, hair-dyes, etc., without alcohol | „ 13,60 | „ 24,— | „ „ „ |
| Perfumes and cosmetics of every description, containing alcohol, such as perfumes, aromatic waters, elixirs, etc. | „ 29,75 | „ 52,50 | „ „ „ |

The import-duty on toilet-soaps, however, has remained unchanged. Nitrobenzene has been raised from 1,40 to 4,0 roubles per pood. Chemico-pharmaceutic preparations, previously paying 1,50 roubles, are now charged 5 roubles per pood.

It is to be hoped that the negotiations now about to be commenced between the two Governments, may lead to advantageous treaties on the “most-favoured nation” basis.

The project of the new Austrian Customs-Tariff also shows but unimportant alterations in the rates applying to our goods; and as far as this market is concerned, it may be confidently expected that the treaties will bring no changes of any consequence.

The situation in the Transatlantic export-markets is unfavourable, especially in Central and South America. Above all, the fluctuations in the exchange in Mexico and Brazil have a restraining effect on the purchasing power and credit of those countries.

On the other hand, the settled economic conditions in the United States of North America, still undergoing an enormous development, operate beneficially; the situation there has consolidated to such an extent, that even the Presidential Election of next year may have no influence on it.

The Chemical Industry will take only a very unimportant part in the Universal Exhibition to be held at St. Louis in 1904, as the last Exhibitions at Chicago and Paris have followed each other so rapidly, that there is a lack of novelties. Moreover, chemical products do not form suitable material for exhibition-purposes, a fact to which we have frequently called attention.

Our export trade to Japan, the Dutch Indies, the Philippines and Australia has been animated.

In Europe the state of the trade has been normal, and does not call for any remarks.

In order to extend our commercial relations with the Capital of the Empire, Berlin, and to offer our clients all the advantages of a modern installation, we have on April 1st opened a branch-office at the Spittelmarkt No. 4—7.

The same is the case with Hamburg, where our office is for the present at Neueburg 6.

We have included in the programme of our operations the manufacture of artificial mustard oil.

As an Appendix to the present Report, we publish for the first time a work on a new subject, entitled:

> "Contributions to the knowledge of the pharmacological and physiologico-chemical behaviour of some volatile substances".

This work, executed in the Institute for Pharmacology and Physiological Chemistry at Rostock i. M. under the direction of Professor Dr. R. Kobert, will be continued. We believe that we are justified in our supposition that it will meet with a considerable amount of interest.

In the half-year under review, the numerous and important movements in the values of several leading articles have brought about a very animated business. The mild winter in Central Europe has prematurely promoted the vegetation of many plants used as raw material in our industry, and has increased the danger of ultimate injury by subsequent frosts. It is to be hoped that these fears will not be realised.

**Almond Oil, pressed from apricot-kernels.** On this subject it is reported from Marseilles, that the upward movement in Syrian apricot-kernels has communicated itself to all other sources of supply. It is said that in the whole of Syria at most 200 to 300 bales are still to be found. The prices have advanced in consequence from 68 to 76 francs, and they would be still higher, if the Californian kernels had not placed a check upon the rise. We have not yet followed the advance with our prices of essential and fatty oils, as we are for the greater part covered by contracts at low rates, but in a few months' time we may also be compelled to raise our quotations.

**Almond Oil, Germ. Pharm. IV, pressed from sweet almonds.** The high prices of Bari and Sicilian almonds continue to rule, and no change must be expected before next autumn. In Puglia the 1902 harvest has given a yield of only 40 000 to 50 000 bales instead of the 100 000 bales anticipated, and they have all been bought up by speculators. The same is the case with the last Sicilian harvest. As other cheaper qualities do not come under consideration for the manufacture of oil, these figures will have to be taken into account until the advent of autumn.

**Oil of Amber.** Oil of amber does not, strictly speaking, belong to the essential oils, as it is obtained as a by-product in the dry distillation of amber for the production of succinic acid, and therefore owes its origin to a pyrogenic reaction. The rectified oil, *Ol. succini rectificatum* of some Pharmacopœias, was formerly, and is probably still used medicinally on a small scale, chiefly maybe as a remedy against toothache, an addition to liniments, etc. It appears that this oil is much esteemed in England, as the demand for it from that country is fairly brisk.

As we obtain the crude oil of amber direct from the producer, and rectify it ourselves, we are in a position to give an absolute guarantee of the purity of our distillate; but it is not quite easy to obtain the rectified oil of the brightest possible colour, and special measures have to be taken to produce even a distillate of only a bright-yellow colour. Very little is known of the physical constants of rectified oil of amber, and for this reason we give below a short table of the properties of some oils rectified by ourselves. This table shows that the product supplied by us is always of identic constitution.

| $d_{15^\circ}$ | $\alpha_D$ | $n_{D20^\circ}$ | Acid Number | Ester Number |
|---|---|---|---|---|
| 0,9281 | + 22° 32′ | 1,50820 | 6,5 | 8,95 |
| 0,9259 | + 24° 28′ | 1,50802 | 5,1 | 6,8 |
| 0,9277 | + 24° 36′ | 1,50957 | 5,78 | 3,85 |
| 0,926 | + 24° 40′ | 1,50857 | 5,09 | 4,37 |
| 0,9295 | + 26° | 1,51083 | 5,5 | 5,0 |

All these oils were soluble in 4 to 4,5 volumes of 95 per cent. alcohol.

For this reason we were all the more surprised, when recently several consigments sent to England formed the subject of complaints. The samples of oils sent to us for comparison, to which the oil we were to supply should correspond, differed in such a pronounced manner from our distillates, that we could not help looking upon them with great suspicion. For four samples which had a much brighter colour than our rectified oil, we obtained the following values: —

| $d_{15^\circ}$ | $\alpha_D$ | $n_{D20^\circ}$ | Acid Number | Ester Number |
|---|---|---|---|---|
| 0,8835 | + 3° 4′ | 1,48863 | — | 4,9 |
| 0,8437 | — 1° 53′ | 1,46367 | 5,4 | 3,3 |
| 0,873 | + 3° 14′ | 1,48122 | 12,7 | 6,0 |
| 0,8941 | + 12° 55′ | 1,48633 | 2,1 | 2,7 |

All these samples were more readily soluble in 95 per cent. alcohol than the oils mentioned before. An addition of alcohol could not, however, be detected.

The essentially lower specific gravity, the lower rotatory power, and the change in the index of refraction, pointed to the fact that all these oils contained larger proportions of lower boiling constituents than our distillate. A detailed examination, with which we are at this moment still occupied, will prove whether these oils may be claimed to represent pure oils of amber, or whether they have undergone some "improvement" by the addition of other resin-distillates.

**Oil of Ambrette-seeds.** The well-known natural phenomena in Martinique have been used as a pretext for a rise in the price of ambrette-seeds. The holders of stocks, however, did not meet with any reciprocal feeling on the part of the consumers, and were soon compelled to drop their tactics.

Material is now available in greater abundance than ever.

We were the first to produce oil of ambrette-seeds, and to place it on the market. It has now secured a firm footing in the high-class perfumery-trade. The liquid oil of ambrette-seeds which we added to our lists in October last year, also finds great favour; from this oil the solid odourless constituents, which in the manufacture of the ordinary distillate pass over along with the latter, have been removed. For use in soap-perfumes, where a little more substance is desired, the concrete oil might perhaps be preferred for practical reasons, but for all other purposes the new liquid product is recommended. The high quotation of the latter is not by any means a fancy price, but fully agrees with the intrinsic value and the richness of this preparation.

**Angelica Oil.** Our own cultivation of angelica-plants, extending over about 12 acres in the immediate vicinity of our factory, has yielded last year such a rich crop of roots as never before. For this reason we have, after many years' scarcity, once more an abundant stock of angelica oil at low prices.

The method of distillation at our Works is most rational, as only such quantities of roots are gathered from day to day as can be submitted to distillation. By these means it is possible to prevent heating which in working up fresh roots causes so much trouble, and to produce an oil of unparalleled quality.

**Anise Oil.** It is at the present moment too early to state with certainty, how on the whole the sale of Russian oil has been, and what stocks of this oil are still in existence, but a certain firmness of the market is unmistakable. The forced sales of large parcels of crude oil, which took place in the previous year, have now only occurred on a moderate scale, and the prices would already be decidedly higher, if it had not been for the fairly considerable quantities of oil of 1901 which have been carried forward into the new season. The value of this article will chiefly depend on the weather-conditions prevailing during the next few months, but it appears to us that a decline of any consequence is out of the question, if only for this reason, that the present quotations are below the normal average value.

The export of anise from Libau, the principal anise-shipping port of Russia, amounted

in 1900 to 27518 poods, of which 7744 poods to Germany
„ 1901 „ 18659 „ „ „ 6004 „ „ „

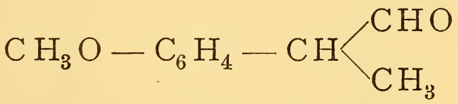
but it is possible that more important quantities than the above have found their way direct by rail from the anise-districts into Germany. The anethol-manufacturers had no lack of raw material. The Roumelian anise, already mentioned in our last Report, may possibly acquire some importance in the next few years. This anise yields a product of the highest quality, and should be preferred to the Russian seed on account of its purity.

New oxidation-products of anethol and analogous bodies with propenyl side-chain are discussed in Joseph Bougault's thesis[1]). If to a 1 per cent. solution of anethol in 96 per cent. alcohol, an excess of mercuric chloride is added, and then gradually a solution of about 1 per cent. iodine, the latter is immediately completely absorbed until 2 atoms iodine have been used up with one molecule anethol. The first superfluous drop then imparts a yellow colour to the liquid. On this Bougault bases a method for the determination of anethol and similar bodies with propenyl side-chain. But it can only be employed in the absence of bodies with double linkage, phenol- or amine-character, as these also react with iodine[2]). The determination is carried out as follows: To the alcoholic solution of anethol, diluted to about 1 to 2 per cent., there is added 10 cc of an alcoholic solution of mercuric chloride (containing 6 per cent.), after which a titrated iodine solution is added drop by drop until the liquid is permanently coloured yellow. 254 g iodine correspond to 148 g anethol.

The reaction[3]) which occurs in this process, is as follows: iodine and mercuric chloride form in the first instance iodine chloride, which, under the influence of the water of the alcohol, next splits up into hydrochloric acid and hypoiodous acid. The latter then attaches itself to the double linkage of anethol. This view is supported by the fact, that the same products are also formed when mercuric oxide and iodine are employed:

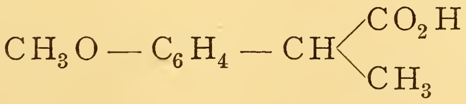
$$H_2O + 2\,C_{10}H_{12}O + HgO + 4\,I = HgI_2 + 2\,(C_{10}H_{12}O \cdot IOH).$$

An excess of mercuric oxide produces a body which shows all the properties of an aldehyde, and which possesses the formula $C_{10}H_{12}O_2$. The same body is also formed, when the addition-product obtained with mercuric chloride is submitted to further treatment with mercuric oxide. The constitution of this aldehyde is expressed by the following formula:



$$CH_3O - C_6H_4 - CH\left\langle\begin{matrix}CHO\\CH_3\end{matrix}\right.$$

for, when oxidised with silver oxide, it passes over into p-methoxyhydratropic acid



$$CH_3O - C_6H_4 - CH\left\langle\begin{matrix}CO_2H\\CH_3\end{matrix}\right.$$

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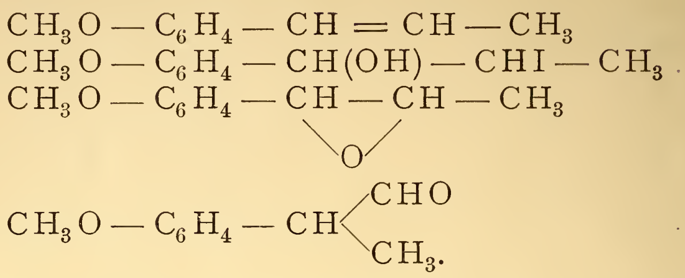
[1]) Thèse pour obtenir le grade de docteur, Paris 1902.

[2]) Wijs, Zeitschrift für angew. Chemie **1898**, 291.

[3]) For this reason the method is not applicable in practice to the determination of anethol contained in essential oils, as it only occurs in combination with bodies possessing double linkages, such as terpenes, methyl chavicol.

of the melting point 57°, and should therefore be designated as p-methoxyhydratropic aldehyde. Its formation is thus explained by Bougault:



$$CH_3O - C_6H_4 - CH = CH - CH_3$$
$$CH_3O - C_6H_4 - CH(OH) - CHI - CH_3$$
$$CH_3O - C_6H_4 - \underbrace{CH - CH}_{O} - CH_3$$
$$CH_3O - C_6H_4 - CH\begin{cases} CHO \\ CH_3. \end{cases}$$

It forms a colour- and odourless liquid with a nauseous, burning taste, boils at 255° to 256°, and has the specific gravity at 15° of 1,069. Its bisulphite compound can be crystallised from water. The oxime obtained in the usual manner melts at 96°.

The acid belonging to it, or better still the bisulphite double-compound of the aldehyde, can by further oxidation be converted into the ketone

$$CH_3O - C_6H_4 - CO - CH_3 \text{ (melting point 38°)}$$

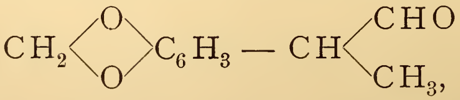
and the acid

$$CH_3O - C_6H_4 - COOH \text{ (melting point 88° to 89°).}$$

Entirely analogous to anethol is the behaviour during these various reactions of isosafrol, methyl isoeugenol, and isoapiol. The bodies with allyl side-chain (such as methyl chavicol, safrol) also react in the same manner with iodine and mercuric chloride or mercuric oxide, but here the reaction is less pronounced, and an excess of mercuric oxide does not produce the corresponding aldehyde. A further difference between the two classes of bodies is this, that the addition-products from bodies with propenyl side-chain, when treated with silver nitrate, produce iodide of silver, and the aldehyde belonging to it, whilst those from bodies with allyl side-chain form iodide of silver but no aldehyde. On the other hand, the addition-products from all the bodies referred to, are reconverted into the crude material by zinc and glacial acetic acid.

The author has produced the following bodies by precisely the same methods as in the case of anethol:

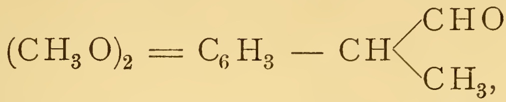
1. From isosafrol, methylene-3,4-dioxyhydratropic aldehyde



$$CH_2\left\langle\begin{matrix} O \\ O \end{matrix}\right\rangle C_6H_3 - CH\begin{cases} CHO \\ CH_3, \end{cases}$$

a liquid free from colour and odour. Boiling point 279° to 280°; $d_{15} = 1{,}203$. Melting point of the oxime 71°. Melting point of methylene-3,4-dioxyhydratropic acid 80°, and of methylene-3,4-dioxyacetophenone obtained from this acid 87° to 88°.

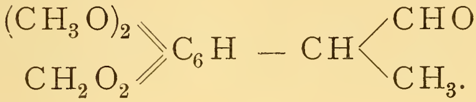
2. From methyl isoeugenol, dimethoxy-3,4-hydratropic aldehyde



$$(CH_3O)_2 = C_6H_3 - CH\left\langle\begin{array}{l}CHO\\CH_3,\end{array}\right.$$

a solid body of the melting point 44°. Melting point of the oxime 77°. The acid belonging to it, dimethoxy-3,4-hydratropic acid, melts at 60°, and the dimethoxyacetophenone formed from it, at 48°.

3. From isoapiol, dimethoxymethylene dioxyhydratropic aldehyde



$$\left.\begin{array}{r}(CH_3O)_2\\CH_2O_2\end{array}\right\rangle C_6H - CH\left\langle\begin{array}{l}CHO\\CH_3.\end{array}\right.$$

This is a colourless liquid, boiling at 305°, and having a specific gravity at 15° of 1,246. It is almost insoluble in petroleum ether. The acid belonging to it, dimethoxymethylene dioxyhydratropic acid, melts at 97°, and the dimethoxymethylene dioxyacetophenone produced from it, at 92°.

**Basil Oil.** The freshly-distilled essential oil from *Ocimum Basilicum* L. (*Selasih hidjau*) rotates the plane of polarised light 0,35° to the right, according to the observation made at the agriculturo-chemical laboratory of the Botanic Garden of Buitenzorg1). If the oil is decomposed into fractions by steam distillation, and if the 10 per cent. first passing over are collected separately, this portion shows a dextrorotation of + 5°, whilst the residue rotates 0,6° to the left. This residue, when heated, shows a remarkable optical behaviour. If, namely, it is heated up to nearly its boiling point, which lies at about 215°, and it is then cooled down, it is found that the previously slightly lævorotatory residue has become dextrorotatory (+ 2° in a 200 mm tube). But if it is heated for a prolonged time to a high temperature, the dextrorotatory power increases to + 3,4°, and appears to remain there permanently. On the other hand, by distillation in vacuo, only a body with a considerably lower dextrorotatory power can be isolated from the residue.

This peculiar optical behaviour of basil oil will be submitted to further examination.

**Bay Oil.** We have lately received such important consignments of genuine bay-leaves, that we were again able to supply exclusively our own distillate of the highest possible quality.

In addition to the 6 low-grade oils mentioned in our last Report, another large parcel of about 2300 lbs. imported in London from

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1) Annual Report **1901**, 58.

Guadeloupe, has meanwhile also been placed on the market. The quality of this oil also shows abnormal properties. Whilst the content of phenols (eugenol and chavicol) of normal distillates fluctuates between 59 and 65 per cent., two samples of this Guadeloupe oil contained only 38 and 41 per cent. phenols. The specific gravity of the one was 0,934, that of the other 0,926; the optical rotation was — 2°46′ and 3° 10′; against this, our own distillate has a specific gravity of 0,980 and a rotatory power of — 1° 48′. We do not believe that the two samples mentioned above were adulterated, but attribute the differences to an irrational method of distillation.

In place of the so-called extra-strong bay oil which we previously kept in stock, we now supply an absolutely terpeneless quality, which in respect of its solubility answers still higher requirements than the former.

**Cajeput Oil.** According to reports from Macassar, the distillation in the Moluccas has suffered through severe drought. In various districts the plants have been completely destroyed, and only a limited quantity of oil has been distilled. Similar conditions have prevailed in the Straits Settlements, and as a consequence the values have risen considerably both in Singapore and in Macassar. As soon as the stocks in Holland, amounting at the close of the year to about 2000 bottles, have to some extent become depleted, a general increase in the prices, of about 30 per cent., will also be bound to take place in Europe.

**Calamus Oil.** We have already on a previous occasion [1]) referred to the results, recently published jointly by Thoms and Beckstroem [2]), of their work on calamus oil. From these it appeared that asarone, which in the proportion of about 7,5 per cent. forms a constituent of this oil, has a genetic relation to the aromatic body of the oil. The asarone-content also explains the high methyl number, to which Benedikt and Grüssner [3]) had already called attention. For, apart from minute quantities of eugenol and asarylic aldehyde, calamus oil does not contain any compounds with methoxyl-groups. Beckstroem [4]) therefore proposes to make use of the asarone-content, in addition to the physical constants, in estimating the value of calamus oil.

**Camphor Oil.** Nothing new can be said of this article. We hear from Japan that the Camphor Monopoly Bill will again be laid before Parliament in the new Session, in May of this year.

A matter of exceptional interest was the report that a limited Company has been formed in New York under the style of "The Port

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[1]) Report October **1902,** 15.

[2]) Berliner Berichte **35** (1902), 3187 and 3195.

[3]) Chemiker-Zeitung **13** (1889), 1088.

[4]) Berichte d. deutsch. pharm. Ges. **12** (1902), 266.

Chester Chemical Company", which has for its object the production of camphor by synthetic process. The share-capital amounts to 1 000 000 dollars, in 10 000 shares of 100 dollars each. According to the prospectus which we have before us, the world's consumption of camphor is said to amount to 8 000 000 lbs., that of the United States to 2 000 000 lbs.

It is claimed that the camphor produced synthetically is decidedly purer than the natural article (probably crude camphor) as it is received from Japan, or Formosa, for the purity of the latter is given as 88—90 per cent., that of artificial camphor as 99 per cent. The process is protected by patents.

The factory has been established in Fox Island, with plant for an annual output of 2 000 000 lbs. The immediate production is said to amount to 600 000 lbs.

The crude material employed is oil of turpentine, and the yield is 98 lbs. camphor from 1 barrel of the oil.

With the proposed maximum output of 2 000 000 lbs., the company expect to pay dividends of 50 per cent.

It appears to us that in the calculation the cost of turpentine oil of 6 $^1/_2$ cents per lb. is taken too low, in view of the present market-quotations, whilst the selling-price of camphor at 50 cents per lb. is taken a little too high. The Company may perhaps prosper, so long as the price of crude camphor in Japan is not reduced to such an extent that the estimates are upset. This new competition would probably only affect the value of the article, when the production exceeds the demand in the United States, and when the Company would be forced to export its product.

The prospectus of the Company contains the following interesting communications on the camphor production in Asia, taken from the reports of the American Consul in Formosa:

> "Hitherto camphor has been produced from the wood of the camphor-tree which grows in Japan, China, and chiefly on the island Formosa. The production of Japan has fallen to 300 000 lbs., that of China has never exceeded 220 000 lbs., whilst that of Formosa in 1895 reached a total of 7 000 000 lbs., and in the last four years amounted on the average to about 6 000 000 lbs. For all practical purposes, Formosa therefore covers the world's requirements, and its production yields an annual revenue of about $ 800 000 to the Japanese Government. In order to protect the industry, it is now obligatory to plant immediately a new tree for every camphor-tree which is cut down. The production in Formosa is moreover a monopoly, and is protected by 1500 armed guards who also control the afforestation as prescribed by law."

**Cananga Oil.** The stocks available in Holland and at Antwerp are only very insignificant, and consist partly of old stocks of inferior, viscid quality which gives a considerable loss in rectification, and which compares unfavourably in net cost with the fresh article imported direct. Of the latter we have recently received important consignments, which enable us to offer an exquisitly fine, rectified, water-white oil at a very moderate price. The present quotation is certainly worthy of notice, for, according to reports from Java, at the present low values the manufacture is only carried on on a small scale, and it is expected that this diminished production will very soon find expression in the quotations.

**Caraway Oil.** The prices of Dutch caraway-seed have undergone but unimportant fluctuations in the course of the last six months. Several attempts made to drive up the values have been unsuccessful, and it would appear that the stocks are still too large to carry through, in the face of the new harvest, an increase in the quotations with any lasting result.

According to reports which have come to hand, the quantity sown this year would be approximately the same as that of 1902; for this reason, an upward movement would only be justified if the result of the harvest were injuriously affected by unfavourable weather-conditions.

From Sweden and Norway a few isolated small parcels were offered at disproportionately high prices. East Prussia and Finland supplied only insignificant quantities; on the other hand, several truck-loads of German caraway-seed were placed on the market, and were rapidly taken up by the consumers.

The prices of carvol, caraway oil, and carvene are at present well worthy of consideration.

**Cassia Oil.** The fluctuations of the last six months moved between the narrow limits of 1 d. to 2 d. per lb., according to the exchange of silver. Latterly, the high-grade oil containing 80 to 85 per cent. aldehyde, which is the one most in demand, has been somewhat more plentiful. The qualities which have lately come under our notice have not called for any remark, and it may therefore be assumed that the adulterators have given up their nefarious trade. But all the same, it will be well, in view of the Chinese character, to continue checking the quality by means of the determination of aldehyde.

Business in cassia oil has been remarkably slow. This is also confirmed by the figures of the Hongkong export. These figures, which comprise oils of cassia and of star-anise, were as follows: —

| | | | | | | |
|---|---|---|---|---|---|---|
| | in the year | 1902 | only | 3635 | cases |
| against | „ „ „ | 1901 | | 6423 | „ |
| | „ „ „ | 1900 | | 4261 | „ |
| | „ „ „ | 1899 | | 3374 | „ |
| | „ „ „ | 1898 | | 4461 | „ |

Of the quantity of 1902, the shipments to America consisted of 1308 cases, against 2090 cases in 1901.

The last Chinese quotations, at the end of February, were: —

| | | | |
|---|---|---|---|
| for 70 to 75 per cent. oil | $ 195,— per picul | = 2/8 | per lb. d/d Hamburg |
| „ 75 „ 80 „ „ „ | $ 205,— „ „ | = 2/9 | „ „ „ „ |
| „ 80 „ 85 „ „ „ | $ 215,— „ „ | = $2/10^3/_4$ | „ „ „ „ |

The stock at Hongkong amounted to about 300 cases.

At the present prices we consider this article a good subject for speculation.

**Cassia Oil "Schimmel & Co."** Although pure cinnamic aldehyde, free from chlorine, cannot at the present quotations compete with Chinese cassia oil, there are a fair number of consumers who use the first-named excellent product regularly for special purposes.

Pure cinnamic aldehyde has also been used of late to cover the disagreeable odour of many technical and pharmaceutical products. This applies in the first instance to benzene and ether (collodion). It should also be employed largely in all cases where hitherto cassia oil has been used as a spice, i. e. more particularly in the manufacture of the better-class confectionery, cakes, biscuits, condiments for cakes, and such like. In all these articles it is a question of the pure cinnamon-cassia flavour, and this is embodied in the pure aldehyde as in no essential oil. The manufacture, unfortunately, is not remunerative so long as the high-grade qualities of Chinese cassia oil are so low-priced, for the quotations of these two products must to a certain extent be proportionate to each other.

**Oil of Cassie flowers.** As mentioned by us on a previous occasion¹), we succeeded at the time in isolating from the oil of cassie flowers (*Acacia Farnesiana* Willd.), in addition to methyl ester of salicylic acid and a ketone of a very pleasant violet-like odour, also benzyl alcohol, by means of phthalic anhydride. Recent examinations have shown that in all probability linalol and geraniol are also present. Further, we were lately able to obtain a crystalline compound, by shaking with bisulphite solution a fraction of the oil boiling from 95° to 105° at 11 mm. When this compound was boiled with soda solution, an aldehyde was soon split off, which was immediately identified by its intense characteristic odour as decylic aldehyde.

In a solution of glacial acetic acid it readily formed with sodium acetate and semicarbazide hydrochloride, a semicarbazone melting at 97°. By recrystallisation from benzene and petroleum ether, the melting point of the compound could not be raised to any appreciable extent,

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¹) Report April **1901**, 18.

as the quantity of this aldehyde obtained up to the present was still very small. But in any case the aldehyde is identic with decylic aldehyde, whose semicarbazone melts at 102°. We obtained another aldehyde from a fraction boiling at 11 mm between 100° and 112°. This yielded with semicarbazide a solid semicarbazone, which, after repeated recrystallisation from alcohol, melted at 200° to 201°, and which was found to be the semicarbazone of cumic aldehyde. When this was heated with dilute sulphuric acid, an aldehyde was regenerated, which does not differ in its odour from cumic aldehyde. The melting point of the semicarbazone of the cumic aldehyde isolated from oil of cumin also lies at 200°.

At this moment we are still engaged on the further examination of the essential oils of *Acacia Farnesiana*, and of *Cassie Romaine*, and it is our intention, after a sufficiently thorough study, to report on this subject in detail.

A German Patent (No. 139 635) has been granted to us for the use of the newly discovered bodies in the production of artificial oil of cassie flowers.

**Cedarwood Oil, Atlas** (Libanol Boisse). An exceptionally lively interest has been shown for this novelty, and at various clinical institutions examinations are now in progress on the therapeutical value of this product. If they confirm the favourable results obtained in the French hospitals, the use of this oil may become very extensive.

More recent information of a practical character has not been received from France.

Emilien Grimal[1]) reports in two communications the results of an examination made by him in our laboratory, of the essential oil of the Atlas cedar, *Cedrus atlantica,* a variety of *Cedrus Libani.* The oil examined had a peculiar odour, which is chiefly due to a ketone $C_9H_{14}O$ detected in the oil. The physical constants of the oil were as follows: $d = 0{,}9508$; $n_{D20^\circ} = 1{,}51191$; $[\alpha]_{D20^\circ} = +60^\circ 32'$. The oil dissolved in 8,5 parts of 90 per cent. alcohol, and only in 115 parts of 70 per cent. alcohol. Acid number 1,16; saponification number 6,92; saponification number after acetylation 33,84.

In distilling the oil, 80 per cent. passed over between 270° and 295°. 800 g of the oil were fractionated; in the portions first passing over, small quantities of acetone were detected, and about 40 g were obtained of a fraction boiling between 180° and 215°, which contains the ketone $C_9H_{14}O$. This ketone yielded a semicarbazone of the

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[1]) Compt. rend. **135** (1902), 582 and 1057.

melting point 159° to 160°, and an oxime which could not be obtained in the solid form, but which on brominating yielded a dibromide melting at 132° to 133°.

From the higher-boiling portions of the oil there was further obtained, as principal constituent, d-cadinene of the following constants: boiling point 273° to 275°; d = 0,9224; $n_{D20°} = 1,5107$; $[\alpha]_{D20°} = + 48° 7'$.

The hydrochloride produced from the latter showed the melting point 117° to 118°, and differs from the one hitherto known only by the opposite rotatory power, $[\alpha]_{D20°} = + 25° 40'$.

The cadinene regenerated from the dextrogyrate hydrochloride by Wallach's method, by means of sodium acetate in glacial acetic acid, showed the following constants: boiling point 274° to 275°; d = 0,9212; $n_{D20°} = 1,5094$; $[\alpha]_{D20°} = + 47° 55'$.

The hydrobromide melted at 124° to 125°.

The sesquiterpene also differs from the cadinene only by the optical rotation. A pure dextrogyrate cadinene had not hitherto been known.

**Cedarwood Oil, Florida.** It was recently found possible to reduce selling prices, as the offers of genuine cedarwood-chips were larger than before, and the manufacturers of lead-pencils were voluntarily making concessions. The distillation-expenses in our new factory are also essentially lower.

**Celery Oil, from the fresh herb.** The stock of this beautiful preparation has been completely cleared. We doubt very much whether the manufacture of this oil will again be taken up by us, as the number of consumers who are able to appreciate it is limited. This oil is one of those — like, for example, the garlic oil we used to manufacture — which are only appreciated when they are no longer obtainable.

**Cinnamon Oil, Ceylon.** The prices of fine cinnamon-chips have undergone fairly large fluctuations, until at last the downward tendency gained the upperhand. As a consequence, cinnamon oil could be produced under favourable conditions, and could be offered at such low prices as hardly ever before.

**Citronella Oil, Ceylon.** The prices of this important article reached their lowest position in October last year at about 8½ d. per lb. The distillation was then completely suspended on account of continuous rainfall in the citronella-districts, and this led to a rise in the prices up to 9¾ d. This last figure represents approximately the present market-value. The quotations had to be raised proportionately.

The exports from Ceylon have slightly receded in 1902. They were:

| | | |
|---|---|---|
| in | 1902 | 1 294 750 lbs. |
| against „ | 1901 | 1 430 168 „ |
| „ | 1900 | 1 409 050 „ |
| „ | 1899 | 1 478 756 „ |
| „ | 1898 | 1 365 917 „ |
| „ | 1897 | 1 182 867 „ |

The figures for the various countries were as follows: —

| | |
|---|---|
| to the United Kingdom . . . | 556 096 lbs. |
| „ „ America . . . . . . . | 538 970 „ |
| „ „ Germany . . . . . . | 146 518 „ |
| „ „ Australia . . . . . . | 26 408 „ |
| „ „ China . . . . . . . | 17 115 „ |
| „ „ France . . . . . . . | 2 376 „ |
| „ „ Singapore . . . . . | 1 867 „ |
| „ „ India . . . . . . . | 5 400 „ |
| Total | 1 294 750 lbs. |

The low value of the article has lately, unfortunately, again led to numerous and very peculiar adulterations, such as have never been observed before.

In our Report of October 1899, page 23, we mentioned already, that citronella oils are met with in commerce, which, although they are unadulterated, yet do not form a clear solution with 80 per cent. alcohol, and therefore do not pass Schimmel's test. But we then said that oils which only just formed a cloudy solution, and with which no oil-drops are separated out from the solution, could not be considered objectionable, as the insolubility could only be attributed to the resinification of the (light) sesquiterpene present in citronella oil; on the other hand, it should be absolutely insisted upon, that on prolonged standing no small drops of mineral or fatty oil are separated out from the alcoholic solution, neither at the surface, nor on the bottom of the vessel.

Since then we have very rarely been in a position to examine such insoluble, but unadulterated oils. The majority of the oils characterised by insolubility was adulterated; for this reason, we had no occasion to depart from the condition imposed by us, that citronella oil must form a clear solution even in 10 volumes 80 per cent. alcohol.

Parry[1]) has subsequently called attention to the fact, that the oils whose insolubility in 80 per cent. alcohol must be attributed to a high

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[1]) The Chemist and Druggist **59** (1901), 142; compare Report October **1901**, 17.

content of sesquiterpene, dissolve clear, or at most with a very slight turbidity, in 81 to 83 per cent. alcohol, whilst with oils which have been mixed with only very small quantities of petroleum, the turbidity does not diminish even when 85 per cent. alcohol is used.

But along with the gradual decline in the price of citronella oil there was a great increase in the number of insoluble oils which were submitted to us for examination, and we found that even the somewhat stronger alcohol recommended by Parry did not regularly suffice for solution. The oils differed from unadulterated oils barely in specific gravity, but little in rotatory power, most in the index of refraction which was essentially lower than otherwise. Now, when in a specially striking case a rather large sample was placed at our disposal, we determined the physical constants of the portion insoluble in 80 per cent. alcohol. We found: $d_{15^\circ}$ 0,8411; $\alpha_D$ — 11° 21′; $n_{D20^\circ}$ 1,46872. The separated insoluble oil did not dissolve in 10 volumes 90 per cent. alcohol, but made a cloudy solution with about 8 volumes 95 per cent. alcohol. In order to obtain further data, a part of the original oil was carefully fractionated with water vapour; for the two fractions first passing over we ascertained the following constants:

|  | $d_{15^\circ}$ | $\alpha_D$ | $n_{D20^\circ}$ |
|---|---|---|---|
| I | 0,8145 | — 19° 6′ | 1,44741, |
| II | 0,8278 | — 21° 24′ | 1,45371, |

whilst a pure Ceylon citronella oil taken for comparison, and reduced into fractions of equal quantity, gave the following figures for the more volatile portions:

|  | $d_{15^\circ}$ | $\alpha_D$ | $n_{D20^\circ}$ |
|---|---|---|---|
| I | 0,8599 | — 50° 44′ | 1,47058, |
| II | 0,8608 | — 48° 46′ | 1,47156. |

It follows that to the citronella oils which do not pass the solubility-test, a comparatively highly volatile body, of very low specific gravity, and an exceptionally low index of refraction, has been added. It is open to doubt, whether it is here a question of adulteration with a fraction of petroleum or petroleum ether, or of the addition of resin spirit. Parry and Bennett who simultaneously with us made similar observations on adulterated citronella oil, and who have already published these¹), are inclined to believe that it is a question of adulteration with resin spirit, without, however, giving proofs, which in any case it would be very difficult to supply. In a short time we shall have an abundance of material for examination, and we hope then to be able to clear up this question to some extent.

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¹) The Chemist and Druggist **62** (1903), 88.

It follows from the foregoing that from an oil adulterated in such manner, the adulterant can be separated by fractional distillation, and detected by its physical constants. For this reason Parry and Bennett, in a communication[1]) published shortly before the closing of our Report, propose the following standard: that the first fraction, consisting of 10 per cent. of the oil under examination, distilled under reduced pressure (20 to 40 mm) must have a specific gravity not below 0,858, and a refractive index, at 20°, not below 1,4570, and further, that citronella oil must dissolve either clear, or at most with the slightest opalescence, in 10 volumes of 80 per cent. alcohol at a temperature of 20°.

We can only express our complete agreement with this proposal. The solubility-test in 80 per cent. alcohol (Schimmel's test) must be maintained, although it may perhaps be suitable to change the temperature of 15° originally proposed by us, into one of 20°; the distillation-test will make it also possible to identify those oils, which, being but slightly adulterated, have passed the solubility test.

* * *

Under the designation "Java lemon olie" we have lately received several samples of oils, which can neither pass for lemongrass nor for palmarosa oil, and which should rather be considered as a kind of citronella oil, although they slightly differ from the latter in the odour. The mother-plant from which this oil is obtained, is presumably a species of *Andropogon*: we know nothing definite about this, but will endeavour to ascertain further details of the origin of this oil.

The samples obtained from different sources show a fair amount of similarity in their constants, as will be seen from the following short table:

| $d_{15^\circ}$ | $\alpha_D$ (in 100 mm tube) | $n_{D20^\circ}$ | Total content of $C_{10}H_{18}O$ |
|---|---|---|---|
| 0,8889 | + 13° 26′ | 1,46466 | 49,09 % |
| 0,8914 | + 10° 6′ | 1,46684 | 50,9 „ |
| 0,8809 | + 14° 52′ | 1,46496 | 49,18 „ |

The oils dissolve readily in 80 per cent. alcohol, but when the concentrated solution is diluted, turbidity occurs uniformly. To all appearances they do not contain geraniol, but this statement is subject to further verification, as in every case we have only had small samples at our disposal, and therefore were unable to make a thorough examination.

From the sample mentioned last we have isolated the aldehyde contained in it, by shaking with bisulphite solution. In the odour it completely resembled citronellal, whose physical constants it also possesses: boiling point 205° to 208°, $d_{15^\circ}$ 0,8567, $n_{D20^\circ} = 1,44791$; but it was found to be lævogyrate, as we observed $\alpha_D = -3°$. This

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[1]) The Chemist and Druggist **62** (1903), 408.

is consequently the first time that l-citronellal has been detected as a constituent of an essential oil. The melting point of the semicarbazone which was produced for the further identification, and was prepared according to Tiemann's directions, was found at 74°.

In the portions of the oil which did not react with bisulphite solution, cineol could be detected with certainty; they probably also contain limonene, or a mixture of limonene and dipentene.

A sample of citronella oil which takes about an intermediate place between Ceylon and Java citronella oils, was received by us some time ago from the Government Laboratory in Jamaica. We found for this oil: $d_{15^\circ} = 0{,}8947$, $\alpha_D - 4^\circ\,16'$, and $n_{D20^\circ}$ 1,47098. It also showed a low acid number, and contained 86,4 per cent. total $C_{10}H_{18}O$, with a citronellal-content of 25,43 per cent.

In a note appearing in the "Tropenpflanzer"[1] we find that in the Botanical Garden at Victoria in the Cameroons, under the name *Andropogon citratus*, a species of grass is cultivated, which, according to an examination by Strunk, yields an oil which is seemingly identic with citronella oil. Strunk distilled 10 kilos of the fresh grass with water, and obtained a yield of 0,38 per cent oil. With the primitive means at his disposal he was able to ascertain that this oil contains about 15 per cent. of an aldehyde, which appears to be identic with citronellal.

According to the foregoing the grass cultivated at Victoria, of which it had not hitherto been possible to determine the species as the plant never reached the flowering stage, may possibly be identic with *Andropogon Nardus* L., which in the East-Indies is cultivated on a large scale for the production of citronella oil.

It has repeatedly attracted our attention, that when it is a question of their origin, the *Andropogon* grasses are frequently confounded with each other. The thought which first occurs is, that such confusion is caused by the omission of the name of the author after the designation of the species. But this does not apply in every case, for there are some exactly-defined species indicated as the mother-plants of oils which, according to our information, could not possibly be produced from them. We will give some examples of this. Tschirch, in his work "Indische Heil- und Nutzpflanzen"[2] mentions on page 128 *Andropogon Schoenanthus* L. as the mother-plant of lemongrass oil. The same statement is made in the chapter *Gramineae* edited by Hackel, in Engler and Prantl's "Natürlichen Pflanzenfamilien"; the oil obtained from it is said to be met with in commerce as

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[1] Volume 7 (1903), 37.

[2] Berlin 1892. R. Gaertner.

"lemon oil". Sadebeck[1]) also states, that *Andropogon Schoenanthus* L. is cultivated in some parts of East Africa, and that the fragrant lemongrass oil is distilled from it. But at the same time he mentions also, that this oil is used for adulterating rose oil, and thereby (and also by referring to the synonymous words rusa, palmarosa, or Turkish geranium oil) he identifies it with palmarosa oil. Finally, the annual report of the Buitenzorg botanical gardens also mentions *Andropogon Schoenanthus* L. (sereh) as the mother-plant of lemongrass oil.

With reference to a lemongrass oil from Jamaica which is said to be distilled from this species of grass, see under "lemongrass oil".

**Clove Oil.** Since our Report of October 1902, the prices of Zanzibar cloves have gradually advanced by a few marks per 100 kilos, until about the end of January last the rise came to a stop, and the value even declined again little by little to about the October-level. The present state of the prices may be designated as normal, healthy, and there can be no objection to the laying in of an abundant supply of clove oil.

In our new factories we have made extensive arrangements for the distillation of cloves on the largest scale, in the true sense of the word. The establishment of a private custom-house in our factory-buildings is a great advantage in this connection, as cloves and all other spices may be distilled free of duty if under control of the Customs' officers, a control which extends to the denaturalising of the spice after distillation.

The following statistics, taken from official Consular reports in the "Deutsches Handels-Archiv", may be found interesting.

Cloves. The exports were: —

| | Weight in pounds: | Value in rupees: |
|---|---|---|
| in 1898 . . . . . . . . . . . | 10856566 | 2155956 |
| „ 1899 . . . . . . . . . . . | 16593340 | 2958487 |
| „ 1900 . . . . . . . . . . . | 11788095 | 2372227 |
| „ 1901 . . . . . . . . . . . | 11962069 | 2465373 |

They were made up as follows: —

| | 1898 | 1899 | 1900 | 1901 |
|---|---|---|---|---|
| | | Weight in pounds: | | |
| Europe . . . | 4138086 | 8028780 | 5235388 | 4470632 |
| America . . | 729960 | 648970 | 719600 | 252000 |
| Asia . . . | 5912800 | 7599517 | 5769293 | 7081471 |
| Africa . . . | 75720 | 316073 | 63814 | 153966 |
| | | Value in rupees: | | |
| Europe . . . | 797375 | 1394217 | 1031952 | 888110 |
| America . . | 149402 | 110108 | 150079 | 50700 |
| Asia . . . | 1194032 | 1397837 | 1177754 | 1496053 |
| Africa . . . | 15147 | 56425 | 12442 | 30510 |

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[1]) Die Culturgewächse der deutschen Colonien. Jena 1899, p. 247.

It will be seen that the exports to India have increased considerably, those to Europe slightly, whilst the exports to America have greatly gone down. As regards the European ports, the exports were in detail: —

| | 1899 | 1900 | 1901 |
|---|---|---|---|
| | Weight in pounds: | | |
| Rotterdam | 4 473 240 | 2 674 160 | 2 330 764 |
| London | 1 432 475 | 1 404 968 | 1 841 493 |
| Marseilles | 292 215 | 217 000 | 133 000 |
| Hamburg | 1 249 850 | 715 260 | 125 720 |
| | Value in rupees: | | |
| Rotterdam | 786 212 | 537 810 | 466 168 |
| London | 254 852 | 274 520 | 364 955 |
| Marseilles | 51 229 | 49 800 | 25 200 |
| Hamburg | 204 267 | 122 912 | 23 220 |

London, which at one time was the principal port for clove-exports, has therefore improved its position in the year under review. Rotterdam has, however, still an advantage of half a million pounds.

Clove-stems were exported: —

| in | 1898 | 1899 | 1900 | 1901 |
|---|---|---|---|---|
| | | Weight in pounds: | | |
| to Europe | 584 640 | 3 605 245 | 1 743 426 | 1 290 868 |
| ,, Asia | 305 561 | 216 484 | 220 447 | 210 140 |
| ,, America | 336 875 | 555 940 | 98 000 | 140 000 |
| | | Value in rupees: | | |
| ,, Europe | 24055 | 104351 | 70453 | 66556 |
| ,, Asia | 14 845 | 6748 | 11 621 | 13350 |
| ,, America | 19657 | 31 708 | 7 700 | 10600 |

The export to Europe was shipped: —

| in | 1898 | 1899 | 1900 | 1901 |
|---|---|---|---|---|
| | | Weight in pounds: | | |
| to Hamburg | 456 890 | 2 980 110 | 1 478 226 | 1 212 668 |
| ,, London | 74 900 | 370 335 | 83 160 | 33 700 |
| ,, Marseilles | 38 850 | 179 900 | 28 000 | 31 500 |
| ,, Rotterdam | | unknown | | 112 000 |

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In our April Report of last year, on page 24, we stated that, according to our observations, among others benzoic acid was also contained in clove oil, and we pointed out that it was probably present in the oil, if only in minute quantity, in the form of its methyl ester. We were namely able to isolate this ester from the first runnings though not in a perfectly pure state, by frequently repeated fractional distillation, and subsequent suitable treatment of a fraction which came under consideration for this body on account of its boiling point. The first portions of the oil passing over betwen 40° and 94° (8 to 9 mm), distilled after treatment with bisulphite solution between 161° and 220°. The first of these fractions, boiling at 161° to 165°, was tested for pinene, but yielded no solid nitrosochloride; similarly, no solid terpene derivative could be obtained from the subsequent fractions, which, judging by their physical constants and the odour, consisted chiefly of terpenes. The constants of the two fractions distilled over sodium were as follows: 1. boiling point 165° to 170°, specific gravity 0,8567, optical rotation — 2° 31′ (50 mm), and 2. boiling point 170° to 180°, specific gravity 0,8631, optical rotation — 1° 11′ (100 mm). The oil passing over at 180° to 210° served for the isolation of the benzoic ester. It was oxidised at ordinary temperature with a 1 to 2 per cent. solution of potassium permanganate, until the violet colour of the solution, which was gradually added to the oil in small quantities, remained unchanged. In this manner we obtained a liquid which had a distinct odour like methyl ester of benzoic acid, and boiled at 190° to 200°, and which, being slightly lighter than water, would still contain considerable quantities of foreign admixtures. As in spite of this the saponification number was comparatively high (101,1) it was obvious that the oil had a high ester-content. By repeated careful fractionating we endeavoured, but unfortunately without success, to separate from it a fraction with a still greater ester-content. In consequence of paucity of material we were then compelled to abandon further attempts to produce it in the pure state, and to content ourselves with having proved that as a matter of fact an ester of benzoic acid was present in the oil. The saponification yielded a pure white acid crystallising in leaflets, which had the melting point 121°, could readily be sublimed, and showed all the properties of benzoic acid. When heated with methyl alcohol and concentrated sulphuric acid, it formed methyl ester of benzoic acid with its characteristic odour. We would still point out that the boiling point of the ester fraction in question very closely approaches that of methyl ester of benzoic acid (199°). By means of saponification we succeeded in identifying the compound, which was present along with the ester, as methyl heptyl ketone. The oil driven off with steam from the saponification liquor, possessed a refreshing rue-like odour. The boiling point was at 191° to 196°. The capacity of reacting with bisulphite liquor, and of forming a semicarbazone with semicarbazide in acetic solution, showed that the body was a ketone, or an aldehyde respectively. The semicarbazone melted at 118° to 119°, and when submitted to elementary analysis gave values corresponding to those of the semicarbazone of methyl heptyl ketone.

1. 0,1606 g of the substance yielded 0,3530 g $CO_2$ and 0,1448 g $H_2O$.
2. 0,1510 g „ „ „ „ 0,3321 g „ „ 0,1401 g „

|  | Calculated for $C_{10}H_{21}ON_3$: | Found: |  |
|---|---|---|---|
| C | 60,30 per cent. | 59,94 per cent.; | 59,98 per cent. |
| H | 10,55 „ „ | 10,15 „ „ | 10,31 „ „ |

The methyl heptyl ketone produced for the purpose of comparison by heating a mixture of calcium caprylate and acetate, yielded a semicarbazone of the same melting point. A mixture of the two semicarbazones melted at 118° to 119°, a proof that both bodies were identic, and that the product isolated from clove oil was methyl heptyl ketone. The presence of this ketone in oil of cloves is all the more interesting, as it had up to the now only been found in rue oil¹). When the opportunity arises we will return to this body, and then identify it further. According to our present observations methyl heptyl ketone reacts with some difficulty with sodium bisulphite. To this may possibly be attributed the fact that we detected the ketone of clove oil in fractions which had already been shaken with bisulphite liquor.

In our last year's April Report²) we discussed a new method (published by Verley and Bölsing) for the quantitative estimation of alcohols and phenols, which is based on this, that the alcohols (or phenols) in question are esterified in the presence of pyridine by means of a known quantity of acetic anhydride, and the acetic acid not thereby combined is titrated back. As the method was specially recommended by Verley and Bölsing for the determination of eugenol in oil of cloves, we have taken this particularly into consideration in testing the process, and have examined on the one hand eugenol mixtures of known content, on the other hand numerous clove oils, both by this method and by the one introduced by Umney. We desire to state here that some considerable time ago we slightly modified Umney's method to this extent, that, instead of a 10 per cent. potash liquor for extracting the clove oils, we use a 5 per cent. soda-solution. The results thereby obtained are perfectly satisfactory.

As contrasted with this, the experience obtained by us with the acetylation-method proposed by Verley and Bölsing is unfortunately such, that we are unable to confirm the statements made by these gentlemen as to the reliability of their method. Already with the artificial mixtures very important differences could be observed as compared with Umney's method, differences which became even more pronounced with the natural clove oils.

It should be mentioned here particularly, that we, of course, paid the most scrupulous attention to the conditions of temperature, and that the errors observed cannot therefore be attributed to this. The

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¹) Report April **1901**, 52. — Berichte der deutsch. pharm. Ges. **11** (1901), 3.
²) Report April **1902**, 24.

following table which contains some of the results obtained by us, may serve as an illustration of the foregoing:

| | Eugenol-content | |
|---|---|---|
| | according to Umney (5 per cent. NaOH) | according to Verley and Bölsing |
| Mixture with 10 per cent. eugenol | 9,5 per cent. | 13,2 per cent. |
| ,, ,, 50 ,, ,, ,, | 49,5 ,, ,, | 51,33 ,, ,, |
| ,, ,, 75 ,, ,, ,, | 75,0 ,, ,, | 73,58 ,, ,, |
| Pure eugenol . . . . . . . . | 100,0 ,, ,, | 102,3 ,, ,, |
| English oil of cloves . . . . . | 90,5 ,, ,, | 79,94 ,, ,, |
| ,, ,, ,, ,, . . . . . . | 73,0 ,, ,, | 74,12 ,, ,, |
| ,, ,, ,, ,, . . . . . . | 80,0 ,, ,, | 69,53 ,, ,, |

These few examples may already suffice to justify our unfavourable opinion on the method proposed by Verley and Bölsing. It is all the more surprising that we have not arrived at approximately as satisfactory results as Verley and Bölsing, as they used normal liquor for titration, but we only semi-normal solution. Further, it is not quite clear on what grounds Verley and Bölsing made the statement, that in the case of differences between Umney's method and theirs, the latter should always be preferred; for they themselves admit that with artificial mixtures Umney's method also gives figures which agree most satisfactorily. The fact that the results obtained by their method agree with those of the process recommended by Thoms is not at all convincing, as the latter gives approximate values only when the conditions mentioned in the directions are carried out most accurately — a matter which is very difficult to accomplish. For practical purposes moreover this method generally takes up too much time.

After all we still believe that the method proposed by Umney, modified by us in the above-mentioned manner, is the most practical and reliable method for the determination of eugenol. According to this process, 10 cc oil are shaken for a considerable time with a 5 per cent. soda liquor in a burette or cassia flask, and the mixture then left standing, but the vessel is occasionally turned lightly round on its vertical axis in order that oil drops adhering to the sides of the glass may also rise to the surface. The portions of the oil which have not combined with alkali are estimated volumetrically, and the eugenol-content is ascertained from the difference between the original quantity of oil and the non-phenols. In order to avoid all misunderstanding we would point out, that we can only guarantee the eugenol-content of oils of clove on the basis of the method just described. Further, we wish to call particular attention to the fact that it is here a question of percentages by volume, although with normal oils of clove the difference between percentages by weight and by volume should not be very large.

H. von Soden and W. Rojahn[1]) have been able to isolate from the hydrocarbons of an oil of clove stems, naphthalene[2]), a body which up to now had not been detected as a constituent of an essential oil.

**Oil of Copaiba.** Oil of copaiba has been adopted officially only by the British Pharmacopœia, and it is there required to have a specific gravity of 0,900 to 0,910, lævorotatory power, and solubility in an equal volume of absolute alcohol. The degree of lævogyration is not given, but in the article "Copaiba", i. e. copaiba balsam, it is stated that the essential oil, contained up to 40 per cent in the balsam, must have a rotatory power of — 28° to — 34°. That this condition is evidently due to an error is a matter to which F. W. Short[3]) has first called attention; Parry, as appears from a recently published communication[4]) by him, is also of opinion, that many oils of copaiba, although unadulterated, do not possess such a rotatory power. According to our own experience, the extreme limits within which the rotatory power may fluctuate, should be taken as — 7° and — 35°.

But, according to Parry, much adulterated copaiba balsam has, especially in recent times, been placed on the market, from which either a dextrogyrate (up to + 28°) oil is obtained, or one which is very strongly lævorotatory (— 50° to — 60°). If such oils are to be judged, it may always be taken for granted that they are adulterated; the change in the rotatory power in the first-named case would lead to the conclusion that so-called African copaiba balsam had been added, whilst in the second case it might be assumed that gurjun balsam had been mixed with the material used for distillation. Oil of gurjun balsam, also called East Indian copaiba oil, would no doubt, when added to copaiba oil, raise the latter's specific gravity, whereas the oil of African copaiba reduces the solubility in absolute alcohol required by the British Pharmacopœia.

**Cypress Oil.** In the cohobation of the distillation waters there is here also obtained a very volatile, yellow-coloured distillate, in which can be detected without difficulty methyl alcohol, diacetyl, and furfurol, bodies which have already been found repeatedly in distillation waters. They were identified in the usual manner: methyl alcohol by the acid oxalate; diacetyl was separated as monophenylhydrazone, or osazone; and furfurol was recognised by its boiling point, its colour-reaction with aniline and toluidine, and was also

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[1]) Pharm. Zeitung **47** (1902), 779.

[2]) The same substance has been found by the authors in the essential oil from the bark of a storax.

[3]) Pharm. Journ. **64** (1900), 54.

[4]) The Chemist and Druggist **62** (1903), 332.

characterised by the melting point of its phenylhydrazone. The last-named body can also be very readily identified by the semicarbazone, which, being scarcely soluble in water, is precipitated already from a dilute aqueous solution by semicarbazide acetate. It is obtained in this manner in the form of brilliant white laminæ which turn slightly yellow when kept, especially when exposed to the light. The semicarbazone melts at 197° with decomposition.

**Dill Oil.** From Spain we received a sample of dill oil which had been distilled exclusively from the dill plant, and which differed in its properties in a marked degreee from normal dill oil. Its physical constants were as follows: $d_{15^\circ}$ 0,9282, $\alpha_D + 45^\circ 47'$, $n_{D20^\circ}$ 1,49638; it was insoluble in 80 per cent. alcohol, but formed a clear solution with about 5 volumes of 90 per cent. alcohol. Judged by the odour, the oil appeared to have a large phellandrene-content; this supposition was soon confirmed, for when the oil was tested for phellandrene in the usual manner, it gave an exceptionally strong reaction. A trial to determine the carvone-content by titration with hydroxylamine hydrochloride, showed that it amounted only to about 16 per cent.

When fractionated in vacuo, by far the greater part of the oil, (four-fifths) passed over at the boiling temperature of terpenes; it was found to be almost pure phellandrene, which perhaps still contained small quantities of other terpenes. Next followed a comparatively small intermediate fraction, which, however, had only a very faint odour like carvone. The boiling point of the residue was fairly high, and the distillate was heavier than water. As there were grounds for supposing that the dill oil might contain dill-apiol, which Ciamician and Silber have found in the oil from East Indian dill, this portion was repeatedly submitted to fractional distillation in vacuo. In this manner there was finally obtained an oil which had a faint yellow colour, and which passed over constantly between 155° and 156°, at 8 mm pressure. As it was only a question of proving whether this body actually contained dill-apiol, a small quantity of the oil was heated in a sealed tube for several hours to 160° with an alcoholic solution of sodium ethylate. The reaction-product which separated out when water was added, had a slightly higher boiling point than the crude material, and when slowly cooled it gradually solidified into a hard crystalline mass, which was dried on a tile in order to remove small quantities of liquid matter, and was then repeatedly recrystallised from dilute alcohol. As was clear from the melting point 43° to 44° of the crystals and that of their product of bromination, it was actually a question of dill-isoapiol.

When the portion containing apiol was distilled, there remained in the flask a mass with a very high boiling point, which solidified on cooling, and which could be purified by recrystallisation from boiling absolute alcohol. This, however, is probably not a hydrocarbon, but a wax-like substance.

As dill oil is met with both free from phellandrene (our own distillates from the fruit of the dill have never given us as such a phellandrene-reaction) and also containing phellandrene, the presence of this hydrocarbon must perhaps be attributed to the fact that the oil has been distilled not exclusively from the fruit, but from both the fruit and the herb, and the phellandrene-content will vary according to the quantity of the latter.

## Essential Oils, Sicilian and Calabrian.

The Imperial German Consul at Messina, Mr. Eduardo Jacob, has again, as in previous years, supplied us the detailed report on essential oils which is given below, thereby ensuring the gratitude of everyone interested in this trade. These reports are all the more valuable, as they appear in the middle of the season, and do not follow the official roundabout way by which they would only attain publicity when the season is long since past.

It will be seen from the following statistical tables of the exports of essential oils from Sicily and Calabria in the year 1902, that the export of last year has exceeded that of the previous year by 264 515 kilos and 2 882 228 Lire.

Very rich harvests of bergamot- and lemon-fruit have made it possible for the export-trade here, to place in the year under review large quantities of oil at the disposal of foreign consumers, and the latter have shown no hesitation to make use of the favourable situation, as they were able to buy, especially lemon oil, at exceptionally low prices.

This enormous increase in the exports during last year confirms what has already been pointed out in previous Reports, viz., that the world's consumption of Sicilian essential oils, and principally of lemon oil, is constantly growing, a fact which may be calculated to put a check on any further fall in the prices of lemon oil.

Export of essential oils.

| | in 1901 | | in 1902 | |
|---|---|---|---|---|
| a) from Messina: | quantity Kilos | value Lire | quantity Kilos | value Lire |
| to North German Ports . . . | 13 676 | 205 140 | 21 773 | 304 822 |
| „ Austria . . . . . . . . . | 50 648 | 759 720 | 75 280 | 1 053 920 |
| „ Belgium . . . . . . . . | 1 368 | 20 520 | 2 225 | 31 150 |
| „ Denmark . . . . . . . . | 2 241 | 33 615 | 3 085 | 43 190 |
| forward | 67 933 | 1 018 995 | 102 363 | 1 433 082 |

| | in 1901 | | in 1902 | |
|---|---|---|---|---|
| a) from Messina: — | quantity Kilos | value Lire | quantity Kilos | value Lire |
| forward | 67 933 | 1 018 995 | 102 363 | 1 433 082 |
| to France | 36 312 | 546 195 | 43 609 | 610 526 |
| ,, United Kingdom | 211 342 | 3 170 130 | 235 108 | 3 291 512 |
| ,, Holland | 10392 | 155 880 | 8 345 | 116 830 |
| ,, Russia | 9 331 | 139 965 | 10631 | 146 834 |
| ,, Scandinavia | 6 216 | 93 240 | 7 308 | 102 312 |
| ,, Spain and Portugal | 1 064 | 15 960 | 1 721 | 24 094 |
| ,, Turkey | 1 560 | 23 400 | 1 726 | 24 164 |
| ,, United States | 266 614 | 3 999 210 | 436 566 | 6 111 924 |
| ,, South America | 3 510 | 52 650 | — | — |
| ,, Australia | 35 369 | 530 535 | 39749 | 556 486 |
| ,, Egypt | 1 313 | 19 695 | 1 672 | 23 408 |
| ,, Greece | 360 | 5 400 | 704 | 9856 |
| ,, India | 625 | 9 375 | 1 330 | 18 620 |
| ,, Malta | 60 | 900 | — | — |
| ,, Other countries | 500 | 7 500 | 12487 | 147 818 |
| Total: | 652 501 | 9 789 030 | 903 319 | 12 646 466 |
| b) from Reggio: — | | | | |
| to Austria | 26 810 | 402 150 | 31 062 | 434 868 |
| ,, France | 24 315 | 364 725 | 32 459 | 454 426 |
| ,, North German Ports | 5 890 | 88 350 | 3 804 | 53 256 |
| ,, United Kingdom | 20663 | 309 945 | 24 032 | 336 448 |
| ,, Malta | 200 | 3 000 | — | — |
| ,, United States | 27 440 | 410 100 | 31 388 | 439 432 |
| ,, Other countries | 415 | 6 225 | 2 580 | 36 120 |
| Total: | 105 733 | 1 584 495 | 125 325 | 1 754 550 |
| c) from Catania: — | | | | |
| to Austria | 1 650 | 24 750 | 2 671 | 37 394 |
| ,, United Kingdom | 350 | 5 250 | 1 715 | 24 010 |
| ,, North German Ports | 200 | 3 000 | — | — |
| ,, Other countries | 210 | 3 150 | 52 | 728 |
| Total: | 2 410 | 36 150 | 4 438 | 62 132 |
| d) from Palermo: — | | | | |
| to Austria | 12 650 | 189 750 | 7 433 | 104 062 |
| ,, North German Ports | 1 315 | 19 725 | 20 | 280 |
| ,, France | — | — | 2 970 | 41 580 |
| ,, United Kingdom | 36 410 | 546 150 | 31 535 | 441 490 |
| ,, United States | 9 350 | 140 250 | 9 049 | 126 686 |
| ,, Other countries | 612 | 9 180 | 1 408 | 19 712 |
| Total: | 60 337 | 905 055 | 52 415 | 733 810 |
| Total exports: — | | | | |
| from Messina | 652 602 | 9 789 030 | 903 319 | 12 646 466 |
| ,, Reggio | 105 633 | 1 584 495 | 125 325 | 1 754 550 |
| ,, Catania | 2 410 | 36 150 | 4 438 | 62 132 |
| ,, Palermo | 60 337 | 902 055 | 52 415 | 733 810 |
| Grand Total: | 820 982 | 12 317 730 | 1 085 497 | 15 196 958 |

that is to say, in the year 1902 264 515 kilos and 2 882 228 Lire more than in 1901.

The figures of the exports of the last ten years are as follows:

| | | | | | |
|---|---|---|---|---|---|
| 1893: | 588334 kilos, | value 9356814 L. | 1898: | 667293 kilos, | value 9015083 L. |
| 1894: | 666740 „ | „ 8308148 „ | 1899: | 797145 „ | „ 10722445 „ |
| 1895: | 554191 „ | „ 8081870 „ | 1900: | 842246 „ | „ 10972295 „ |
| 1896: | 514067 „ | „ 7579424 „ | 1901: | 820982 „ | „ 12314730 „ |
| 1897: | 732092 „ | „ 9719133 „ | 1902: | 1085497 „ | „ 15196958 „ |

**Bergamot Oil.** This year's distillation has left much to be desired. A much smaller quantity of fruit was worked up than in the previous year, and the oil-content also did not justify the hopes which had been entertained. It was fortunate that abroad a large proportion of the previous year's rich harvest had remained unsold, and that the demand in November and up to January was comparatively small; if there had been a strong demand, the price of this article would have risen considerably already at the beginning of the manufacturing season. In view of the above-mentioned small demand from abroad, the speculators, who at Reggio had formed a combine, were unable, in spite of the greatest efforts, to drive up the prices during the manufacturing season, and their endeavours were not crowned with success until in the course of last month a stronger demand began to assert itself on the market.

The present situation is this, that the comparatively small export has left considerable stocks of bergamot oil over for the new season, stocks which amount to fully 25000 kilos.

At the present time the bergamot-trees are already in leaf, thanks to a winter free from gales, and they justify the hope of a good harvest. If this supposition is confirmed by a rich development of blossoms and a good germination of fruit, the speculators will probably lose courage, and they may show greater willingness than hitherto to realise their holdings. For this reason there is no great belief in a further rise of the prices; on the contrary, the presumption is that in the summer months it will be possible to buy cheaper than now.

**Citron Oil.** S. Gulli has now published the contemplated supplement to his previous notes on citron oil[1]), and thereby added a valuable contribution to the knowledge of this oil. The oil previously examined by him, prepared from "*cedri*", agreed (as we wish once more to point out) in its physical constants with the oil which we had at the time under examination, but differed in a marked degree from that which Burgess had before him. The oil recently tested by Gulli, which had been made from "*cedrini*" (derived from *Citrus medica gibocarpa* or *citrea*) corresponded in its physical constants to

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[1] The Chemist and Drugg. **62** (1903), 22.

the oil described by Burgess. Gulli, namely, found: $d_{15^\circ}$ 0,851, and $\alpha_D + 80^\circ 50'$, and for another oil also prepared from "*cedrini*", $d_{15^\circ}$ 0,850, and $\alpha_D + 79^\circ$.

The author further found that the oil of sweet lemon (derived from *Citrus Limonum dulcis)* represents an excellent adulterant of citron oil, for mixtures of equal quantities of common lemon oil, or sweet lemon oil, with oil of sweet orange, possessed properties almost identic with those of citron oil. But such mixtures can immediately be distinguished from genuine citron oil by the fact that they are perfectly clear, whilst citron oil soon after preparation becomes turbid, with separation of fine white crystals of the form of small needles.

Dr. Gulli was good enough to send us samples of the two above-mentioned oils prepared by him. Unfortunately, both oils reached us in a turbid condition owing to crystals having separated out, and we are therefore unable to accept such behaviour as characteristic of citron oil alone. After removing the crystalline precipitate by filtration, we found for the *cedrini* oil: $d_{15^\circ} = 0{,}8541$, $\alpha_{D21^\circ} = +81^\circ 7'$ and $n_{D20^\circ} = 1{,}47480$; and for the oil of sweet lemon: $d_{15^\circ} = 0{,}8579$; $\alpha_{D21^\circ} = +64^\circ 15'$, and $n_{D20^\circ} = 1{,}47568$, whilst Gulli gives for the latter $d = 0{,}856$ and $\alpha_D = +64^\circ 30'$. Our observations consequently agree fairly well.

But the determination of the specific gravity and the rotatory power alone is not sufficient to distinguish genuine from adulterated citron oil; this is clear from a further article on this subject by the chemists of the London Essence Company[1]). In their opinion, adulteration can readily be detected in the same manner as already proposed by Burgess and Child for lemon oil, viz., by separating the oil to be tested into different carefully measured fractions, and determining the physical constants of such fractions. For a sample of pure citron oil with $d_{15^\circ} = 0{,}852$, $\alpha_D = +80^\circ 5'$ and $n_D = 1{,}4749$, the authors give the following as typical values:

| Fraction | $\alpha_D$ | $n_D$ | Aldehyde-content |
|---|---|---|---|
| 10 per cent | $+85^\circ 55'$ | 1,4730 | — |
| 80 „ „ | $+86^\circ 5'$ | 1,4735 | — |
| 7 „ „ | $+16^\circ 30'$ | 1,4806 | 53 per cent. |

The two first fractions would therefore have a higher rotatory power than the original oil, which would not be the case if the oil had been adulterated. The chemists of the London Essence Company also refer to the presence of crystals as being a characteristic of citron oil.

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[1]) The Chemist and Druggist **62** (1903), 57.

All these notes on citron oil which have been published in recent times, have been lucidly arranged in a small pamphlet issued in January last by the London Essence Company.

If we now summarise all what has been said on the subject, we find that the varieties of citron yield oils of totally different properties; the *cedri* (as has been proved by Gulli and ourselves) yield an oil which has a somewhat higher specific gravity, and a little less rotatory power, than that from *cedrini*, whilst the latter is clearly richer in hydrocarbons.

We have also had *cedrini* oils repeatedly before us (1898/99), and we found for this oil in two cases: —

$$d_{18^\circ} = 0{,}8507; \quad \alpha_{D20^\circ} = +78^\circ\,39';$$
$$d_{15^\circ} = 0{,}853\;; \quad \text{„} \quad = +77^\circ\,53'; \; n_{D20^\circ} = 1{,}47519.$$

These results agree very well with those communicated by Burgess and lately also by Gulli.

In future it will therefore be necessary to discriminate severely between these two oils, a view which is supported by S. Gulli in a recently published note on citron oil[1]). It is obviously desirable to maintain the name citron oil for the oil prepared from *cedri*, and in the absence of a better name, the *cedrini* oils will meanwhile have to be designated as such.

**Lemon Oil.** The position of this article was in September 1902 as follows: —

With the rich lemon-harvest of the winter 1901/02, the consumers abroad had during the first nine months of 1902 covered the whole of their requirements for the year, and even more, in the most abundant manner. A falling-off in the demand caused in Sicily a decline in the prices to a level which had never been reached before; this again attracted the interest of speculators abroad, who could be persuaded all the more readily that it would be well to take advantage of the situation, as the lemon oil of the previous season was good in every respect, and the oil had in the course of the summer also proved its excellent keeping qualities.

An abundant supply to the consumers abroad of the previous season's oil, at low prices, appeared all the more opportune, as the prospect of the new harvest, of the winter 1902/03, was not favourable, and much higher prices were asked for new forward oil than for old spot oil.

As a matter of fact, the result of the new lemon-harvest has been about half of that of the previous one, and as in the case of the

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[1]) The Chemist and Druggist **62** (1903), 454.

bergamot and the orange, whose yield of oil was only small, the lemon also showed a lower oil-content, as compared with other years.

If, in spite of this, the prices of lemon oil have up to now remained comparatively low, the reason of this must be found in the fact that buyers abroad, who were abundantly supplied with the previous year's product, have sent in new orders only on a small scale, and this has rendered the accumulation of a certain stock of new oil possible.

The following statistics of the export will supply the proof of this:

Export Season:

| 1901/02 | | 1902/1903 | |
|---|---|---|---|
| December 1901 | 96985 kilos | December 1902 | 73440 kilos |
| January 1902 | 132509 „ | January 1903 | 95975 „ |
| February 1902 | 74056 „ | February 1903 | 97846 „ |

The stock held at Messina in December made it possible for the exporters to fulfil their obligations also in January and February, without having to fall back on the daily supplies of lemon oil.

The exports of last month, however, have almost exhausted the available stocks, and the export-trade can from now only rely on the quantities offered from day to day.

But, as experience shows that at Messina a considerable shortage for forward deliveries at late dates is the rule, and as moreover the consumption has not yet covered its requirements for the next nine months, whilst on the other hand the manufacturing season will come to an end at an early date on account of lack of fruit, and the stocks held by manufacturers and speculators probably amount to no more than one fourth of the previous year's stocks, there can be little doubt that an improvement in the prices within a not very distant time may be expected.

Of what importance such improvement may be, cannot at this moment be said with any certainty; it depends upon the extent to which buyers abroad have to rely on the market here until the time of the next harvest, and also upon the expectations for the season 1903/4 which will be raised by the development of the new blossoms.

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The following compounds have been found up to the present in lemon oil, excepting bodies which are not volatilisable by steam, viz., pinene, camphene, phellandrene, limonene, methyl heptenone, octyl and nonyl aldehydes, citronellal, terpineol, citral, linalyl and geranyl acetates and a sesquiterpene. On removing by distillation in vacuo the hydrocarbons of a low boiling point, i. e. pinene, camphene, phellandrene and limonene, with which pass over also methyl heptenone and partially the fatty aldehydes and the citral, and on separating then by steam-distillation the volatile from the non-volatilisable constituents, a concentrated lemon oil is obtained, showing a lævorotation, unlike the rather strongly dextrogyrate raw material. This lævorotation has always been considered as particularly characteristic for terpeneless lemon oil, indeed a rotation of at least — 7° to — 8° was insisted upon for this preparation.

Among the compounds met with in concentrated lemon oil are optically active only citronellal, terpineol, linalyl acetate and the sesquiterpene, the latter being known to rotate, though not in which direction; of these bodies citronellal is dextrogyrate, whereas terpineol and linalyl acetate turn the polarised light to the left, the former doing so less than the latter. The content of terpineol and linalyl acetate in concentrated lemon oil is not very considerable and it may therefore be safely supposed that the lævorotation caused by these bodies is at least counterbalanced by the dextrogyration of the citronellal, the likely consequence being optical inactivity or even slight deviation to the right.

These reflections lead forcibly to the conclusion that the lævorotation, claimed up to the present so persistently for terpeneless lemon oil, must be attributed exclusively to its sesquiterpene-content.

However, if lemon oil is freed from its terpenes, in order to increase its solubility and prevent certain troubles, it is but logical to remove also the sesquiterpene, same impeding likewise the solubility of lemon oil. But on separating the sesquiterpene a concentrated lemon oil is obtained, the properties of which differ from those required up to now for terpeneless lemon oil, the most remarkable event being the changed rotatory power.

Terpeneless lemon oil, in the true sense of the word, will always be lævogyrate, whereas oils freed from terpenes and sesquiterpene should be either optically inactive or slightly dextrogyrate. It will indeed soon be found in practice that the sesquiterpeneless preparation deserves the preference, for it is already soluble in about 6 to 10 parts 60 per cent. alcohol, whereas terpeneless oil requires often twice as much if not more of 70 per cent. alcohol.

On this occasion we ascertained the sesquiterpene of lemon oil to belong to the category of the light sesquiterpenes, its physical constants being: — boiling point 125° to 127° (8 mm pressure); $d_{15^\circ}$ 0,8843; $\alpha_D = -42^\circ$ and $n_{D20^\circ} = 1{,}49034$. So far we have not succeeded in obtaining crystallised derivatives by means of which this hydrocarbon might be identified.

**Mandarin Oil.** It is well known that a few years ago H. Walbaum[1]) succeeded in identifying in our laboratory the fluorescent constituent of oil of mandarin peel as methyl ester of methyl anthranilic acid. E. Charabot[2]) has recently found that the same body is

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[1]) Report October **1900**, 31. — Journ. f. pract. Chemie II. **62** (1900), 135.
[2]) Compt. rend. **135** (1902), 580.

present in far greater proportion, viz., up to about 50 per cent., in the oil from mandarin leaves, so that this oil may be considered as the natural source of this important perfume. The oil examined by Charabot, which had been obtained by steam-distillation from the leaves of the mandarin tree, turned the plane of polarised light + 6° 40′; the saponification number was 160. The ester was detected and isolated by Walbaum's method. Its melting point lay at 19°. The compound was recognised as methyl ester of methyl anthranilic acid by elementary analysis, and by the acid of the melting point 179° occurring during saponification, which showed all the properties of methyl anthranilic acid.

**Mandarin Oil "Schimmel & Co."** This product, prepared in accordance with our German Patents Nos. 122568 and 125308, enjoys already a considerable amount of favour. It is chiefly used for aromatising high-quality confectionery and bonbons.

With regard to the physiologico-chemical behaviour of methyl ester of methyl anthranilic acid, which represents the most characteristic constituent of mandarin oil, interesting experiments are mentioned on page 121, which experiments prove that this substance is tolerated by warm-blooded animals in large doses without the slightest injurious effect.

**Oil of Orange, sweet.** As predicted, the conditions for the manufacture of this oil during the present season were very unfavourable. The orange-harvest did not everywhere give satisfactory results, and was particularly poor in those districts, whose fruit, as compared with that of other districts, is characterised by low keeping-qualities, and which is therefore chiefly used for working up into orange oil. Nevertheless, a good oil-content was anticipated, and sales for forward delivery were being made on the basis of about 11,50 marks per kilo cif. Trieste.

But the first pressing trials already proved that the oil-content was very low, and that the manufacture at the above-mentioned price was bound to result in loss. The manufacture of orange oil was therefore not commenced with the usual energy, but was only started with a limited number of hands.

A very brisk export-trade in fruit in cases, and the year by year increasing number of whole truck-loads sent to the Upper Italian markets, absorbed moreover a greater quantity of fruit for purposes of consumption than at other times, so that the owners of orange-gardens, in spite of the attractive prices of orange oil, yet found it more advantageous to sell the fruit for consumption than to supply it to the manufacturers for expression.

We are therefore now face to face with a very small production, and the stocks still in hand may possibly at this moment not exceed 5000 to 6000 kilos. Nobody will therefore be surprised by a further increase of the prices beyond their present level.

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The manufacturing season now lying behind us has been extremely interesting, as it has brought to the light various anomalies respecting the chemico-physical constants of the different oils.

Rarely has in previous years the effect of the atmospheric conditions during the ripening period of bergamots, oranges and lemons, come so prominently into relief, as in the half-year just closed. A matter which is specially striking, is the poor content of essential oil of all the various *Citrus* fruits.

Orange oil showed on the whole a higher specific gravity than hitherto; sweet Sicilian oil had a lower rotatory power than in previous years, but sweet Calabrian oil, on the other hand, a higher rotation. Oil of bitter orange had a strikingly high specific gravity — both in Calabria and in Sicily, — the average being 0,854 to 0,856; the Calabrian oil had a normal rotatory power, but the Sicilian an exceptionally low rotation.

Various differences, as compared with previous years, could be detected in lemon oils from certain districts which are subject to other climatic conditions than the district adjoining the Strait of Messina, particularly the on the average higher specific gravity of this year's lemon oil in most of the producing districts of the island, with exceptionally low gravity in some others.

With regard to the prospects of the coming harvest, nothing can as yet be stated with certainty. The smaller crop of last season, and the fact that the trees (which are already in full foliage) have been brought into an excellent condition by copious rainfall during the winter, justify the supposition that the next harvest will have good and abundant results if no unfavourable weather-conditions occur during the flowering season.

But good harvests are most necessary, as in the opposite case, in view of the low stocks of all these oils, the prices of all the various kinds would harden rapidly, and the market during the next nine months would be exposed to disagreeable and trade-disturbing fluctuations.

**Eucalyptus Oil.** 'Globulus' oil is at present very scarce and quoted higher. Algerian sellers have not carried out their contracts, and the chances for the Australian product are consequently more favourable. The 'Amygdalina' quality containing phellandrene is abundantly in stock.

J. H. Maiden has again supplied some contributions to the knowledge of the eucalyptus species, to which we can here refer only briefly, as they are essentially interesting from a botanical point of view. In the first place we would mention a work on *Eucalyptus Behriana* F. v. M.[1] in which are discussed the characteristic differences between that species of eucalyptus and *E. hemiphloia* F. v. M., *E. populifolia*, *E. largiflorens*, *E. odorata* and *E. incrassata* var. *dumosa.*

A further short work deals with *Eucalyptus Macarthuri* D. and M., whose presence in Tasmania is confirmed. As this species of eucalyptus presumably will become important on account of the oil it yields, which is rich in geranyl acetate, Maiden recommends that the trees, in the interest of the oil distillation, should not be felled, but that only the branches should be cut off.

In the long list of Australian useful trees[2] the author also mentions *Eucalyptus haemastoma*, *E. haemastoma* var. *micrantha*, and describes these along with *E. punctata* D. C. which is frequently mistaken for the *grandiflora*-kind of *E. resinifera*, and is popularly known as *Grey gum.*

Treatises by the same author, on *E. Baueriana* Schauer and *E. calycogona* Turcz., are found in the Proc. of the Linn. Soc. of N. S. W. 1902, Vol. II, and on *E. tereticornis* Smith and *E. rostrata* Schlechtendal, in the Bulletin de l'herbier Boissier, 2$^{d}$ series, 1902.

We desire to avail ourselves of this opportunity, to call the attention of those of our readers who take an interest in the extraordinarily varied family of eucalypts and in the essential oils obtained from their individual species, to the recently published work by R. T. Baker and H. G. Smith: "A research on the eucalypts especially in regard to their essential oils."[3]

Both authors have now for a long time been connected with the Sydney Technological Museum, the first chiefly as botanist, the other as chemist, and they have occupied themselves particularly with a thorough examination of the family of eucalypts, and, indeed, their names have been repeatedly mentioned in these pages in discussing their previous work.

The present work, which is provided with very good habitat-pictures, and also illustrations of branches of the individual species with the organs which are the most important for the identification and differentiation, represents an epitome of everything that has up to now become known of eucalypts, both from a botanical and a chemical point of view. The fact that the authors have on this occasion taken their

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[1] Trans. of the Royal Soc. of South Australia **1902**.

[2] Agricultural Gazette of N. S. Wales, **1902**.

[3] Sydney, 1902.

own researches specially into consideration, is a matter for which one can hardly find fault with them, but for this very reason it may be assumed, that the views thus set forth by them will not always meet with unanimous approval on the part of their more immediate colleagues. The discussion of the individual eucalyptus-species is conducted from the chemical point of view, i. e. according to the principal constituents present in the individual oils. This is followed by a reproduction of various works by H. G. Smith from the 'Proceedings of the Royal Society of N. S. Wales' respecting the composition and constituents of a few eucalyptus oils, and finally details are given on the method of distilling eucalyptus oils, as in vogue in Australia, which method is elucidated by well-executed pictures. The work ends with a clearly arranged table which permits ready reference to the properties and constituents of any eucalyptus oil.

This publication meets a real want, and is all the more to be welcomed, as with the large number of eucalyptus species described and the still larger number of synonyms, it was not at all, or hardly, possible for anyone who had not made a special study of this subject, to find the way in such a chaos.

**Fennel Oil.** We are in the pleasant position of now being able to supply our own distillate from purified Galician seed of which we have since January received every month a number of truck-loads.

**Gardenia Oil.** E. Parone[1]) has published a work on the properties and chemical composition of the essential oil of gardenia, from which we abstract the following:

The gardenia oil obtained by maceration from the fresh gardenias gathered during the flowering season, has a yellowish colour, and possesses at 20,5° the specific gravity 1,009. The specific rotation is $[\alpha]_D = + 1{,}47°$, at 20°, in a 50 mm tube. At ordinary pressure the oil commenced to boil at 204° with partial decomposition; at a pressure of from 12 to 15 mm the bulk passed over between 84° and 150°. Parone has detected the following bodies as constituents of gardenia oil: benzyl acetate, styrolyl acetate, [acetate of the methyl phenyl carbinol $C_6H_5 \cdot CH \cdot (OCOCH_3) CH_3$], linalol, linalyl acetate, terpineol, and methyl ester of anthranilic acid.

Benzyl acetate represents the principal constituent of gardenia oil, whilst the aroma peculiar to the oil is chiefly due to the styrolyl acetate.

**Geranium Oil.** Within the last 6 months the prices of the Algerian oil have declined to a not inconsiderable extent, and they may possibly drop still lower, as, according to our personal experience, the cultivation is now carried on on a much larger scale. A suspicious

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[1]) Boll. Chim. Farm. **41**, 489, according to Chem. Centralblatt **1902**, II, 703.

fact is also this, that efforts are made to conclude contracts running over several years, which safeguard the seller but not the buyer, as, in case of a failure of the harvest, the former is covered by the "force majeure" clause, leaving the purchaser to do the best he can.

Réunion oil is at present very animated. Although prompt oil is fairly scarce and is kept still high, the prospects of the new distilling-season commencing in April appear to be favourable, and a large part of the yield has already been placed in advance at very acceptable prices.

As to ourselves, we have through our representative at St. Denis strongly participated in this favourable state of affairs, and we now quote this article considerably lower, in accordance with the average of our purchases; the following statistics show that at such an exceptionally low price no risk is incurred: —

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Quotation | on | 1st | April | 1894, | 44 | marks | per | kilo |
| " | " | 1st | " | 1895, | 44 | " | " | " |
| " | " | 1st | " | 1896, | 43 | " | " | " |
| " | " | 1st | " | 1897, | 40 | " | " | " |
| " | " | 1st | " | 1898, | 32 | " | " | " |
| " | " | 1st | " | 1899, | 30 | " | " | " |
| " | " | 1st | " | 1900, | 30 | " | " | " |
| " | " | 1st | " | 1901, | 38 | " | " | " |
| " | " | 1st | " | 1902, | 40 | " | " | " |
| " | " | 1st | " | 1903, | 30 | " | " | " |

Our highest quotation was in 1891, at 48 marks per kilo. For large contracts we invite correspondence.

Spanish geranium oil, which in point of quality is not approached by any other kind, remains with the limited production an article of luxury. For certain purposes this oil is indispensable.

The prices of the Indian distillate, also called palmarosa oil, have suffered a heavy fall, in consequence of a considerably increased production combined with an absence of inclination to buy. This fall, as compared with the values of the previous season, amounts to about 50 per cent. Hitherto this oil was only distilled in Khandesh, in Bombay Presidency, but lately the production has also been taken up on the coast of Madras whence fairly considerable quantities have this year already been placed on the market via Bombay, a fact which has also influenced the prices. It may be taken for granted that this new source of supply will in future form a strong competitor, and that the prices will permanently remain low, which would promote the consumption. At the present values the article will have all the more interest for the soap-manufacturers, as the parcels which have appeared on the market were chiefly of such a fine quality as had not been met with last year. Our very large stock consists exclusively of such.

The same is the case with gingergrass oil, which has never before been of such good quality, or so moderate in price. Efforts made to ascertain further particulars as to the origin of this oil have remained unsuccessful, and for this reason no guarantee can be given of either the origin or the uniform composition of the supplies. But in any case, the parcels at present in stock do not appear to contain foreign admixtures. We are earnestly continuing our efforts to elucidate the existing mystery, and, as has been the case with so many other products of Asia, they are bound to lead at last to the desired end.

**Jasmine Oil "Schimmel & Co."** The consumption of this perfume, which we were the first to produce and introduce into commerce, is constantly increasing, no matter what the result may be of the harvest of jasmine-flowers in the South of France. At the same time, the prices of the flowers may be influenced to a certain extent by the competition of the artificial oil, and it would not surprise us if an improvement of the natural products from jasmine-flowers by means of the artificial oil were found to be practical, and would become more general.

**Oil of Juniper-Berries.** The reports from Hungary announcing a failure of the harvest of juniper-berries, have been fully confirmed. For the first time in our long experience there has been a lack of Hungarian oil of juniper-berries, i. e., the oil which is obtained as a by-product in the "Borowiczka"-distillation. This oil is not normal, but has had the best readily soluble portions abstracted by the brandy. But when the demands are not too high, it is very useful when rectified, and under the designation "rectified" it represents the ordinary commercial quality of this article.

Normal pure distillates from berries are our two first qualities; these are distilled by ourselves from the best Italian berries, rich in aroma, and most carefully purified. This kind of berries, as is well known, is also preferred for the finest brands of geneva. We have used these exclusively this year, as Hungary had practically nothing at disposal for exportation.

**Kaempferia Oil.** Some time ago¹) P. van Romburgh detected in the essential oil of *Kaempferia Galanga* L., ethyl p-methoxy cinnamate as principal constituent. When recently examining the liquid portions of the oil, the same author²) obtained a fraction boiling between 155° and 165° (30 mm), which could be split up by saponification into

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¹) Report October **1900,** 38.

²) On some further constituents of the essential oil of *Kaempferia Galanga* L. Kon. Akademie van Wetenschappen, Amsterdam, May, 1902, 618.

cinnamic acid and ethyl alcohol, and which, therefore, consisted of ethyl cinnamate. This body, which represents almost one-fourth part of the oil, could only be separated with difficulty from a substance of nearly the same boiling point. The separation could finally be accomplished by treating the mixture with 80 per cent. alcohol, in which the bulk of the ester dissolved. The remaining portion was purified by boiling with potash, treatment with a solution of bromine in chloroform, and shaking with concentrated sulphuric acid. In this manner van Romburgh obtained an inactive, colour- and odourless liquid of the boiling point 267,5° (738 mm) and the specific gravity 0,766 at 26°, which on cooling solidified completely. By analysis and determination of molecular weight, the formula $C_{15}H_{32}$ was obtained. The only hydrocarbon of this composition known up to the present is pentadecane, described by Krafft, whose properties so closely agree with those of the body found, that the identity of the two cannot be doubted. More than half the liquid portion of Kaempferia oil consists of this paraffin.

**Lavender Oil.** According to the most recent reports from the departments Alpes-Maritimes and Basses-Alpes, the stocks held at first hand are practically exhausted, and the prices are almost left at the mercy of the middlemen. As a matter of fact, 19 to 20 francs has been paid for fine qualities.

In the departments Vaucluse, Hérault, Drôme and Gard, the stocks are also nil. For many years there has not been such lack of this eminently important article, and we are afraid that before the new harvest the position will come to a head in a manner never dreamt of. The whole world's requirements depend solely upon the production of the above-named departments, and these requirements, according to all indications, are incessantly increasing. Although no statistics on this subject are in existence, the enormous development of the toilet-soap industry, and the numerous specialities for which lavender oil is employed in large quantities, leave no doubt whatever on this point.

Through the good offices of Mr. Jean Gras of Cannes we are in a position to present again illustrations of some portable stills for lavender oil (Fig. 1, 2 and 3), all of which are from the district of Séderon (Basses-Alpes) which supplies good-quality oils, containing about 30 to 36 per cent. ester. These installations are situated at a height of some 3000 to 3300 feet above the sea-level; the highest point in the vicinity is the Mont Ventoux (6273 feet high). In these altitudes water is frequently scarce, so that for purposes of condensation water from tanks, or even the almost hot water running out of the Florentine flasks must be used, a method of cooling which naturally must have an unfavourable effect on the quality on the oil.

Nr. 1.

Nr. 2.

In French lavender oil there had up to now been detected: linalol; linalyl acetate, butyrate and valerianate (?)[1]; geraniol[2]; pinene; cineol[3]; and coumarin[4]. By an examination which we recently again took up, we have been able to increase the knowledge of this oil by a few important bodies. We worked up 4 kilos of a genuine oil from the South of France, which had the following physical constants: specific gravity 0,8902; optical rotation $\alpha_D$ —7° 6′; saponification number 116,5, corresponding to an ester-content of 40,7 per cent. linalyl acetate. In order to prevent decomposition as far as possible, we distilled in vacuo right from the beginning. Between 30° (40 mm) and 125° (5 mm) the whole quantity of oil passed over, apart from about 350 grams of a resinous residue.

With fuchsin and sulphurous acid, the first portions, boiling between 95° and 125°, showed a strong aldehyde-reaction. From this, and also from the fact that a crystalline compound was thereby obtained in minute quantity, from which sodium carbonate liberated a substance which strongly excited coughing, it may be assumed that valeric aldehyde was present in the first runnings.

Traces of amyl alcohol also appear to be present in lavender oil. For example, it was possible to obtain from the fraction boiling from 125° to 140°, with phthalic anhydride, a small quantity of a liquid boiling from 129° to 133°, which violently reacted with sodium, with formation of a colourless compound. From the latter an oil was separated off with water, which had the characteristic odour of amyl alcohol.

l-Pinene. We have once more thought it worth while to demonstrate the presence of this hydrocarbon which we had already previously detected in lavender oil. It was found without difficulty in a fraction of the boiling point 153° to 159° (72° to 75° at 21 mm), with the specific gravity 0,8641, optical rotation $\alpha_D$ — 6° 10′, by means of the nitrosochloride of the melting point 103°, and the nitrolbenzylamine melting at 122°.

Cineol. This body, which also had been discovered previously, was contained in a fraction boiling between 175° and 177°, and having the optical rotation $\alpha_D$ — 1° 10′. The iodol compound produced in large quantity, melted after purification from alcohol at 112°. The presence of the two last-named bodies in lavender oil may thus be accepted as definitely proved. Other terpenes, such as phellandrene, dipentene, and limonene, could not be detected.

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[1] Report April **1892,** 22. — Journ. f. prakt. Chem. II. **45** (1892), 590.

[2] Report April **1898,** 31.

[3] Report October **1893,** 26. — Journ. f. prakt. Chem. loc. cit.

[4] Report October **1900,** 40.

Ketone $C_8H_{16}O$. This substance to which in part lavender oil owes its refreshing odour, had hitherto not yet been more closely identified by its physical constants, as the production of the body in the pure state is attended with considerable difficulties. At the same time, we were able to give some details as to its boiling point and odour, and also of a solid derivative. As we suspected a ketone in the body, on account of its fruit-like odour, but as it formed no solid compound with bisulphite, we endeavoured to purify it at ordinary temperature by oxidation with a 1 per cent. solution of permanganate. The oil, freed in this manner from readily oxidisable admixtures, boiled for the greater part at 159° to 166°, and had the specific gravity 0,8445. We obtained from it a semicarbazone which crystallised from benzene in brilliant leaflets of the melting point 116° to 117°. An elementary analysis gave values which point to the semicarbazone of a ketone $C_8H_{16}O$:

0,1534 g of the substance yielded 0,3282 g $CO_2$ and 0,1427 g $H_2O$.

| Found: | Calculated for $C_9H_{19}ON_3$: |
|---|---|
| C = 58,34 per cent., | C = 58,38 per cent. |
| H = 10,33 ” ” | H = 10,27 ” ” |

The ketone could therefore be the methyl hexyl, or the ethyl amyl ketone. In view of its boiling point (boiling point of the ethyl amyl ketone 164° to 166°), and of the property of not reacting with sodium bisulphite, its identity with the latter might be assumed. This is supported by the fact that the melting point of the methyl hexyl ketone-semicarbazone lies at 123°, i. e. 6° higher. A mixture of the two semicarbazones of different origin melted already below 110°, which is a proof that the derivative melting at 116° to 117° cannot be identic with that of the methyl hexyl ketone. The result obtained by oxidation with chromic acid also speaks in favour of ethyl amyl ketone. According to Wagner's[1]) rules regarding the progress of oxidation with aliphatic monocarbonyl ketones, the preponderating formation of caproic acid was to be expected. We oxidised whilst heating for several hours on a water bath with frequent shaking. The oily acid with the odour of valeric acid, isolated from the reaction-mixtures, yielded a silver salt which could be recrystallised from water, and whose silver-content completely agreed with that calculated for silver caproate:

I. 0,2204 g of the substance yielded 0,1067 g Ag.
II. 0,1025 g ” ” ” ” 0,0497 g ”

| Found: | Calculated for $C_6H_{11}O_2Ag$: |
|---|---|
| I. Ag = 48,41 per cent., | Ag = 48,43 per cent. |
| II. Ag = 48,50 ” ” | |

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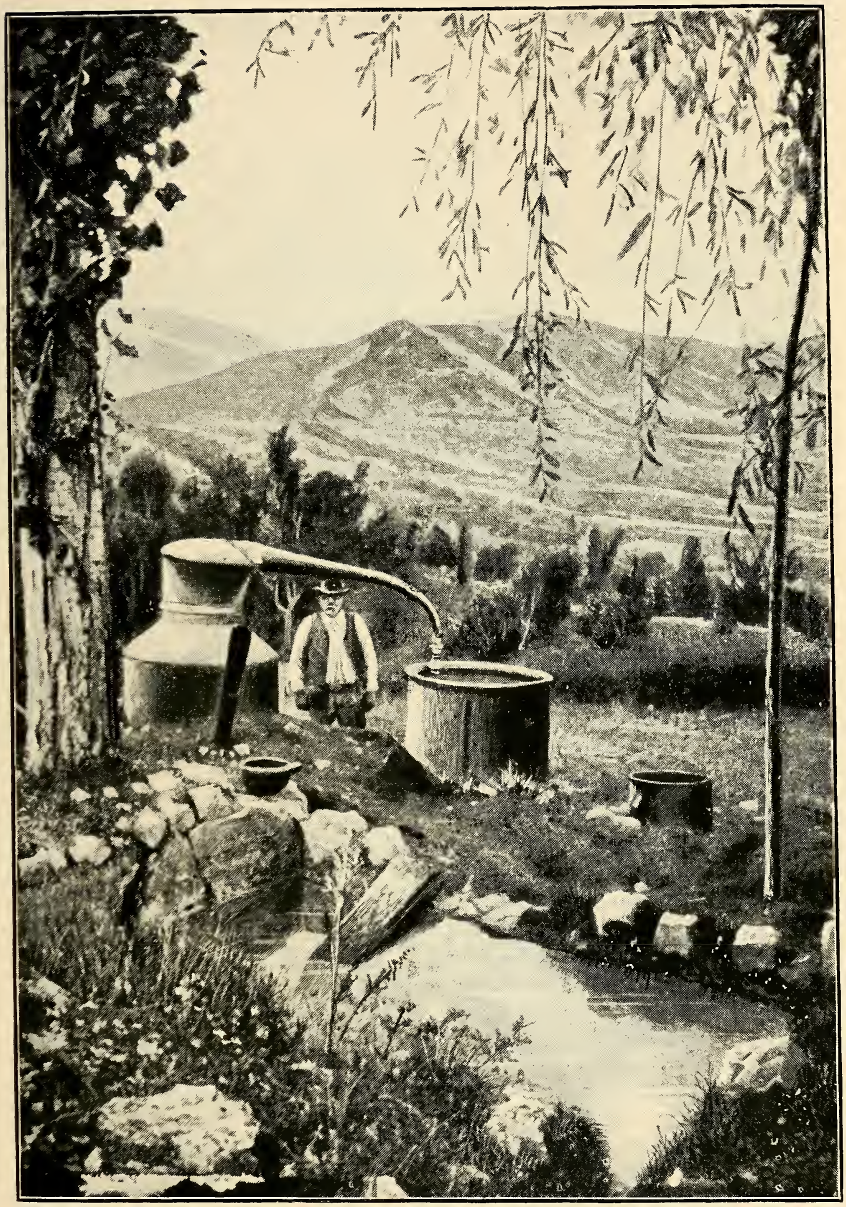
[1]) Journal für practische Chemie II. **44** (1891), 257 et seq.



Nr. 3.

The ketone had therefore been oxidised chiefly into caproic acid. Unfortunately, ethyl amyl ketone is difficult to approach by synthetic process. For this reason, we were as yet unable to compare it, with regard to its properties, with the ketone from lavender oil. The ketone has up to the present not been detected in any essential oil, and its discovery is therefore all the more interesting. The quantity contained in lavender oil may amount to at most 0,2 per cent. In our next Report we hope to be able to supply the physical constants which are still wanting.

d-Borneol. This alcohol was isolated from fractions boiling between 85° and 92° (7 to 8 mm), whose physical constants lay between the following limits: specific gravity 0,9069 to 0,9223; optical rotation $\alpha_D$ — 3° 49′ to — 2° 35′; saponification number 213 to 237. The fractions were saponified with alcoholic potassa, and the alcohols of the boiling point 96 to 103 (13 mm) thereupon obtained were esterified with phthalic anhydride. From the solution of phthalic ester salt, freed from oil by extraction with ether, resulted on saponification an alcoholic mixture of a pronounced borneol odour. By fractionating at ordinary pressure a slightly dextrogyrate oil of the boiling point 205° to 220° was separated off, which did not solidify in a freezing mixture, but which, on oxidation with Beckmann's mixture, yielded large quantities of camphor. The latter was driven off with steam from the oxidation-liquid, and obtained as a solid body of the melting point 175° (after subliming). Its oxime melted at 118° to 119°. This proves the presence of d-borneol in lavender oil, and the borneol occurs in it not only in the free state, but also combined with acetic acid.

Attempts to produce the phenyl urethane of the borneol from the above-mentioned fraction boiling at 205° to 220°, were not successful, — possibly in consequence of an admixture of geraniol.

In the portions of the above-mentioned fractions which could not be esterified with phthalic anhydride, and in others of a slightly higher boiling point, we have repeatedly endeavoured to detect terpineol. Although the portions used for the examination had an odour reminding of terpineol, the latter could not be identified either as a solid body, or by means of its phenyl urethane.

Geraniol. We had previously already shown that geraniol is present in lavender oil, but up to the present it was not known whether geraniol occurs as a free alcohol and as ester, or only in one of these forms. We have now been able to prove that both forms are contained in the oil. For the purpose of detecting free geraniol, we treated a considerable quantity of oil of the boiling point 89° to 93° (6 to 7 mm) with phthalic anhydride. From the solution of the phthalate, which had been frequently extracted with ether, there resulted, after saponification, an alcohol of the boiling point 225° to 232°, which had the unmistakable odour of geraniol. The phenyl urethane crystallising from petroleum ether in the form of needles, melted at 80° to 81°.

The fractions boiling at 93° to 94°, 94° to 103°, and 103° to 106° (7 mm), were rich in esters of geraniol; their saponification numbers were on the average 170. By repeated careful fractionating we succeeded in isolating among others a fraction of the boiling point 100° to 102° (8 to 9 mm) the specific gravity 0,9125, and the saponification number 210,6. The latter corresponds to a content of 73,5 per cent. of an ester $C_{10}H_{17}O \cdot COCH_3$. The alcohol of the boiling point 102° to 109° (8 to 9 mm) resulting from this on saponification, was recognised by the odour as geraniol. When triturated with powdered calcium chloride, it formed a solid cake. From this solid compound, purified with petroleum ether, there was regenerated with water pure geraniol of the following constants: boiling point 105° (8 mm); specific gravity 0,8825; optical rotation $\alpha_D = -0°\,2'$. The melting point of its diphenyl urethane was found at 81° to 82°.

The mixture of acids liberated from the saponification-liquors of the above-mentioned fractions, passed over between 105° and 230°. The bulk of this consisted no doubt of acetic acid, whose pungent odour was characteristic of a fraction boiling at 110° to 120°. The silver salt, however, gave figures which did not completely agree with those required for silver acetate. In spite of this, there is no room for doubt that the salt analysed represented mainly acetate of silver. The figures of the silver salt crystallising from water in well-developed needles, were as follows: —

0,3227 g of the substance yielded 0,2050 g Ag.
Found: 63,53 per cent. Ag. Calculated: 64,67 per cent. Ag.

The difference between the value found and that required may no doubt be explained by a slight admixture of a salt with a lower silver-content. The fractions 130° to 170°, and 170° to 200°, gave values which point to butyric and valeric acids respectively. Both these acids have previously been detected by us in lavender oil. An acid boiling at 200° to 230° formed a silver salt, whose content of silver agrees with that of silver caproate: —

0,2284 g of the substance left 0,1108 g Ag.
0,2404 „ „ „ „ yielded 0,2804 g $CO_2$ and 0,1025 g $H_2O$.

| | Found: | Calculated: |
|---|---|---|
| C = | 31,81 per cent., | 32,29 per cent. |
| H = | 4,74 „ „ | 4,93 „ „ |
| Ag = | 48,51 „ „ | 48,43 „ „ |

According to the above-mentioned results, lavender oil contains, in addition to free geraniol, also the latter's acetic and caproic esters.

Coumarin. We have also directed our attention once more to the detection of this body which has a not unimportant bearing on the lavender odour, and which has already been repeatedly isolated by us from lavender oil. It was detected in the highest ester-containing portions of the oil, boiling at 103° to 126° (5 mm), when it was found as the distillation-residue of the acids isolated from the saponification-liquor of these fractions. After recrystallisation from alcohol it had the melting point 67° to 68°, and the characteristic pleasant oour.

Finally we would mention an occurrence which had already been observed in the first examination of lavender oil made in our laboratory. This is the simultaneous occurrence of the odour like formaldehyde, and the formation of a gelatinous sticky substance, when fractions of the boiling point 78° to 90° (5 mm; 195° to 215° at ordinary pressure) are distilled, a fact of which we are at present unable to explain the cause.

As might be expected, our work¹) on the ester-question does not meet with the approval of Mr. E. Parry²). He thinks fit to dispose of this matter with some disdainful remarks, and for the rest maintains his assertions. As we have already mentioned in our previous Report³) that for us the ester-question was settled once for all, there is no occasion for us to return to the subject.

**Lemongrass Oil.** The value of this article has undergone considerable fluctuations. The lowest point was reached in November, at 4 d. per oz., whilst at the present time it cannot be bought below 5 1/4 d.

The export from Cochin amounted in 1902 to only 2350 cases, but, on the other hand, fresh sources of supplies have appeared, which in the near future may possibly make competition to the present monopoly.

To all appearances the cultivation of *Andropogon* grasses in the West Indian islands, to which we referred in our last October Report, is extending. We have lately received two further samples of *Andropogon* oils from the Government laboratory in Jamaica. On one of these oils we have already reported under the heading citronella oil; the other one was, like the previous one from Antigua⁴), designated

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¹) Report October **1902**, 46.
²) The Chemist and Druggist **61** (1902), 1028.
³) Report October **1902**, 48.
⁴) Report October **1902**, 50.

as having been obtained from *Andropogon Schoenanthus,* but it has such a pronounced odour of lemongrass oil, that we have no hesitation in calling it by that name. It compares favourably with the Antigua oil by its considerably higher aldehyde-content (83,5 per cent., against 48,2 per cent. for the other) but it shares with the latter its insolubility in 70 and 80 per cent. alcohol; 90 per cent. and absolute alcohol form at first a clear solution, but when more is added, they cause strong turbidity. In its physical constants the oil does not show any specially great differences from those observed at other times; we found $d_{15^\circ} = 0{,}8922$, $\alpha_D$ (100 mm) = — 0° 9′, and $n_{D20^\circ} = 1{,}48825$.

**Oil of Leptospermum scoparium.** C. E. Atkinson[1]) describes the essential oil of this shrub, which is called *manuka* by the natives of New Zealand, as a brown liquid having an aromatic odour and an acrid astringent taste. Its yield is but small. The physical constants are as follows: specific gravity 0,916 (12°), congealing point — 17°. It boils between 223° and 280°, chiefly about 260°.

**Linaloe Oil.** The supplies from Mexico in recent times have been totally insufficient, and moreover now and then of unreliable quality. The prices have advanced by several marks. The export in 1901 amounted to 12212 kilos.

**Oil of Sweet Marjoram.** In our Report of October 1902 we gave on page 51 an abstract from a work by Genvresse and Chablay on the constituents of oil of sweet marjoram. Shortly after the publication, Professor Genvresse wrote to us that the oil, which he had believed to be oil of sweet marjoram, was not obtained at all from *Origanum Majorana,* but from *Calamintha Nepeta*, a plant distributed in the Mediterranean countries, which also belongs to the labiates, and which in the South of France is wrongly designated as marjoram. We have now before us a detailed publication[2]) by the two above-mentioned authors, in which they specially refer to this matter.

As we have already mentioned, calamintha oil contains a small quantity of l-pinene, a hitherto unknown ketone $C_{10}H_{16}O$, to which the name calaminthone has been given, and, in the portions boiling about 225°, pulegone. Calaminthone boils under 745 mm pressure at 208° to 209°, and at 20° has the specific gravity 0,930. The oxime produced from it melts at 88° to 89°, and in ethereal solution combines with dry hydrochloric acid gas into an addition-product melting at 165°; the melting point of the semicarbazone lies at the same

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[1]) Pharm. Journ. **69** (1902), 369.

[2]) Compt rend. **136** (1903), 387.

temperature. Calaminthone yields as products of reduction menthone and menthol. With the exception of the position of the double linking which still remains to be ascertained, the constitution of this ketone has thus been determined with a fair amount of certainty.

**Matico Oil.** Fromm and van Emster have recently published[1]) the results of the examination of a matico oil which originated from our factory and which was marked 'heavy portions'[2]). This oil had the specific gravity 1,123 at 15°, and differed in a marked degree from the oil hitherto examined, by the total absence of asarone and matico camphor. About 70 to 75 per cent. passed over between 275° and 289°, and contained chiefly only one body, which the authors call matico ether, and whose formula was found as $C_{14}H_{18}O_4$. It represents a bright-yellow faintly fluorescent oil, volatilising with water vapour only with difficulty, which has the boiling point 282° to 285°, and the specific gravity 1,136 (at 17°). When kept for a prolonged time in a dark place matico ether acquires a brown colour, an occurrence which does not take place when the substance is left standing in sunlight.

Chemically matico ether behaves very indifferently. It is attacked by hydriodic acid with loss of pure methyl iodide. The methoxyl determinations after Zeisel correspond to the value of two methoxyl groups. When oxidised with a 5 per cent. solution of potassium permanganate, the new body yields a neutral product of the melting point 88°, and an acid having a melting point of 138°. The former is an aldehyde of the formula $C_{10}H_{10}O_5$, and is called by the authors matico aldehyde. With silver oxide it is oxidised into the acid $C_{10}H_{10}O_6$ maticoic acid. This is identic with the acid of the melting point 138° obtained direct by oxidation of matico ether.

From the portions of matico oil boiling above 275°, there can be isolated by oxidation with a 2 per cent. solution of potassium permanganate, in addition to matico aldehyde, also homomaticoic acid, whose melting point lies at 96°, and to which the formula $C_{11}H_{12}O_6$ belongs. Like matico aldehyde and maticoic acid, this acid also contains two methoxyl groups.

If the fraction of the examined oil which boils above 275° (dissolved in glacial acetic acid, chloroform, petroleum ether, or carbon disulphide) is mixed with an excess of bromine, the bromide $C_{11}H_{13}O_3Br_3$ is obtained, which melts at 116°.

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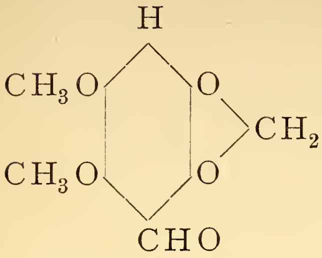
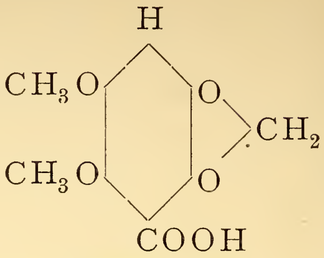
[1]) Berliner Berichte **35** (1902), 4347.

[2]) We would point out, that it was here not a question of a normal oil, but only of the portions which during distillation had separated out on the bottom of the receiver, and which therefore were heavier than water. We have observed that oils whose distillation-material contains a large admixture of fruit heads, are comparatively richer in heavy constituents than those which have been distilled from leaves only.

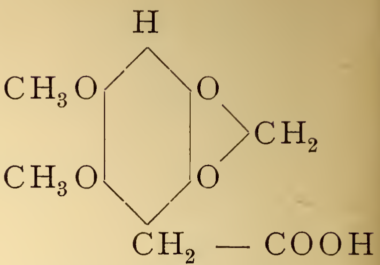
The authors make a provisional attempt to harmonise the results obtained with the following formulæ:



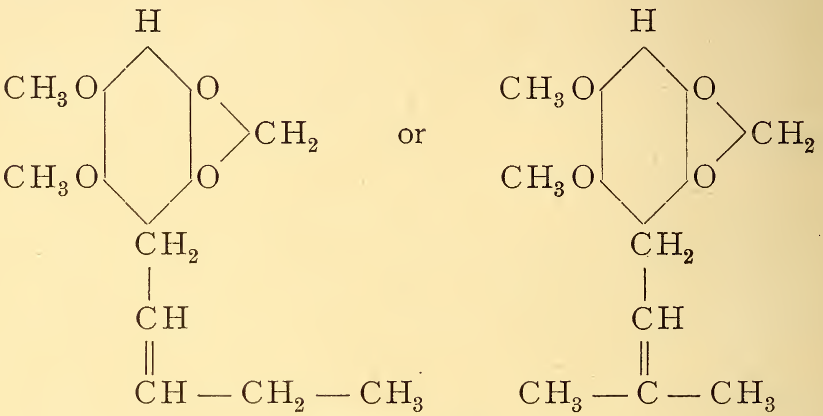
Matico aldehyde



Maticoic acid



Homomaticoic acid



Matico ether.

**Mustard Oil.** The prices of the sorts of mustard-seed which come under consideration for the preparation of genuine mustard oil, have declined somewhat in the course of last autumn, although for example Indian mustard has not yet come back to the low level of the years 1895 and 1896. So-called mustard-cakes — the pressed-out mustard-seed which has been freed from fatty oil — were supplied in truck-loads from Russia at moderate prices. Expressed oil of mustard is used in Russia for alimentary purposes.

**Mustard Oil, artificial.** Since our new factory-buildings offer sufficient room to take up the manufacture of new articles, we have incorporated artificial mustard oil into our programme of manufactures. Our installations enable us in case of need to meet all competition.

We are prepared to prove this assertion by facts, and ask our friends to consider our quotations when in the market for this article.

The quality of our product naturally reaches the highest degree of perfection.

**Myrtle Oil.** There has been such a strong demand for the fine Spanish distillate, that we have only been able to execute the orders in part. The myrtle grows at some spots on the Riviera in enormous quantities. This is, for instance, the case in the neighbourhood of San Remo, on the slopes of the valley leading to Ceriana, at the foot of Monte Bignone. It is surprising that no portable still has yet been put up there, but that, on the contrary, this source of supply is left absolutely unused.

**Neroli Oil.** In our last Report[1]) we published an examination of neroli oil made in our laboratory, in which we communicated the presence in this oil (not yet demonstrated by anyone else) of pinene, camphene, dipentene, terpineol, phenyl acetic acid, benzoic acid, and decylic aldehyde, and also by means of linalyl phenyl urethane (discovered by us), once more detected linalol which was already known as a constituent of the oil. A few weeks afterwards a work on neroli oil by A. Hesse and O. Zeitschel[2]) was also published, in which they confirmed both the presence of camphene and terpineol, and also that of linalol, geraniol and linalyl acetate, bodies whose presence as constituents of this oil had first been communicated by Tiemann and Semmler[3]).

Hesse and Zeitschel in their publication[4]) call our examination of neroli oil a "preliminary communication", which was to be followed by a "publication". We are bound to protest against this misleading and wholly unwarranted description of our publication. The facts rather are these, that through our earlier publication, Hesse and Zeitschel had been placed in the position that they could only confirm a part of our results. A rectification of this matter has just appeared in the "Journal für practische Chemie"[5]). In the same work the supposition put forward by Hesse and Zeitschel, that the neroli oil examined by Tiemann and Semmler had been largely adulterated with petitgrain oil, and that consequently their work in this connection was of no importance for the knowledge of the composition of neroli oil, was rejected as not substantiated.

Indol, which had hitherto only been detected by P. Engels[6]) in neroli pomade, has now also been isolated by Hesse and Zeitschel from neroli oil, in which it is present in extremely small quantity. They further found traces of acetic and palmitic acids, and a sesquiterpenic alcohol $C_{15}H_{26}O$ (nerolidol) boiling at 276° to 277°. Judging from the low specific gravity of the latter (0,880 at 15°), it appears

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[1]) Report October **1902**, 54.

[2]) Journal für practische Chemie II. **66** (1902), 481.

[3]) Berliner Berichte **26** (1893), 2711.

[4]) Journal für practische Chemie II. **66** (1902), 484.

[5]) Vol. **67** (1903), 315.

[6]) Berliner Berichte **32** (1899), 2612. — Journal für practische Chemie II. **66** (1902), 504.

to be an aliphatic compound. The alcohol has a faint odour and is therefore of no importance for the aroma of neroli oil.

On separating[1]) the geraniol from the terpineol and linalol, by means of phthalic anhydride according to the process worked out in our laboratory, they obtained a mixture of geraniol and an alcohol isomeric with geraniol, which latter could approximately be separated from the geraniol by treatment with dry calcium chloride, with which, as is well-known, the last-named body forms a solid compound. The alcohol, separated from the solid calcium chloride compound of geraniol by suction, although still considerably contaminated with geraniol, yet differs sufficiently from the latter, so that the assumption appears to be justified, that an alcohol differing from geraniol is present in the constituent which no longer reacts with calcium chloride. In the odour the alcohol greatly resembles geraniol. In the opinion of the authors it has a finer and fresher odour. For the rest, the product (to which the name nerol has been given) differs from geraniol by an "apparently uniform" diphenyl urethane[2]) melting at 73° to 75°, by the slightly lower boiling point, and by the property of forming no solid compound with calcium chloride.

In addition to the free alcohols geraniol and nerol, their acetic esters geranyl acetate and neryl acetate are, according to Hesse and Zeitschel, also present in neroli oil. Neryl acetate also greatly resembles geranyl acetate in the odour and other properties. With regard to quantity, it is stated that neroli oil contains about 4 per cent. geraniol + nerol, and about the same quantity of the two acetates.

According to our experience (see under petitgrain oil) the statements concerning nerol must for the present be accepted with reserve, as it has not as yet been found possible to separate this body completely from the geraniol, and to identify it with sufficient certainty.

For the aroma of neroli oil, nerol and its acetate have no greater importance than geraniol and its acetic ester, from which in our opinion they do not differ in any very marked degree.

Hesse and Zeitschel have next occupied themselves with the examination of oil of orange-blossom water, and of orange-blossom extract. In the former they detected phenyl acetic acid, phenyl ethyl alcohol, geraniol, and nerol. The oil had the following properties: $d = 0{,}915$; $\alpha_D = +2° 50'$; ester-content 6 per cent.

Owing to the greater solubility of the alcoholic constituents of the orange-blossom and of methyl anthranilate in water, the water-oil contains a comparatively larger amount of these bodies than neroli oil.

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[1]) K. Stephan, Journ. für pract. Chemie II. **60** (1899), 248.

[2]) In this connection, compare our observations under petitgrain oil, on page 62.

The essential extract-oil, which can be readily obtained from orange-blossom extract by treatment with alcohol and steam distillation, showed the following constants: $d = 0{,}913$; $\alpha_D = -2^\circ$; ester-content 41 per cent. calculated on linalyl acetate; content of methyl anthranilate 6,5 per cent. It differs from neroli oil by a much higher ester-content.

We have recently detected in neroli oil, phenyl ethyl alcohol, by its urethane melting at 80°, and we have found that the presence of jasmone is probable, for we obtained from the corresponding fraction a semicarbazone of the melting point 200° to 204°.

**Neroli Oil (artificial) "Schimmel & Co."** Our original product has reached a very high degree of perfection through the important results of our examinations which we published on pages 52 to 58 of our Report of October 1902, and which we have turned to account in practice. We have made special arrangements for the production of the natural plant-constituents contained in the oil, for which we are very favourably situated.

Our original product should not be confounded with the many inferior mixtures which are much puffed up in the trade and are hawked about at all prices. Where cheapness is a consideration, it is in any case much better to buy a product like ours, and to cheapen it oneself with petit-grain or bergamot oil.

**Oil of Nutmeg.** Although the light waste material which is used for the manufacture of this oil really forms an article by itself, its price has not been left untouched by the great advance in the price of nutmeg. For a time the demand for the essential oil was exceptionally strong.

**Orris Oil.** We have received, from a wholly reliable and best informed quarter, the following special report on the present situation of the Florentine market:

> The harvest of 1902 gave a total yield of about 1000 tons, or 1 000 000 kilos, since the producers, encouraged by the rising prices in November, also gathered the two-year old roots, and at the same time did not in every locality reduce the new planting to such an extent as at the end of last summer appeared to be the case.

| | |
|---|---|
| If we add to the above-mentioned crop of . . . . . | 1000 tons |
| the old stocks still on hand . . . . . . . . . . . | 400 ,, |
| we commence with a total quantity of . . . . . . . | 1400 tons. |
| Against this, deliveries from the beginning of September to the end of February 1903 amounted to about . . | 470 ,, |
| leaving a balance at present of about . . . . . . | 930 tons. |

> But further important quantities have already been sold for gradual forward delivery, and based upon the deliveries which have taken place up to the present, it may be assumed that when the new crop comes in, some 500 or 600 tons may still be available of the above 930 tons. To this must then

> be added the result of the coming harvest, which it is as yet impossible to estimate. It may roughly be taken at from 800 to 1000 tons, according as the market-quotations at the harvest-time may induce the producers in a greater or smaller degree to gather the two-years' roots. At the end of November, the prices cif. Hamburg were 40 marks for pickings and 44 marks for assorted roots, and in a few cases higher prices were paid, but with the increasing result of the harvest the speculating mood and gradually also the demand from abroad became more feeble, which reacted adversely on the quotations. As a consequence, the roots can now again be bought:
>
> pickings at 34 to 35 marks cif. Hamburg, and
> assorted roots at 36 to 38 marks cif. Hamburg,
>
> not large quantities, but at any rate parcels which impecunious owners now and again put on the market. A further depression in the prices is aimed at from French quarters, although in that case it is hinted pretty clearly, that large parcels would readily be bought at a few marks lower rates for delivery not only in 1903, but also in 1904 and 1905. But naturally nobody here wishes to expose himself for the future at such prices, whilst the already much-suffering producers are least of all desirous of encroaching upon the market at still lower selling prices, though these may possibly have to be conceded later on, whether the growers like it or not, if the foreign buyers remain passive for some time longer. The over-production during the last few years has unfortunately been disastrous to the producers and to all other interested parties, but it is clear that with a gradually diminishing production, normal conditions, and with the latter also normal prices, may once more come back, if not in the immediate future, at least before long.

We have contracted for several hundred tons of the finest natural Florentine roots at the very lowest quotations of the day, and on the strength of these transactions have also sold very important quantities of orris oil. Never before has the perfumery-trade been able to procure this indispensable product at such incredibly low prices, and to use it on such a liberal scale, that violet-preparations can now be produced of unparallelled quality.

In the event of making purchases or placing contracts, the liquid orris oil in tenfold concentration, which we were the first to produce and to place on the market, should be seriously taken into consideration, as, in consequence of decidedly lower manufacturing expenses, it comes cheaper than the concrete oil. Since we introduced it into commerce, it has been used exclusively by a large number of perfumers. It is a matter of special satisfaction to us, that we have created in liquid orris oil a product of the very highest rank, which is of such sterling quality, that it only requires a single trial and calculation in order to recognise at once the advantages which it offers.

As has been the case with every one of the numerous new preparations produced by us in the last few decades, the great majority of our competitors have immediately appropriated also this new creation of ours. We desire to state this here once more, in order to avoid a confusion in the ideas.

We hear that the project of the etablishment of a factory for the production of orris oil in the root-growing districts of Tuscany, which we described in our last Report, has up to now not taken any tangible form, owing to the illness of the originator of the idea, Mr. Pegna. When calmly considering the scheme, that gentleman may no doubt arrive at the conclusion that it is not feasible to gather such a large number of root-producers under one flag as would here be the case; and, further, that the cost of production, in spite of the saving in carriage, would be much higher in the case of a factory which produces nothing but the single article orris oil, than with an existing etablishment which at the same time manufactures hundreds of other articles.

**Patchouli Oil.** Since our last Report our supplies of patchouli-leaves have reached us punctually, with the single exception of a parcel of 60 bales per s. s. "Bergedorf", which steamer, as is well known, caught fire when off Messina, and reached Hamburg after great delay. Fortunately the goods had suffered no damage whatever.

According to reports from the Straits Settlements, the article is now most difficult to procure, as it is impossible to obtain the leaves dry during the rainy season. In consequence of this the prices advanced by about 50 per cent., and as it cannot be doubted that the price will remain at this level, the quotations of patchouli oil had to be raised further. For imported oil 50 marks per kilo is already asked. Our product stands in respect of quality above that oil.

We hear from a reliable source that in Java patchouli-plantations have been laid out, from which possibly a crop may be expected before the end of the year. This new source of supply can, under the present conditions, only be welcomed.

**Peppermint Oil, American.** This important article has passed through a very agitated period. At the time when our last Report was written, there was not the slightest suspicion of the events which subsequently occurred. The value at that time was about $ 2,— per lb., that is to say fairly normal, and we did not consider it out of the question that with some speculative enterprise it might go slightly higher. We had no idea that at that very time a gang of speculators had already commenced their operations, speculators who were daring enough to buy up 90 per cent. of the existing stocks in order to carry through a corner such as for this article had never been seen before. Within a few weeks the prices were driven up to $ 5,— per lb., and were maintained at that level for several months.

In view of the results of the harvest and the increased cost of production, nobody would have been surprised to see an advance up to $ 3,—, but this bewildering state of affairs bore from the first the stamp of the clumsiest exaggeration, and was naturally opposed by all consumers of peppermint oil. As a consequence business in this article came completely to a standstill. The consumption was restricted to the utmost limits, or else attention was directed to the stocks which were brought to the light at all the principal markets, and which the speculators had not taken into consideration. Moreover France, Italy and Russia placed important quantities on the market and filled many a gap. But the movement received the death-blow when it was found that the bulk of the goods sold by the speculators lacked the properties which good American oil usually possesses. The enormous profit of the corner was not considered sufficient, and it was attempted also to play tricks with the quality. In particular, adulteration with Japanese oil was aimed at; of this oil (as will be found by referring to the statistics on page 61 of this Report) larger quantities than usually were shipped direct from Japan to New York, Philadelphia, San Francisco, Tacoma and Seattle, and heavy purchases were also made in London and Hamburg, with the object of depriving the European market of cheap material. These adulterations were first observed on the English market, but they were also proved by us in quite a large number of samples, and that in oils received from one of the principal speculators who boasts particularly of the "absolute" purity of his oil. Further down we return to this subject. It is only natural that the belief in a continuation of the high prices was greatly shaken by such proceedings. In addition to Japanese oil, erigeron oil is also said to have been used for the adulteration.

Thanks to such preposterous methods, and in the absence of all sympathetic feeling on the part of the European firms chiefly connected with the trade in peppermint oil, the speculators did not succeed in driving the prices up to $ 6,—, as was the intention. Already in January want of money caused a certain weakness, and offers were made under hand at $ 4,50.

At present the price is nominally $ 4,—. Large parcels of the brand H. G. Hotchkiss were recently realised at $ 3,75 to $ 3,50.

In London the speculation in peppermint oil has already claimed a victim. A Mincing Lane firm, heavily engaged in this article, has early in March suspended payment.

In the present conditions it is in the highest interest of every consumer to cover only the most necessary requirements. We have reduced the prices of our two brands **FB** and **FS & Co.** by 4/- per lb.

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As already mentioned, the rise in the prices of American peppermint oil has amongst others also led to extensive adulteration. In our laboratory numerous samples were examined which showed pronounced differences in specific gravity and optical properties from the normal distillate, but which above all attracted attention by their difficult solubility. It is a matter of course that these oils also showed a very low menthol-content. We mention below a few oils which had been adulterated to a specially large extent, in order to show the impudence with which these adulterations are carried out: —

| | $d_{15^\circ}$ | $\alpha_D$ | Total alcohol % | Solubility |
|---|---|---|---|---|
| 1 | 0,8888 | $-15^\circ 40'$ | 33,8 | Insoluble in 10 volumes 70 per cent. alcohol. |
| 2 | 0,8886 | $-17^\circ 24'$ | 35,2 | |
| 3 | 0,937 | $-12^\circ 44'$ | 45,9 | |
| 4 | 0,8867 | $-\ 9^\circ 41'$ | 26,1 | |

What has been said above applies particularly to the last-mentioned oil, which, contrary to the other three oils, only formed a cloudy solution even in 15 to 20 volumes absolute alcohol. A more detailed examination showed in this case an addition of about 60 per cent. mineral oil, an adulteration which must be characterised as unheard of.

The same observations have been made by Parry who, in "The Chemist and Druggist"[1]), publishes the examination of a number of American peppermint oils which show entirely similar deviations from normal oil as the examples mentioned by us. He states that he has lately had before him more adulterated oils than pure ones.

On a previous occasion Parry had already pointed out a case of adulteration of peppermint oil with light oil of camphor[2]). Such oils are characterised by exceptional insolubility and low menthol-content, and especially by the fact that the fractions obtained on distillation below 200° to 205°, are much larger than in the case of pure peppermint oil.

**Peppermint Oil, Italian.** In our Report of October 1902 we gave on page 66 particulars of Italian peppermint oil. A few peppermint oils also originating from Piemont have been examined by C. Ed. Zay[3]); we reproduce below in tabulated form (I to III) the actual results obtained by the author, and add for purposes of comparison the values which we have since obtained in examining some other samples of the same origin (IV to VI).

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[1]) Vol. **61** (1902), 948.

[2]) The Chemist and Druggist **61** (1902), 520.

[3]) Staz. sperim. agrar. ital. **35**, 816; according to Chem. Centralblatt **1903**, I, 331.

| | $d_{15^\circ}$ | $\alpha_{D16^\circ}$ | $n_{D16^\circ}$ | Total menthol | Ester-menthol | Free menthol |
|---|---|---|---|---|---|---|
| I. | 0,916 | — 2° 34′ | 1,468 | 55,5 % | 9,72% | 45,78% |
| II. | 0,9171 | — 10° 41′ | 1,467 | 58,6 „ | 7,10 „ | 51,5 „ |
| III. | 0,9256 | — 7° 4′ | 1,468 | 45,0 „ | 6,01 „ | 38,99 „ |
| IV. | 0,9122 | — 16° 21′ | 1,46733 (20°) | 52,5 „ | 7,89 „ | 44,61 „ |
| V. | 0,916 | — 13° 17′ | 1,46783 (20°) | 53,07 „ | 9,66 „ | 43,41 „ |
| VI. | 0,9157 | — 12° 34′ | 1,46783 (20°) | 50,95 „ | 9,87 „ | 41,08 „ |

The oils IV to VI examined by us did not form a completely clear solution with 70 per cent. alcohol, and the solutions in 80 per cent. alcohol which were at first clear, became cloudy when more solvent was added.

We wish to avail ourselves of this opportunity to correct a slight error which has crept in the previous article. It is mentioned there, that the menthone-content of the sample amounted to 23 per cent.; in reality it only amounts to 8,16 per cent., and this result agrees very well with a further examination which was subsequently made with another sample. The mistake was, that the difference in the saponification numbers of the acetylised oil before and after the conversion of menthone into menthol, was given as the menthone-content.

**Peppermint Oil, Japanese.** According to information from our friends in Japan, dating from the end of October last year, the result of the last harvest is as follows: —

| | | | |
|---|---|---|---|
| Bingo Bitchin | 1st crop | 4000 | catties. |
| „ „ | 2nd „ | 30000 | „ |
| „ „ | 3rd „ | 26000 | „ |
| Yonezawa | 1st „ | 25000 | „ |
| „ | 2nd „ | 15000 | „ |
| | Total | 100000 | catties |
| | or about | 60000 | kilos, |

against 80000 catties, or about 50000 kilos, in 1901. It was therefore fairly normal, and sufficient for the demand.

If, in spite of this, the value of the article is exceptionally high, the fault lies solely and exclusively with America, for the purchases on American account were made in such haste, that the Japanese soon discovered what the object was of these transactions.

Our cheapest purchase was in July last year at 3/3; since then the rise occurred as follows: —

| | | | | | |
|---|---|---|---|---|---|
| Cheapest quotation in | July | 1902, | about | 3/3 | per lb. |
| Average „ „ | August | „ | „ | 4/4 | „ „ |
| „ „ „ | September | „ | „ | 5/- | „ „ |
| „ „ „ | October | „ | „ | 5/- | „ „ |
| „ „ „ | November | „ | „ | 7/6 | „ „ |
| „ „ „ | December | „ | „ | 8/6 | „ „ |
| „ „ „ | January | 1903, | „ | 13/- | „ „ |

With the January quotation the highest price was reached. The prices then remained at the same level, and when in February and March several large parcels were sold by auction in London and fetched prices between 8/- and 9/-, the tendency became less firm, and the prices since then are nominal.

We are convinced that the fall in the quotation of Japanese oil will go hand in hand with that of American oil, the same as was the case with the rise. On the supposition that this argument is correct, it is at present advisable to exercise caution in purchasing.

The shipments of liquid Japanese oil since 1st August last year were as follows: —

| | | | |
|---|---|---|---|
| to | Hongkong | 7097 | catties |
| „ | London | 2700 | „ |
| „ | Hamburg | 2700 | „ |
| „ | Havre | 2475 | „ |
| „ | New York | 1350 | „ |
| „ | San Francisco | 1125 | „ |
| „ | Philadelphia | 900 | „ |

The comparatively large shipments to Hongkong would probably be bound chiefly for Hamburg and London, as our direct importation during that time is decidedly larger than the figures given for Hamburg.

**Peppermint Oil, Mitcham.** In the better qualities there is a total absence of offers, and it would be a difficult matter to hunt up parcels of any importance in England. With the enormous prices of American oil, there is a very brisk demand for English oil. In spite of the notorious lack of pure original distillates, "Mitcham" oil is hawked about at all prices, down to 52 marks per kilo, prices which can only raise a smile on the face of those who are behind the scenes.

Experiments made by E. Charabot and A. Hébert¹) have shown that mineral salts which have been applied to the soil in the neighbourhood of a plant, effect a reduction in the water-content of the latter. The experiments were made with the peppermint plant, which was submitted to the action of common salt, calcium chloride, sal ammoniac; the sulphates of sodium, potassium, ammonium, iron, and manganese; the nitrates of sodium, potassium, and ammonium; and di-sodium phosphate. The most powerful action is exerted by nitrates, especially sodium nitrate; the least powerful by di-sodium phosphate.

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¹) Compt. rend. **136** (1903), 160.

**Petitgrain Oil.** In November last year the report was circulated, that negotiations were being carried on between the distillers in Paraguay for the formation of a "ring", in order to monopolise the production, and as a consequence a prospect was held out of higher prices. But as we learn from a reliable source, this syndicate has not succeeded on account of the opposition from one of the oldest and most important producers, and the situation will therefore practically remain as before. The export of petitgrain oil from Paraguay amounted in 1901 to 17044 kilos, value 25566 gold pesos (1 peso = 4 s.). The quantity as given may agree with the facts, but the value is placed much too low, which shows once more that statistical figures have only a comparative value.

It might be assumed that the geraniol-like alcohol, designated by Hesse and Zeitschel as nerol, also occurs in petitgrain oil which is closely related to neroli oil. von Soden and Zeitschel[1]) have meanwhile produced from saponified petitgrain oil, by treatment with phthalic anhydride and calcium chloride, a fraction which had the properties mentioned by Hesse and Zeitschel. It is stated that petitgrain oil contains about 2 per cent. of this body. The boiling point of the preparation which in the opinion of the authors is now only contaminated with about 10 to 15 per cent. geraniol, is given by them as 225° to 227°, at atmospheric pressure; $\alpha_D = 0°$, d = 0,880. The odour is said to be decidedly fresher than that of geraniol. The compound absorbs 4 atoms bromine. Boiled with acetic anhydride, it yields quantitatively an ester having an odour resembling that of geranyl acetate. The boiling point of the ester at 25 mm is 134°; d = 0,917.

The formate is formed in the cold when a mixture is made with concentrated formic acid; it has an odour like geranyl formate. Boiling point 119° to 121°, at 25 mm; d = 0,928.

These compounds are naturally not uniform bodies, but contaminated with the corresponding esters of geraniol. It is suspected that nerol, along with geraniol, is present in most oils which contain the last-named body. von Soden and Zeitschel do not state on what grounds they assume that the admixture of geraniol in the preparation produced by them amounts to only 10 to 15 per cent.

As we have also occupied ourselves since some time with the examination of petitgrain oil (see our Report of October 1902, page 68) we have, in isolating the alcohols which are present in this oil, also directed our attention particularly to the separation of a compound having the properties of nerol, from the geraniol fraction of this oil.

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[1]) Berliner Berichte **36** (1903), 265.

We are in a position to confirm von Soden and Zeitschel's statement that here also, after removing the terpineol and linalol by means of phthalic anhydride, a mixture of alcohols remains, which unites only partially with calcium chloride. The product which we purified by treating it twice with calcium chloride, showed a boiling point a little lower than geraniol.

The principal fraction boiled under atmospheric pressure at 225° to 227°, or from 106° to 107,5° at 7 to 8 mm; the following fraction from 227° to 228° at atmospheric pressure, or from 107,5° to 109° at 7 to 8 mm.

The odour of these fractions very much resembles that of geraniol, but differs from that of citronellol. The diphenyl urethane was produced with 4 g of the principal fraction. We readily obtained a solid product which after being recrystallised once from dilute alcohol, melted indistinctly at from 60° to 64°. The melting point could not be raised in any marked degree (65° to 66°), in spite of repeated recrystallisation from alcohol. Only by partly dissolving the preparation in cold petroleum ether, and allowing the solvent to evaporate, we were able to obtain crystals which showed the melting point 73° to 75°, indicated by Hesse and Zeitschel for neryl diphenyl urethane. The melting point of this product was, however, after further recrystallisation from petroleum ether, raised to 80° to 81°, i. e. the melting point of geranyl diphenyl urethane.

It remains, therefore, open to doubt, whether the melting point given by Hesse and Zeitschel for neryl diphenyl urethane, is correct.

We will now compare the physical constants of the 'nerol' produced by us (which essentially agree with the figures given by v. Soden and Zeitschel), with the constants of the pure geraniol regenerated from the solid calcium chloride compound:

| Nerol | Geraniol |
|---|---|
| Boiling point 225° to 227° | Boiling point 229° to 230° |
| $d = 0{,}8804$ | $d = 0{,}880 - 0{,}883$ |
| $\alpha_D = + 0^\circ 17'$ | $\alpha_D = \pm 0^\circ$ |
| $n_{D17^\circ} = 1{,}47665$ | $n_{D17^\circ} = 1{,}47660$ |

It will be seen that the differences are so small, that on the ground of a determination of the constants, a differentiation of the compounds is not possible. For this reason it requires several further examinations to establish whether nerol, according to its principal quantity, represents a new alcohol differing from geraniol.

As the nerol produced according to Hesse, v. Soden and Zeitschel is still strongly contaminated with geraniol, we have attempted by another method to purify it further from geraniol.

When geraniol is heated with concentrated formic acid at 80° to 100°, it decomposes, like linalol, almost quantitatively into terpenes and polyterpenes, with loss of water. It might be possible that nerol would be less readily attacked by formic acid, and that, therefore, by heating crude nerol with formic acid, nerol might be produced free from geraniol by means of phthalic anhydride from the saponified mixture of terpenes, polyterpenes, and neryl formate. We accordingly heated 7 grams of the crude nerol (fraction 225° to 227°) obtained by Hesse and Zeitschel's method, with 10 grams concentrated formic acid on a water bath, until the turbidity due to loss of water occurred, and thereupon immediately diluted with water. The quantitative saponification of the washed neutral oil showed that it contained 39 per cent. of a formate, calculated on neryl formate. The bulk of the washed mixture, consisting of terpenes, polyterpenes and the unattacked alcohol, distilled at 15 mm from 80° to 170°. This fraction which still possessed a rose-like odour, was, after adding a small quantity of benzene, with the same weight of phthalic anhydride heated on a water bath, and the acid phthalic ester of the alcohol thereby formed extracted with soda, and all impurities removed by extraction with ether. When the phthalate was heated with soda liquor, an alcohol with a geraniol-like odour was separated, which was obtained by steam-distillation. The quantity was too small to determine whether this alcohol differs from geraniol.

We do not doubt, however, that v. Soden and Zeitschel will soon succeed in producing nerol quite free from geraniol, and in elucidating the nature of this compound which resembles geraniol in such an extraordinary degree.

**Pine-needle Oils.** Of these products, the distillate from *Pinus Pumilio* still plays the most important part; this is now so much in demand, that we had the greatest difficulty in obtaining the necessary supplies. The project, previously mentioned by us, of taking up the distillation on the slopes of the Carpathian Mountains in Hungary, has not yet been realised. The present moment would be favourable for the introduction of a new kind.

The consumption of the fine Siberian pine-needle oil which is absolutely pure and at the same time extremely moderate in price, has developed enormously. Last year it was already used by us in quantities of thousands of kilos. The Swiss distillers already demand higher prices for the extra-fine quality distilled from the cones of *Abies pectinata*. The exquisitely fine oil from *Abies alba* takes, as regards quality, now as before the first rank, and it sells so rapidly that we are never able to accumulate a stock of it.

**Rose Oil, Turkish.** The prices of the better-class brands have on the whole remained unchanged. The purchase-prices of these brands amount to about 600 marks per kilo, whilst ordinary commercial oil can be bought at all prices. Nothing can as yet be said of the new harvest. The winter in Roumelia was very mild, and the rose-bushes do not appear to have suffered.

By far the most important question for the rose-oil trade which at present claims attention, is the position of the Bulgarian Government towards the adulteration-problem, a question which has already been discussed so often in our Reports, and which up to now, for the most diverse reasons, has not yet been solved.

On the initiative of some deputies, there has been deposited at the Bureau of the National Assembly a new project of a law which is to guarantee the purity of rose oil. According to this project every admixture to rose oil, of whatever nature, is prohibited under penalties, and that not only during distillation, but also during the sale. The distillation is to be carried out in common establishments under control of a Government official; the produced oil is stored in special premises connected with the Agricultural Offices. Every producer receives from the particular Office a voucher giving the quantity, solidifying point, name of the distillation and origin of the roses, and on the strength of such voucher the producers will be able to obtain advances on their oil from the Loan Offices, or they can sell the oil to merchants against delivery of the voucher. Every purchaser can on presenting the voucher demand delivery of the oil mentioned in it. Moreover, the "Caisse Agricole" gives to the purchaser a sealed note which has been endorsed by a notary, on which the quantity purchased and exported is stated. Every consignment which is exported is accompanied by a certificate mentioning the name of the exporter, the place of origin, the guarantee of purity, and the solidifying point.

These certificates are returned by the sender within 6 months to the particular office, after having been signed by the purchaser and his signature legalised.

We are, however, informed that the Government as well as all interested parties are opposed to this project. It is the work of people who have no thorough knowledge of the article, and who do not know that it would be impossible to carry out such a law in practice, and that it would consequently be useless.

With regard to the matter of the Government-seal to coppers, to which we referred last year, a commencement has now been made to provide rose oil with such seal. The coppers have also a label attached with the following inscription: Douane Plovdive-Bulgare, Provenance Bulgare, S. G. D. G. (sans garantie du gouvernement). A tax of 30 centimes is levied for the seal and label.

The utility of these measures is inexplicable to anyone who has a practical insight into the conditions, for the insignia are attached to every copper, no matter whether it contains pure or adulterated oil.

It follows from the foregoing that the question of submitting rose oil to official control, which at the time was introduced with great emphasis, remains unsolved just as before.

According to the particulars recently published by the Statistical Office, the total export of rose oil from Bulgaria amounted in 1902 to 3676 kilos, value 2609159 francs, against 3027 kilos, value 2140538 francs, in 1901. The exports of 1902 therefore exceed those of the preceding year by 649 kilos, and 468621 francs. In the month of December 1902 the exports of rose oil came to 227 kilos, value 151817 francs, of which to Austria-Hungary 5 kilos, value 3425 francs, to the United Kingdom 22 kilos, value 15154 francs; to Germany 29 kilos, value 19753 francs, to Turkey 6 kilos, value 3661 francs, and to France 145 kilos, value 96132 francs.

**Rosemary Oil, Dalmatian.** In view of the high prices and the scarcity of the French distillate, an exceptionally strong demand exists for Dalmatian oil, which has led to a slight increase in the prices. The adulterated qualities which are met with in commerce in large quantities are not affected by the present state of affairs.

As is well known, the distillation of rosemary oil is carried on on the Dalmatian island of Lesina. In our Report of October 1896 we gave a detailed description on the subject, based on personal observations. In the meantime, the situation has undergone a decided change. The distillation is still carried on in the two villages Bruschje and Grablje, which from time immemorial have been the seat of the production; the process was formerly very primitive and took up much time. At the instigation of the Governor of Dalmatia, two limited companies have now been formed for the production of rosemary oil, which work with German steam-distilling apparatus of the most modern construction, and are said to supply an excellent article. It is stated that the peasants are quite enchanted with these installations, and are vying with each other in their work. With the old, difficult manufacturing process, the two villages had an annual revenue of about ₤ 900,— from rosemary oil, whilst in the present season, with much less work, they have already received about ₤ 1200,—. The distillation of sage, which plant grows there in enormous quantities, has also succeeded excellently, and a remunerative trade in oil of sage¹) is also anticipated.

It is a pleasure to find that civilisation is gradually penetrating even into remote districts with prosperity following in its train.

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¹) "Gartenflora", Zeitschrift für Garten- und Blumenkunde 1903, Vol. 4.

**Rosemary Oil, French.** The final result of the distillation in the South of France has fallen below the most modest expectations. The acquisition of larger parcels of pure oil is a matter of the greatest difficulty.

**Oil of Rue.** From the work of Mannich[1]) on the ketones of oil of rue, which has been published again in connected form, we make some abstracts as an addition to what we mentioned on the subject in our last Report[2]). The ketone $C_{22}H_{42}O$, obtained from methyl nonyl ketone in a manner analogous to the condensation of acetone with hydrochloric acid gas, can again be converted into the original ketone by means of 60 per cent. sulphuric acid. The picrate of its amido-guanidine compound melts at 125° to 126°. The methyl heptyl ketone is capable of analogous condensation. The ketone $C_{18}H_{34}O$ thereby formed, boils at 184° to 187° (14 mm), its amido-guanidine derivative has the melting point 130° to 131°.

A German oil of rue recently examined by J. Houben[3]) had the melting point 9,3°, and showed a striking blue fluorescence, which was caused by a compound which could be abstracted from the oil by shaking with dilute sulphuric acid. Owing to the smallness of the quantity of oil which was obtained from the sulphate solution on neutralising the latter, the author was unable to make a further examination of the compound. In this connection we would point out that the same body was discovered by us already some time ago in German oil of rue, and that, according to our observations, it may most probably be identic with methyl ester of methyl anthranilic acid. We would refer to our communication in the October Report of 1901, page 46.

In addition to a small quantity of an acid distilling at 236° to 238°, which was probably caprylic acid, and another small quantity of a phenol-like body of the melting point 156°, Houben isolated from 500 grams oil 355 grams methyl nonyl ketone and 12 grams methyl heptyl ketone. According to his statements, the latter boils, contrary to what Thoms has stated[4]), at 194° to 196° (80° to 82° at 15 mm). The boiling point of methyl nonyl ketone was found at 228° to 230°, at 18 mm pressure at 118°. Thoms gives it as 223° to 224°, v. Soden[5]) and Henle as 230° to 231°. Methyl nonyl ketone has the following constants: specific gravity 0,8295; solidifying point $+13°$.

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[1]) Berichte der deutsch. pharm. Ges. **12** (1902), 267.
[2]) October **1902,** 76.
[3]) Berliner Berichte **35** (1902), 3587.
[4]) Report April **1901,** 52.
[5]) Report October **1901,** 47.

The pure ketone shows no fluorescence. The fluorescent ketone described by Charabot-Dupont-Pillet[1]), was clearly contaminated with the above-mentioned basic constituent.

The methyl heptyl carbinol obtained from methyl heptyl ketone by reduction with sodium in an aqueous-ethereal solution, — a body which from another side has recently been detected in oil of rue (see below) — is a liquid with a pleasant odour, boiling at 193° to 194° (90° to 91° at 12 mm). Dimethyl heptyl carbinol produced from the ketone by Grignard's reaction with methyl magnesium iodide, boils at 96° to 98° (13,5 mm). The carbinol boils at 10 mm pressure at 115°, at 14 mm at 120°; its acetic ester distils at 122° (11 mm). The second reduction-product from methyl nonyl ketone, representing 10 to 15 per cent., is methyl nonyl carbinol pinacone, a solid body of the boiling point 215° (10 mm). Dimethyl nonyl carbinol boils at 117° to 118° (12,5 mm). According to Houben's statements, the conversion of the methyl nonyl ketoxime (after Beckmann) with concentrated sulphuric acid, does not take place in accordance with the observations made by Hantzsch[2]) with ketoximes; for the author found, contrary to Thoms[3]), in addition to acetyl nonyl amine, also a large proportion of caprinic acid amide.

F. B. Power and H. Lees[4]) also report on a number of interesting bodies detected in oil of rue. The origin of the material examined could not be determined with certainty, but the authors believe, on the strength of the resemblance of its chemical and physical constants to those of the oil examined by von Soden and Henle[5]), that it was an Algerian rue oil. It had a bright-yellow colour without fluorescence, the specific gravity $d\frac{15.5^\circ}{16^\circ}$ 0,8405, the optical rotation $\alpha_D - 3^\circ 48'$, and was soluble in 2 parts 70 per cent. alcohol. The quantity of oil used was 1800 grams. By shaking with 20 per cent. sulphuric acid, a basic body was abstracted from the oil, but this body (contrary to the base of rue oil discovered in our laboratory) showed no blue fluorescence, and had an odour reminding of quinoline. The crystals of the melting point 156°, previously found by Thoms[6]) and lately also by Houben in the German oil, were proved by Power and Lees to be salicylic acid, clearly originating from its methyl ester which was obtained in small quantity along with it. The properties of the two ketones which are also present in this oil are as follows:

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[1]) Les huiles essentielles, p. 283.

[2]) Berliner Berichte **24** (1891), 4021.

[3]) Berichte d. deutsch. pharm. Ges. **11** (1901), 3.

[4]) Journ. chem. Soc. **81** (1902), 1585.

[5]) Pharm. Ztg. **46** (1901), 277 and 1026. — Report October **1901**, 47.

[6]) loc. cit.

Methyl heptyl ketone:

Boiling point 194,5° to 195,5° (763 mm).

Specific gravity $d\frac{14^\circ}{16^\circ}$ 0,8296.

Melting point of the semicarbazone 119° to 120°.

Methyl nonyl ketone:

Boiling point 229° to 233° (759 mm),

„ of the ketone regenerated from the semicarbazone 231,5° to 232,5° (761 mm).

Specific gravity $d\frac{20,5^\circ}{16^\circ}$ 0,8263.

Melting point of the semicarbazone 122°.

Valeric acid, present in the oil perhaps as ethyl ester, was found on saponification of a fraction boiling from 165° to 170°. l-Pinene was contained in the portions of the same boiling point, limonene and cineol in the fractions boiling from 170° to 185°. The presence of this hydrocarbon was proved by the nitrosochloride and the latter's nitrol piperidide. The two last-named bodies could be identified by the tetrabromide (m. p. 103°) and the iodol derivative (m. p. 114° to 115°) respectively, and by the hydrobromide of cineol (m. p. 55° to 56°). From the saponification liquors of the fractions boiling above 185°, an acid was obtained which distilled below 120°, and which was recognised as acetic acid by the analysis of its silver salt. Special interest is also attached to the presence of methyl heptyl and methyl nonyl carbinols in oil of rue, the secondary alcohols produced by Mannich and by Houben from the corresponding ketones. The authors succeeded in detecting the bodies in the fractions of the boiling points 190° to 200° and 210° to 235° respectively. The physical constants of the compounds are as follows:

Methyl heptyl carbinol:

Boiling point 195° to 196°.

„ of the carbinol purified by the acetyl compound 198° to 200° (765 mm).

Specific gravity $d\frac{19^\circ}{16^\circ}$ 0,8273

Optical rotation $\alpha_D$ — 3° 44′ (50 mm).

Methyl nonyl carbinol:

(obtained from the acetyl compound of the crude carbinol)

Boiling point 231° to 233°.

Optical rotation $\alpha_D$ — 1° 18′ (25 mm).

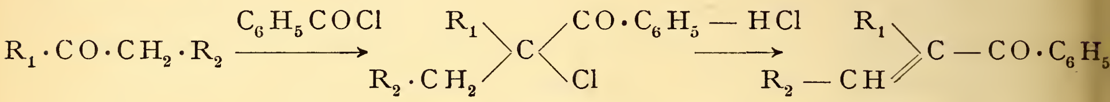
The corresponding acetates boil at 213° to 215° and 245° respectively.

Elementary analysis, and the formation of the ketones of the corresponding boiling points on oxidation of the carbinols with chromic acid, prove that the two products may be considered as methyl heptyl carbinol and methyl nonyl carbinol.

The oil passing over between 250° and 320° has a blue colour and a herb-like odour. The ketone content, according to the authors, amounts to 80 per cent., the content of alcohols to about 10 per cent.

The ketones are present in about equal proportion. The presence of terpenes (pinene, limonene) leads to the suspicion that the oil examined was adulterated.

Power and Lees had at first attempted to separate the ketones of rue oil from the alcohols by treatment with benzoyl chloride, in the expectation that they would subsequently be able to obtain the high-boiling benzoic esters of the alcohols by fractionating. But, as Lees [1]) states in a later work, this method proved unsuitable, as the ketones also yielded high-boiling condensation products with benzoyl chloride, which on further examination were recognised as the benzoic esters of olefinic alcohols. Their formation may be explained by the following formula:



$$R_1\cdot CO\cdot CH_2\cdot R_2 \xrightarrow{C_6H_5COCl} \begin{matrix}R_1\\ R_2\cdot CH_2\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}CO\cdot C_6H_5 - HCl\\ Cl\end{matrix} \xrightarrow{\quad} \begin{matrix}R_1\\ R_2-CH\end{matrix}\!\!>\!C-CO\cdot C_6H_5$$

The compounds correspond to the enol-form of acidyl aceto-acetates produced by Claisen and Haase [2]). On hydrolysis they are reconverted into the original ketones with intermediate formation of homologous vinyl alcohols.

In the course of an examination of oil of rue carried out with Power, Lees [3]) produced from secondary hexyl aceto-acetic ether, by splitting off the ketone, methyl β-methyl hexyl ketone, which was obtained in a yield of 80 per cent. in the form of a pleasant smelling oil of the boiling point 184° at 769 mm, and the specific gravity $\left(d\,\frac{15^\circ}{16^\circ}\right)$ 0,8319. Its oxime is liquid; the semicarbazone shows the melting point 75°.

**Oil of Muscatel Sage,** which is characterised by an odour approaching that of ambergris, has lately been purchased in large quantities, which cannot be replaced until the late autumn. We have only a few ounces at disposal.

**Sandalwood Oil, East Indian.** With regard to the disease which has broken out in some districts among the sandalwood plantations, and which we first mentioned in our Report of October last year, there is now published in number 1 of "The Indian Forester" (January 1903) a very detailed report from the Government botanist, C. A. Barber of Madras, who has inspected these districts by order of the Government. We reproduce below the most essential points of this report: —

> The disease, called "spike", appears to be of recent occurrence; it is believed that the first traces have shown themselves 4 to 5 years ago. Since that time whole tracts have been cleared by it, especially in localities where

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[1]) Journ. chem. Soc. **83** (1903), 145.

[2]) Berliner Berichte **33** (1900), 1242.

[3]) Journ. chem. Soc. **81** (1902), 1594.

the trees grow close together. It is assumed that the disease is infectious, although no strict proofs hereof exist. The disease manifests itself in this manner: the young shoots and leaves, instead of having the beautiful appearance of their kind, commence to grow out stiff and straight. The leaves stand erect like bristles. In the course of the disease the leaves become constantly narrower and more pointed, and from year to year fewer, until they have the appearance of fine ears with 4 rows of bristles. Then the tree soon dies. From all reports it appears that the course of the disease is very rapid, mostly extending only over a few months. The disease does not, as was at first believed, attack only the roots, but the whole plant. No doubt it begins at the roots whose extremities gradually die off, by which the supply of water and salts is cut off. The abnormal conditions which then occur in the formation of the blossoms, must bring about the destruction of the tree. For this reason, the further study of the still unexplained cause of the disease must be directed to the extremities of the roots.

In the same number of the above-mentioned periodical Sir Dietrich Brandis expresses himself on the "Treatment of the Sandal-tree". He suggests the careful study of those plants which appear as "companions" of the sandal-tree. He further recommends a close undergrowth in the sandalwood-plantations. The cultivation should be carried on with self-propagated seedlings, and a sufficient area should be reserved, where the trees, protected from fire and contagion, can develop further in an undisturbed manner. The distances between the plants should be sufficiently large to allow of the free development of the crown of the tree.

It is clear from the foregoing that the British Government is thoroughly following up the evil, and with the help of the capable botanists whom it has in its service, will find ways and means to remove it before it spreads to the other districts. If, against expectation, the disease should extend over all sandalwood districts, the market would, for the time being, receive very large supplies of wood material (as the dead trees represent normal material); but when this is used up, a calamity could scarcely be avoided, until the aftergrowth has advanced far enough to supply a substitute.

The prices of sandalwood oil, through a competition which is constantly increasing in numbers and intensity, have been depressed to a level which is out of all proportion to the cost of production and trouble. Although we take no part in the price-cutting we are unable to accumulate stock, a proof that a reliable and strictly first-quality oil is still appreciated.

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The „Oranje", manufacturers of essential oils at Amsterdam, have issued a circular dated January 22nd 1903, in which they pretend to be particularly well placed for the distillation of Sandalwood oil, owing to contracts with the Mysore Government for the purchase of the wood. As we had reason to believe that this statement was not in accordance with the facts, but merely made for the purpose of "advertising" the firm's importance, we applied direct to the respective officials at Mysore, from whom we promptly received the following reply, which in point of clearness leaves nothing to be desired: —

(General Serial No. 30.)

1903.

*From*

**M. Muttannah, Esquire, R. B.,**
offg. **Conservator of Forests** in **Mysore,**
**Bangalore.**

*To*

Messrs. **Schimmel & Co.,**
**Miltitz, Leipzig,**
via **Brindisi.**

*Dated* } 23rd March 1903.
*Despatched* } Camp Arsikere.
*Received*
*Camp No.* 622 } 1903.
*No.*
*Enclosures Number.*

Sir,

With reference to your letter of the 30th January last, addressed to Mr. J. L. Pigot, late Conservator of Forests in Mysore, I have the honour to inform you that Mysore Sandalwood is always sold by auction, and no contracts exist with any firm or person for the private sale of Sandalwood. The statement published by the "Oranje", that they have important contracts with the Mysore Government, is therefore not true. I accordingly request you to contradict this statement and to give wide publicity to the fact. Thanking you for the information you have been good enough to furnish in the interest of Sandalwood trade,

I have the honour to be,

Sir,

Your most obedient servant,

**M. Muttannah,**
**Offg. Conservator of Forests**
in **Mysore.**

This document needs no further illustration: it shows, what kind of doubtful means are often employed to mislead buyers.

**Sandalwood Oil, West Indian.** The distillation-waters of West Indian sandalwood oil also yield on cohobation a yellow-coloured first fraction containing alcohol, in which methyl alcohol, diacetyl and furfurol could be detected in the manner repeatedly described.

**Savin Oil.** On a previous occasion[1]) we have already mentioned that the first runnings of savin oil contain diacetyl; methyl alcohol, and furfurol, bodies which usually occur along with this compound, could at that time, however, not be detected.

We have now been able to isolate all these three compounds, in considerable quantities, from the cohobation waters of savin oil. The identification took place in the usual manner.

**Spearmint Oil.** At the present time America controls the market of this oil completely, as for many years there has been no question of a German production. The prices, which have risen about 100 per cent., must be paid, whether one likes it or not. For the rest, everything depends on the result of the distillation in the coming autumn.

**Spike Oil.** This oil is in the same position as oils of lavender and rosemary, but with this difference, that here the advance in the prices is about half-way between the other two. As our buyer called our attention in good time to the critical situation, we were able to secure large parcels before the rise asserted itself to its full extent; and we are now in a position to supply our clients in an excellent manner. The stocks in the hands of producers are practically exhausted.

**Star-anise Oil.** Since the date of our last Report, efforts have repeatedly been made in China to drive up the prices, but these have met with no response. In fact, it cannot have escaped the attentive observer, that since several years the speculative spirit for such like articles has disappeared, a spirit which in previous years asserted itself at every opportunity, especially on the London and New York markets. A year seldom passed by without more or less important fluctuations in the prices of Chinese oils. The cause of this disinclination may possibly be this, that the production of star-anise oil has increased, but the consumption has declined owing to the competition of anethol.

The Chinese exports cannot be ascertained, as the statistics give star-anise oil not by itself, but jointly with cassia oil.

The shipments from Tonquin in 1902 were:

| | | |
|---|---|---|
| | 1050 | cases ex Pakhoi |
| | 620 | „ „ Haiphong |
| Total | 1670 | cases of 30 kilos each. |

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[1]) Report October **1900**, 62.

According to reports from Tonquin, the prospects of this year's harvest are exceptionally favourable. The crop is estimated at double that of 1902.

**Oil of Tansy.** The American distillate which in point of quality is entirely reliable, has been carried along with the general upward movement of essential oils of American origin, and has been driven up to almost the double value.

Under these conditions it will be more advantageous to distil this oil here in the coming summer.

**Thyme Oil.** According to a commercial Report issued by the British Board of Trade[1]), it would appear that the manufacture of essential oils in the island of Cyprus is extending more and more. Since some time the manufacture of red thyme oil (which to all appearances is obtained from an *Origanum* species), marjoram oil and rose oil has received special attention, and for these Cyprus seems to offer a large field. For example, the export of red thyme oil amounted in 1899/1900 to 237 lbs., in 1901/01, to 615 lbs., and in 1901/02 to 1086 lbs. The price for the former in England was 3/- per lb., which seems a very fair one considering that pure oil of thyme is sold for at least 5/- per lb. *Origanum* is to be found at present growing wild only, chiefly in the forests, but the quantity growing there is so important, that a much greater quantity of oil could be produced than that distilled last year. Rose oil is at present only produced on a small scale, but this branch of manufacture appears to be also growing. For instance, large plantations of *Rosa damascena* were made last year in the neighbourhood of Milikouri and Pedoula, the centre of the rose-oil and rose-water manufacture.

**Tuberose Oil.** Since A. Verley[2]), four years ago, published his communication on the oil of tuberose-blossoms, this oil has not again been submitted to an examination. Verley had isolated from the essential oil of tuberoses about 10 per cent. of a compound which he calls tuberone. Nothing definite has become known of the properties of this body, which appears to be a ketone, and is said to be composed according to the formula $C_{13}H_{20}O$. Even less is known of the remaining constituents of this oil. In connection with our other chemical examinations of the blossom-oils which are so important for the better-class perfumery, we have also occupied ourselves with tuberose oil. A result of the work which is not yet concluded may be communicated in this place.

The crude material employed for the examination was extract of tuberose-blossoms, as an essential tuberose-oil is not on the market.

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[1]) The Chemist and Druggist **61** (1902), 1026.

[2]) Bull. Soc. chim. III. **21** (1899), 307.

Extract of tuberose-blossoms is a brown salve-like mass, which, like all pure blossom-extracts, consists chiefly of wax and paraffin-like substances which have no value for the odour.

In order to obtain from this the essential oil, 100 g extract were distilled out with water vapour, whereby a milky, turbid, watery distillate was obtained. The essential oil extracted with ether from this distillate after addition of common salt, had the characteristic odour of the tuberose, and showed a distinct blue fluorescence. The latter points to the presence of methyl anthranilate which has repeatedly been detected in flower-oils. The yield of oil only amounted to 5 g, but in any case the extract contains more — perhaps double that quantity — for it is a difficult matter to distil the oil out until all odour has disappeared. At 5 mm pressure the oil distilled from 60° to 140°. With the fraction boiling about 140°, which amounted to over 1 g, and in which tuberone must be present, it was attempted to produce an oxime. After boiling with alcoholic potassa and hydroxylamine hydrochloride, the odour of the fraction had undergone no change. A solid compound could not be separated from the reaction-product. The remaining 4 g oil were oxidised with dilute solution of potassium permanganate, with the application of heat. The oxidation which at first progressed rapidly, became gradually slower, and there remained at last an oil which was oxidised with difficulty, and whose odour reminded of methyl benzoate. This oil, which was fairly volatile with water-vapour, was distilled off in a current of steam. It was heavier than water, but its quantity was too small to allow of an exact determination of the constants. That this oil actually consisted chiefly of methyl benzoate, was shown when it was heated with alcoholic potassa, when a good yield of benzoic acid was obtained. The melting point of the separated recrystallised acid lay at 122°.

The silver salt of this acid contained a quantity of silver calculated for silver benzoate.

0,0956 g yielded 0,0451 g = 47,17 per cent. Ag.
Calculated for $C_6H_5COOAg$ = 47,16 „ „ „

As methyl benzoate is only difficultly attacked by dilute 3 to 4 per cent. solution of potassium permanganate, even when boiled, the method described is suitable for the separation of this compound in oil of tuberoses, and occassionally also in other essential oils¹).

When sulphuric acid was added to the oxidation liquor, an acid of a fatty consistency separated out, which has not yet been submitted to examination. After prolonged standing there sublimed from the mass crystals which melted at 120°, apparently benzoic acid.

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¹) Compare Oil of Cloves

**Verbena Oil.** An examination of verbena oil from Grasse has been published by E. Theulier[1]). The oil, obtained in a yield of 0,072 per cent. from the fresh leaves of *Verbena triphylla*, had a bright yellow colour, reminded in the odour somewhat of lemongrass oil, and showed the following constants: $d_{15^\circ} = 0,919$; $\alpha_D = -16^\circ 20'$; ester-content (calculated on linalyl acetate) 11,20 per cent. The oil was insoluble in 80 per cent. alcohol, but dissolved in an equal volume of 90 per cent. alcohol, and when more of this solvent was added, small white crystals separated out. The same body separated out when the oil was cooled in a freezing mixture; after repeated recrystallisation from strong alcohol it melted at 62,5°, and it is therefore most probably a paraffin-like hydrocarbon. In addition to citral, of which the quantity was found by Theulier to be 20,8 per cent., the oil contained l-limonene (proved by the tetrabromide which was prepared from it, though not in a perfectly pure state); geraniol (separated by the calcium chloride compound, and identified by oxidation into citral), and a probably lævorotatory sesquiterpene.

**Vetiver Oil.** In consequence of an enormous demand for our distillate, we have largely increased the manufacture of this product which is indispensable in the preparation of fine toilet-soaps. We now supply it in any quantity.

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P. Genvresse and G. Langlois[2]) have detected two compounds in vetiver oil, but these have no importance for the odour of the oil. The two oils serving for the examination originated from Bourbon and from Grasse. The neutral Bourbon oil had the specific gravity 0,993 (20°), the optical rotation $+ 23^\circ 43'$ (in alcoholic solution); with the oil from Grasse the specific gravity was 1,012 (20°), and the rotatory power $+ 27^\circ 9'$. The last-named oil had an acid reaction. When submitted to steam-distillation, only one-third of the total oil passed over, of which one part was specifically lighter, and the other heavier than water. The former consists chiefly of a sesquiterpene $C_{15}H_{24}$, vetivene, a colour- and odourless liquid of the boiling point 262° to 263° (740 mm, 135° at 15 mm), the specific gravity 0,932 (20°), and the optical rotation $+ 18^\circ 19'$. It absorbs without solidifying 4 atoms bromine, whereby it acquires a blue colour. The heavier portion of the oil consists essentially of a sesquiterpenic alcohol $C_{15}H_{26}O$, vetivenol, a thickish bright-yellow odourless body with the following physical constants: boiling point 169° to 170° (15 mm), specific gravity 1,011 (20°), optical rotation $+ 53^\circ 43'$ (in alcoholic solution). When the alcohol is treated with acetic anhydride, it forms an acetate; anhydrous

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[1]) Bull. Soc. chim. III. **27** (1902), 1013.

[2]) Compt. rend. **135** (1902), 1059.

oxalic acid acts upon it with formation of the above-mentioned sesquiterpenic hydrocarbon vetivene. The distillation residue contains, in addition to vetivenol, an acid or mixture of acids, a white, viscid mass, acquiring a brown colour when exposed to the air, which yields a soluble potassium salt. The body which bears the characteristic odour of vetiver oil is an ester of this acid and of vetivenol, which is very easily saponified already by water.

**Wintergreen Oil.** According to American reports, the stocks have been greatly reduced by an uninterrupted strong demand, and the prices show an upward tendency. Since the lowest quotation in January 1902 at $ 1,45, they have gradually risen to $ 1,75. The production during last year has been scanty, as even the higher prices paid are not remunerative, in view of the high wages. This state of affairs is the direct consequence of the competition of the artificial oil, which since the great drop in the prices of salicylic acid can be supplied at an absurdly low price, and which, also as regards quality, will be acknowledged by every unbiassed judge to be equal to the natural oil.

Methyl ester of salicylic acid, as is well known, is present in the roots of many polygalaceae. According to recent observations made in the agriculturo-chemical Laboratory of the Botanic Garden of Buitenzorg[1]), it also occurs in the saprophytes *Epirrhizanthes elongata* Bl. and *Epirrhizanthes cylindrica* Bl., which also belong to the family of polygalaceae. The pulp of *Coffea liberica* and *Coffea stenophylla* also contains this ester, but, strange to say, it is not present in the pulp of *Coffea arabica.* On the other hand, methyl ester of salicylic acid has been detected in the pulp of hybrids between *Coffea arabica* and *Coffea liberica.*

**Wormwood Oil.** The American distillate is still quoted at a disproportionately high price, and moreover does not now give satisfaction in the quality. For this reason we prefer to wait until normal conditions return once more. Of French oil, on the other hand, a choice selection is available. First in point of quality stands the oil distilled from the cultivated herb in the neighbourhood of Paris; our quotation refers to this oil.

**Ylang-Ylang Oil, "Sartorius" I.** The hopes expressed by our friends at Manila, that the rise of 50 marks per kilo, which was put in force last autumn, might be sufficient, have unfortunately not been realised; on the contrary, they were absolutely compelled to raise the price by another 50 marks, and they assure us most

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[1]) Annual Report **1901**, 58.

positively that even now their expenses are not covered. There is such a competition in the purchase of the flowers, that the prices are driven up beyond all limits, and the factories will be forced to transfer the distillation to the interior of the island, so as to escape from the conditions which prevail in Manila. On the other hand, the enormous prices paid for the flowers may induce the producers to enlarge the plantations, which would sooner or later lead to an increased supply of flower-material. We have received the most binding promises from our friends, that, as soon as this drop in the values takes place, the prices will be reduced as far as possible. But for the present this is out of the question, for there is everywhere a lack of really fine qualities, and the demand is so large, that we could easily dispose of double the quantity of the Sartorius brand, of which we have as hitherto the sole rights of sale. Our importation during the year 1902 amounted to 49 cases = 250 kilos and 800 grams.

**Ylang-Ylang Oil, "Schimmel & Co."** (German Patent No. 142 859). The favourable state of affairs of the natural flower-distillate has promoted the sale of our synthetic product, and has helped to introduce it into several perfumery-factories. When once it is introduced, it acquires a permanent place, for by the improvements which it has constantly undergone by the discovery of new constituents of the natural oil, it has approached the latter so closely in point of quality, that it can only be distinguished with difficulty from the finest brands. At the present moment it requires already an expert knowledge to detect any difference, and it is really astonishing, in view of the enormous difference in the prices, that here and there clients still hesitate to adopt the artificial oil.

In any case, it should now no longer be judged by previous trials, but new comparisons should be made in order to obtain a correct idea of the quality and fineness of our present product. For since its introduction we have detected a whole series of the most important constituents, which, added in the proper proportion, impart to the artificial oil in a constantly higher degree the stamp of genuineness and truth to nature.

When in the year 1895 we undertook the examination of ylang-ylang oil, only the following bodies were known as constituents of this oil: linalol, geraniol, p-cresol methyl ether, acetic acid, and benzoic acid in the form of esters[1]).

It was, of course, impossible to imitate ylang-ylang oil artificially with these bodies alone, and the further we advanced with our work, the clearer it became, that ylang-ylang oil belongs to that class of oils,

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[1]) Compt. rend. **76** (1873), 1482; Reychler, Bull. Soc. chim. III. **11** (1894), 407, 576, 1045; **13** (1895), 140.

which owe their aroma to the joint action of a large number of different bodies.

In addition to the above-named already known constituents, we have either proved the presence of the following important aromatic bodies with absolute certainty and isolated them, or have indicated their presence as very probable[1]). They are: —

Pinene, creosol, eugenol, isoeugenol, eugenolmethyl ether, benzyl alcohol, benzyl acetate, benzyl benzoate, methyl ester of benzoic acid, methyl ester of salicylic acid, methyl ester of anthranilic acid, and further, an odourless sesquiterpenic alcohol melting at 138°.

In order to protect this discovery we have on 23rd September 1901 applied for letters-patent.

# Novelties.

In November last year we received from Professor Zimmermann, who directs the Botanical Garden at Amani in German East Africa, a sample of wood obtained from a species of tree which is there indigenous. The red-brown wood, in places covered with brilliant crystals, diffused a penetrating skatol-like odour. In order to obtain the odorous substance, the pieces of wood were washed several times with ether. After distilling off the ether, a brown crystalline mass remained behind, which was then distilled out with steam. In this manner we obtained from 112 grams wood, 1,2 gram = about 1 per cent. of white crystals with an intense skatol-odour, which melted at 95°. These are consequently identic with skatol. With hydrochloric acid they formed a hydrochloride melting at 168°. As it was usual to consider skatol essentially as a secretion of the animal organism, the fact, here confirmed, of the presence of not at all unimportant quantities of this powerfully smelling body, is especially interesting.

Skatol was observed for the first time in a plant by Dunstan[2]). He found it in a sample of the wood of *Celtis reticulosa*, collected by Daniel Hanbury and deposited at the museum of the Pharmaceutical Society of London. This tree occurs in Java, Ceylon, and the East Indies. The fresh wood of this tree is also said to have a penetrating and abominable odour.

Up to the present it has not yet been possible to determine the botanical origin of the tree indigenous to East Africa, from which the wood examined by us was obtained.

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[1]) Report April **1896**, 62; April **1899**, 9; October **1901**, 54; April **1902**, 64.

[2]) Pharmaceutical Journal **19** (1899), 1010.

We have further received from Amani a white-coloured wood, which has a much fainter odour of skatol, and which at the same time smells like linalol. Its botanical origin is also unknown.

Professor Zimmermann makes the following remarks on the subject:

> "The wood of this species of tree has in the fresh state a fairly faint and not exactly disagreeable odour. Only when it has reached a certain state of decay it commences to smell strongly and disagreeably, but in a further stage of decomposition it again becomes odourless. It may be assumed that the fresh wood already contains a substance from which through decay the malodorous substance originates."

This observation, which at any rate is very interesting, deserves to be continued further. As we have as yet been unable to obtain a sufficient quantity of material, we have not yet been in a position to make a chemical examination of the white species of wood.

## Notes of recent scientific work concerning terpenes and terpene derivatives.

The desinfecting action of essential oils and their constituents has lately been the subject of several examinations.

Calvello¹) has made comparative tests regarding the bactericide properties of oils of thyme and cinnamon, and other oils, as compared with a 1 per cent. solution of mercuric chloride, and he has found that a 7 to 8 per cent. emulsion of cinnamon oil, or an 11 per cent. solution of thyme oil, in washing the hands, has the same sterilising action as the solution of mercuric chloride, without possessing the disagreeable secondary properties of the latter. The most powerful action is obtained with a 9 per cent. emulsion of cinnamon oil, which effects complete sterilisation.

Marx²), in continuation of previous work by Konradi, has examined terpineol, heliotropin, vanillin and other aromatic bodies for the same purpose.

The development of pathogenic germs, such as the spores of anthrax and *Staphylococcus pyogenes aureus,* is arrested by the above-named substances. A 1 per cent. solution of terpineol destroyed *Anthrax* after 1 hour, and in a 10 per cent. solution it had the same effect on *Staphylococcus*; nitrobenzene effected the same result in a 10 per cent. solution only after 24 hours. Specially powerful is the action of terpineol in combination with soft soap. In bacteria-emulsion the above-mentioned substances, — and preferably again terpineol — effect agglutination,

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¹) Pharm. Ztg. **47** (1902), 759.

²) Centralbl. f. Bakteriol. und Parasitenk. **33**, I (1903), 74; according to Chem. Repert. **27** (1903), 28 and Apoth. Ztg. **18** (1903), 7.

the cause of which is attributed to the oily consistency of the substances, which, however, does not seem to come under consideration for the actual destruction. Marx rather thinks that the bactericide action is due to the capacity of the aromatic substances of rendering oxygen active, and supports this view by the observation that terpineol, (either in the substance or in the form of vapour) almost immediately liberates iodine from potassium iodide, an occurence which with heliotropin and vanillin only takes place after several hours. The bactericide action stands, according to its degree, in direct relation to this activating power.

The fate of a number of terpenes and camphors in the animal organism has been further traced[1]) by Hildebrandt[2]) and also by Fromm, Hildebrandt and Clemens[3]). According to the former, carvone yields a combined glycuronic acid, which, on being split up with sulphuric acid, does not yield the solid oxycarvone found by Harries[4]) (or the isomeric diketone formed from the latter), but an oily oxidation-product which could not be further identified. Santalol showed a behaviour which differed completely from the observations hitherto made. It appeared from the analysis of the potassium salt of the combined glycuronic acid, that during the passage through the animal body, the santalol molecule had undergone a decided diminution, as it was proved that the formula belonging to the term split off by acids, was $COOH \cdot C_9H_{16} \cdot OH$. If it is accepted with Hildebrandt, that the carboxyl group is formed by oxidation of a methyl group, it would be possible to express the loss suffered by the santalol molecule, by the splitting off of the group $C_5H_6$. By means of a modified method of examination (precipitation of the alcoholic solution of potassium salt with basic acetate of lead), the author succeeded in proving, for a series of other compounds, such as fenchone, thujone, and others, an oxidation with formation of a carboxylic acid, in addition to the hydration previously observed. With compounds of the so-called "pseudo-class" of terpenes (Semmler), such as for example sabinene and sabinol, only a hydroxylation was observed. Contrary to p-cymene which in the animal body is converted into cumic acid, there was observed with m-cymene the occurrence of a combined glycuronic acid.

A peculiar departure from the regularities hitherto observed was detected with the product of conversion obtained after administration of camphene. On splitting up, a liquid body of the formula $C_{10}H_{16}O$ was obtained, which was at first regarded as an alcohol, and was called

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[1]) Compare Report April **1902,** 84.

[2]) Zeitschrift für physiologische Chemie **36** (1902), 441 and 452.

[3]) Zeitschrift für physiologische Chemie **37** (1903), 189.

[4]) Berliner Berichte **34** (1901), 2105.

"camphenol". On closer examination it was, however, recognised as an aldehyde, and it was found possible to prove its identity with the camphenilanic aldehyde of the melting point 68° to 70°, produced by Bredt and Jagelki[1]) from camphene and chromyl chloride. The remarkable formation of this body is explained in this manner, that camphene adds two hydroxyls, and the camphene glycol formed appears in the urine combined with glycuronic acid, but during the decomposition with acids is again split up, and is converted, with loss of water, in the manner indicated by Bredt, into camphenilanic aldehyde.

The examination carried on by us to ascertain in how far the refractive index of essential oils may be employed for the purpose of judging their quality and purity, a matter to which we referred about a year ago[2]), is now approaching completion. The figures which we have collected on this subject, a material of a fairly voluminous character, will be published in another place; here, we will only state in anticipation, that by this systematic examination we have by no means been converted, and that we quietly remain on the standpoint hitherto occupied. We do not deny that the determination of the indices of refraction of fractions of essential oils may be used with advantage for the detection of adulterations, and we will even supply further proofs in confirmation thereof, but for the rest we adhere to our opinion, that the time-honoured factors for judging the value, such as specific gravity, rotatory power, solubility in alcohol etc., are fully sufficient to distinguish pure oils from adulterated, and good ones from inferior oils.

The use of the iodine-addition as a method for testing essential oils has been repeatedly proposed, but the results obtained by individual investigators have proved beyond doubt that this method is not suitable for the purpose of ascertaining the quality of an essential oil. In spite of this, the method has recently again been rescued from the oblivion into which it had not undeservedly fallen, by Messrs. Sanglé-Ferrière and Cuniasse, who have employed it in the analysis of various preparations of absinthe[3]) for the quantitative estimation of the essential oils therein contained. Now with the view of rendering the use of this formerly-employed method more common, and to adopt it as a general method for ascertaining the quantity of essential oil in liqueurs etc., the authors have determined the iodine-absorbing capacity of a whole number of essential oils which they had previously

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[1]) Liebig's Annalen **310** (1900), 116.

[2]) Report April **1902**, 82.

[3]) Nouvelle méthode d'analyse des absinthes. Paris 1902, publ. by Ch. Dunod. Compare Chem. Centralblatt **1903**. I, 543.

tested for their purity by determining the physical constants and the solubility in alcohol¹). The process which they thereby employed does not differ in any marked degree from that of Hübl, which is in use for the estimation of the iodine number of fatty oils. The accurately-weighed oil was dissolved in 80 per cent. alcohol, and that solution mixed with 15 to 20 cc of an alcoholic solution of iodine and mercuric chloride; after standing for exactly three hours, the excess of iodine was titrated back with deci-normal solution of sodium hyposulphite.

Messrs. Sanglé-Ferrière and Cuniasse, however, are of opinion that the iodine numbers communicated by them can not only be used with advantage for the quantitative estimation of essential oils in liqueurs or generally in alcoholic solutions, but that they can also serve for the identification and detection of adulterations of essential oils.

Assuming that the above-mentioned method really gives uniform values, it is not quite clear how from the iodine number ascertained, the content of essential oil of for example a liqueur can be found, for it is highly questionable whether the essential oil whose presence is suspected by the odour and taste, is the only representative of this class of bodies. It may be predicted with certainty that the results, in the case of mixtures, cannot be very favourable, as the essential oils do not all possess the same capacity of absorbing iodine. If the essential oil is to be estimated according to quantity, it would seem to us that Mann's method described on page 10 of our Report of October 1902, is far more suitable.

L. Balbiano and V. Paolini²) have made use of an oxidising agent which had hitherto been hardly employed at all in the terpene chemistry, viz., mercuric acetate. The experiments made by them differ in so far from those of Tafel³) — who allowed the same compound to act in the heated state in a closed tube on other bodies — that a solution of mercuric acetate at ordinary temperature is allowed to react slowly on hydrocarbons, olefinic phenol ethers, etc. We reproduce here briefly the results obtained by this method. In the oxidation of pinene with a saturated solution of mercuric acetate during 7 to 8 days, there results as reaction-product, an almost colourless, thickish oil whose odour reminds of camphor, of the formula $C_{10}H_{16}O_2$, i. e. a dioxypinene. It has the specific gravity 1,069 (0°) and boils at 5 mm pressure at 145°, at 20 mm at 170° to 171°. Its property of forming on the one hand with hydroxylamine an oxime of the melting point 138,5°, with semicarbazide

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¹) Journn. de pharm. et de chim. VI. **17** (1903), 169.

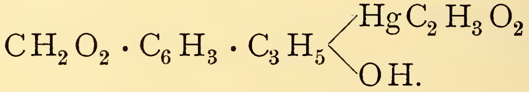
²) Berliner Berichte **35** (1902), 2995.

³) Berliner Berichte **25** (1892) 1619.

a semicarbazone of the melting point 180°, and on the other hand with carbanil a phenyl urethane, proves that it is here a question of a ketonic alcohol. The absorption of 2 atoms bromine shows that the product contains a double linking. Oxidation with permanganate in acid solution converts the dioxypinene into a lactonic acid $C_8H_{12}O_4$ of the melting points 68° to 69° and 89° respectively, which is identic with terpenylic acid.

When anethol is oxidised with mercuric acetate, it yields a glycol $CH_3O \cdot C_6H_4 \cdot C_3H_5(OH)_2$ of the melting point 98°, which chromic acid converts into anisic acid. The diacetyl derivative of the glycol, a thickish oil, boils at 41 mm pressure at 210°.

Whilst isosafrol on treatment with mercuric acetate yields an oxidation product, safrol does not yield one, but, on the other hand, a mercuric compound occurs which is separated out, according to the length of time during which the reagent is allowed to act, either as a syrup, or as a white crystalline body. The authors give the following constitutional formula to it:



$$CH_2O_2 \cdot C_6H_3 \cdot C_3H_5\left\langle\begin{matrix} HgC_2H_3O_2 \\ OH. \end{matrix}\right.$$

In the same manner a mercuric compound is obtained from camphene. As the authors do not give any further particulars of the manner of production or the properties of this body, and do not announce a continuation of their examination, and as we were anxious to render this reaction, if possible, available for the detection of camphene in essential oils, we have occupied ourselves with the examination of this compound. We worked under the same conditions as those given by Balbiano and Paolini for the pinene oxidation. The camphene was dissolved in an equal volume benzene. The separated compound, which was apparently of a crystalline character, was washed with water, alcohol and ether, in which it is insoluble, and was thereby obtained as a pure white, dust-like powder. After unsuccessful attempts to regenerate camphene from it by boiling with water or alkalies, we succeeded in decomposing it with hydrogen sulphide. For this purpose the powder was suspended in water, and hydrogen sulphide introduced into this suspension for 4 to 5 hours, with frequent shaking. From the black compound which was filtered off and washed, a quantity of camphene approximately the same as that employed could be isolated by steam distillation. After recrystallisation from alcohol, the camphene melted at 49° to 50°. Its boiling point was found as 159° to 160°.

The next step was to submit to this reaction an oil which was believed to contain camphene by reason of the isoborneol reaction obtained with it, but from which no camphene as such had as yet been isolated. Up to now it had frequently been necessary to be content with Bertram's isoborneol reaction alone, for the purpose of detecting the presence of camphene in essential oils. But as the occurrence of this reaction might also be due to the presence of a hitherto unknown hydrocarbon, it was desirable to supply the proof by isolating the solid hydrocarbon. We found a welcome subject for examination in the first runnings of Ceylon citronella oil, which, judging from the results obtained with the isoborneol reaction, should contain large quantities of camphene. We used for this purpose the portions passing over between 158° and 162°. The mercuric compound separated off was purified and decomposed in the above-described manner. Strange to say, it was found extremely difficult to isolate the camphene with water vapour from the decomposed compound. We believe that this was solely due to causes of a mechanical nature, for as long as the steam distillation was continued, small quantities of camphene distilled over. Melting and boiling points agreed with those of pure camphene. For further identification we converted the camphene into isoborneol, whose melting point we found at 212°.

## Hydrocarbons.

Pinene. According to the German Patent No. 134553, one of the substances formed by the action of oxalic acid on pinene is camphor. Schindelmeiser¹) has not found this statement confirmed, as chiefly esters of the inactive borneol are obtained.

Camphene. Konowaloff and Kikina²) have obtained nitro-compounds by heating dihydrocamphene and pinene hydrochloride with nitric acid of the specific gravity 1,12. The former yielded chiefly a secondary nitro-body of the melting point 125° to 129°, which on reduction with zinc and hydrochloric acid yielded an amine of the melting point 65° to 130°, and boiling at 194° to 204°. It was more difficult to nitrate pinene hydrochloride; it yielded a mixture of solid (secondary) and liquid (primary and secondary) derivatives. These observations lead to the conclusion, that camphene, camphor, and pinene hydrochloride contain a CH-group, to which no methyl group is attached.

Fenchene. In a long publication which has recently appeared³), J. Kondakow returns to Wallach's explanation of the history of fenchene, mentioned on page 91 of our last year's October Report.

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¹) Journ. d. russ. phys.-chem. Ges. **34** (1902), 954; according to Chem. Centralbl. **1903**, I, 515.

²) Journ. d. russ. phys.-chem. Ges. **34** (1902), 925; according to Chem. Centralbl. **1903**, I, 512.

³) Journ. f. pract. Chemie II. **67** (1903), 94.

In that publication he again claims priority for having accurately defined the constitution of the various hydrocarbons $C_{10}H_{16}$, formed from fenchyl alcohol and fenchyl chloride respectively. He is further of opinion, that, as he had conceived the idea of studying the isomerisation of secondary hydroaromatic alcohols into tertiary, he had also the right to include fenchyl alcohol in the sphere of his examinations, and that therefore there could be no question of an unauthorised invasion of Wallach's sphere of action.

With regard to the remark made by us in the same place, that zinc chloride as a substitute for sulphuric acid in the hydration of hydroaromatic hydrocarbons had been used by Ertschikowsky long before Kondakow, we wish to state, in accordance with a communication made by the latter[1]), that the experiments in question were made by Ertschikowsky at the instigation of Kondakow. For this reason, Ertschikowsky cannot be designated as the one to whom the priority for the use of this method is to be credited.

Phellandrene. According to a previous statement by Pesci, when phellandrene nitrite is reduced with zinc and glacial acetic acid, a diamine boiling at 209° to 215° is formed, which is distinguished by a platinum double salt almost insoluble in water. As Wallach has already established, phellandrene nitrite from eucalyptus oil yields, in addition to non-volatile basic compounds, a base which not only boils 40° to 50° higher than stated by Pesci, but which also shows a totally different behaviour. An examination recently made by Wallach[2]), in which original preparations by Pesci were available for comparison, has now shown that the compounds which Pesci had obtained from the phellandrene of oil of water fennel, differ from those which can be prepared from the phellandrene of Australian eucalyptus oil. This is all the less remarkable, as O. Schreiner[3]) has meanwhile called attention to the fact, that from the phellandrene of eucalyptus oil nitrites of different melting points can be obtained.

If the phellandrene nitrites, obtained on the one hand from eucalyptus phellandrene, and on the other from the phellandrene of water fennel, are reduced according to the method indicated by Pesci, there are obtained from both nitrites diamines which boil at 250°, but which in respect of the formation of salts behave in a totally dissimilar manner. The phellandrene diamine from eucalyptus oil namely yields a difficultly soluble monohydrochloride and a readily soluble platinum double salt; the diamine from oil of water fennel, on the other hand, yields a readily soluble hydrochloride, and a platinum double salt which is

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[1]) Journ. f. pract. Chemie II. **66** (1902), 479.

[2]) Liebig's Annalen **324** (1902), 269.

[3]) Compare Report October **1901**, 61.

difficult to dissolve, and these have the properties ascribed to them by Pesci. With regard to the boiling point of the base, however, Pesci has been in error, for the latter lies at about 260°, i. e. about 50° higher than would be expected from Pesci's statements. But it is correct that, as Pesci mentions, in the reduction of the phellandrene nitrites, in addition to the volatile diamine, also a considerable quantity of a non-volatile base is formed; the latter is still to be submitted to a more detailed examination.

Very welcome contributions to the knowledge of sesquiterpenes and sesquiterpenic alcohols have been supplied by J. Gadamer and T. Amenomiya[1]). These authors examined atractylol, a sesquiterpenic alcohol $C_{15}H_{26}O$ which forms the principal constituent of the essential oil of *Atractylis ovata* Thunbg., and in connection therewith also examined a number of other known sesquiterpenic alcohols and the sesquiterpenes formed therefrom by loss of water.

Atractylol, obtained in the pure state by crystallisation from petroleum ether at a temperature much reduced by means of solid carbon dioxide and ether, possesses a faint odour which when much diluted reminds of lilies of the valley; it melts at 59°, boils at atmospheric pressure without decomposition at 290° to 292°, and is optically inactive. As follows from the behaviour of atractylol towards phenyl isocyanate, and from acylation tests, it must be considered a tertiary alcohol; this view also agrees with the fact that the alcohol, when treated with water-abstracting substances, such as potassium hydrosulphate, is very readily converted into a hydrocarbon $C_{15}H_{24}$ atractylene. When freshly prepared this represents a fairly mobile liquid with a cedar-like odour, boiling point at 10 mm pressure chiefly at 125° to 126°; $d\frac{20^\circ}{15^\circ} = 0{,}9101$, and $n_{D20^\circ} = 1{,}50893$, which when kept polymerises, becomes viscid, and acquires a lemon-like odour. A similar polymerised product is formed when atractylene is produced from atractylene dihydrochloride by boiling with aniline. To the pure non-polymerised hydrocarbon belong two ethylene-linkings, as appears from its behaviour towards bromine and hydriodic acid, whilst the atractylene regenerated from the dihydrochloride represents essentially the polymerised compound, which also differs by its slightly dissimilar physical constants from the hydrocarbon obtained by means of potassium hydrosulphate. An attempt to attach water to atractylene, and to regenerate the alcohol, remained unsuccessful; it was equally impossible to obtain a crystallised nitrosochloride for the purpose of identification.

As already mentioned, the authors, in connection with their examination of atractylol and atractylene, publish communications on

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[1]) Archiv der Pharm. **241** (1903), 22.

çaryophyllene, patchoulene, guajene, and the alcohols belonging thereto, and finally also on oil of carline thistle, but these in the main only confirm already-known facts concerning these compounds.

Of the chemistry of Para caoutchouc little is known. Contrary to other work of older date, Weber¹) held the opinion that caoutchouc represented an aliphatic polyterpene with two double linkings each on one molecule $C_{10}H_{16}$, as he obtained from it tetrahalogen compounds of the formula $(C_{10}H_{16}X_4)_n$. Harries²) supports this view. In the degradation of the caoutchouc molecule he obtained, by means of nitrous acid, under various conditions, nitrosites of a dimolecular terpene, which resembled the nitrosites of dimyrcene, a polymerisation-product of the aliphatic terpene myrcene. The process of reaction appears to be accomplished thus, that first of all nitrosites of a tetraterpene are formed, and on further oxidation diterpene derivatives. In the pyrogenic polymerisation of cyclic terpenes, such as limonene, dipentene, and others, no bodies were obtained which under the same conditions yielded addition-products with $N_2O_3$. Dipentene which is stated to occur in large quantity in the distillation of caoutchouc, but which was only obtained in a yield of about 15 per cent. is, according to Harries, produced by secondary formation from isoprene or the hypothetic diisoprene, and not from caoutchouc direct.

## Alcohols.

For the detection of bodies containing hydroxyl (alcohols, phenols, or oximes) Tschugaeff³) recommends that the substance to be examined be brought into reaction with organic magnesium compounds of the formula $R \cdot Mg \cdot I$, such as $CH_3 \cdot Mg \cdot I$. In the presence of a hydroxyl-group methane is formed according to the equation $CH_3MgI + R \cdot OH = RO \cdot MgI + CH_4$. As these Mg-organic compounds of alcohols etc. are non-volatile, this method can also serve for their separation from volatile indifferent bodies, such as hydrocarbons, as the latter can be distilled off in vacuo.

In the "Archiv für experimentelle Pathologie und Pharmacologie" vol. **48** (1902), 223, E. Erdmann reports more in detail on the pharmacological action of furfur alcohol⁴).

The experiments on animals and on men show that this constituent of essential oil of coffee possesses toxic properties which are not

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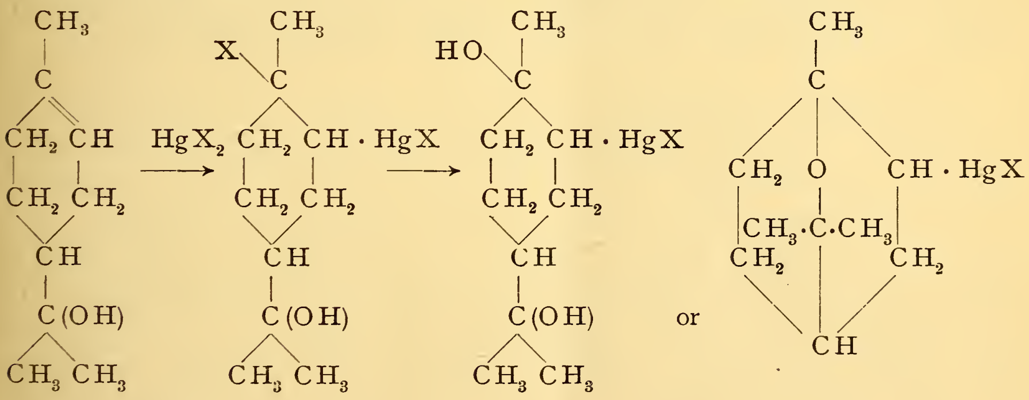
¹) Berliner Berichte **33** (1900), 779; **35** (1902), 1947.
²) Berliner Berichte **35** (1902), 3256; 4429.
³) Chemiker Zeitung **26** (1902), 1043.
⁴) Compare also Report October **1902**, 31.

inconsiderable, and it would therefore appear by no means impossible, that the effects on the respiration and pulsation which occur when coffee is partaken of, must in part be attributed to the presence of furfur alcohol. Further information on the cause of the action of coffee may possibly be obtained from the pharmacological examination of the nitrogenous substance contained in oil of coffee. In apparent contradiction herewith are the statements by K. B. Lehmann and G. Rohrer[1]), who have also occupied themselves with the question of the pharmacological action of distillates from coffee and tea. They confirm by new experiments a previously obtained result, according to which neither the coffee- nor the tea-distillate exerts any action worth mentioning, either temporary or permanent, whatever.

Manasse[2]) has extended the well-known synthesis of aromatic oxyalcohols from phenols and formaldehyde[3]) to a number of other phenols, such as eugenol, thymol, carvacrol and o-oxyquinoline.

Sand and Singer[4]) have recently enlarged the previous work by Hofmann and Sand on the formation of mercuric compounds from unsaturated bodies and mercuric salts, by adding to it terpineol and dimethyl heptenol. They found here also, that salts of mercury $HgX_2$ united in such manner with the double linking, that the group HgX becomes attached to the carbon atom richer in hydrogen; the other attached group X can be readily split off by hydrolysis, and the conversion which takes place is either extra-molecular with substitution by the OH-group, or intra-molecular with loss of water and formation of an oxide-like compound. The following formula of the process of the reaction in the case of terpineol may serve to elucidate this:



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[1]) Archiv für Hygiene **44** (1902), 202; according to Chem. Centr. Blatt **1902**, II, 1067.

[2]) Berliner Berichte **35** (1902), 3844.

[3]) Berliner Berichte **27** (1894), 2409. — German Patent No. 85588.

[4]) Berliner Berichte **35** (1902), 3170.

According to the conditions selected, there are, therefore, obtained the Hg-salts either of cineol, or of two isomeric trans-terpins; by reduction with sodium amalgam or electrolytic hydrogen, trans-terpin of the melting point 156° can be obtained from the latter.

The reaction took place in the same manner when applied to the dimethyl heptenol obtainable from methyl heptenone with $CH_3 \cdot Mg \cdot I$.

Minguin and de Bollemont[1]) have recently continued their work (discussed in our previous Report[2]) on the rotation of the esters of lævo-borneol, and have extended it to the esters of lævo-isoborneol. It was hereby found that the molecular rotatory power only becomes constant from the ester of valerianic acid, a fact which is attributed to the action of the lower acids splitting off water, with formation of inactive camphene, and the esterification of the latter into inactive isobornyl ester. The authors are of opinion that their supposition is confirmed by the fact, that the rotation of the isoborneol obtained from the esters by saponification is only constant in the preparation made from the valerianate, and that the lower homologues always yield isoborneol of constantly decreasing rotatory power. A similar regularity of the rotatory power could not be detected in homologue alkyl esters of camphocarbonic acid, presumably owing to the occurrence of compounds of the isomeric keto- and enol-forms, or of stereomerides.

Substituted glycocollic esters of borneol and menthol have been produced by Einhorn and Jahn[3]) by allowing bases, such as diethylamine and amido camphor, to act on the chloro-acetic acid esters of these alcohols. The diethyl glycocollic ester of menthol may possibly be interesting from a therapeutical point of view, as it forms a readily soluble hydrochloride, and in the organism splits off menthol.

J. Kondakow and J. Schindelmeiser[4]) report on some derivatives of menthol. Like other secondary hydroaromatic alcohols, menthol also yields no uniform body when it is converted into menthyl halogen compounds, but on the contrary forms mixtures of secondary and tertiary compounds, whose quantities vary according to the reagent employed (phosphorus halogen compounds or concentrated acids of hydrohalogen), and to the temperature at which the action thereof takes place. If alcoholic alkali is allowed to act on these mixtures, the tertiary menthyl halogen compounds split off hydrohalogen much more

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[1]) Compt. rend. **136** (1902), 238.

[2]) Report October **1902**, 94.

[3]) Archiv d. Pharm. **240** (1902), 644.

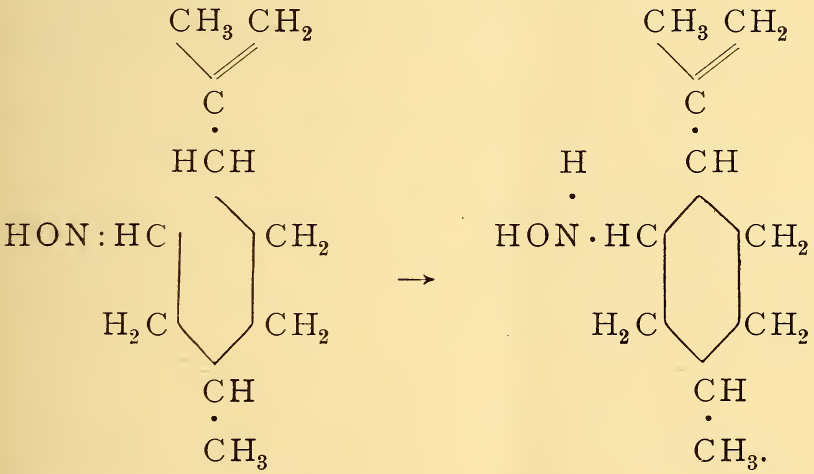
[4]) Journ. f. prakt. Chemie II. **67** (1903), 193.

readily, with formation of hydrocarbon, than the secondary compounds, which are partly again obtained without change.

Kondakow and Schindelmeiser have made a more detailed examination of the menthyl bromide, formed by the action of phosphorus pentabromide or concentrated hydrobromic acid on menthol, and find the above statement confirmed. Of much interest is the observation, that the menthene which is formed from tertiary menthyl bromide, cannot be completely converted by Reychler's process (by the action of trichloro-acetic acid) into tertiary menthol. The small portion of the hydrocarbon which remains unattacked has a somewhat different odour, and also boils higher, than the ordinary menthene; it is possible that it represents a pseudo-menthene.

## Aldehydes.

Citronellal. If citronellal oxime is mixed at a much reduced temperature with several times its weight of about 50 per cent. sulphuric acid, the mixture which is at first clear, becomes cloudy (as F. Mahla[1]) observed) when left standing for several hours, and the acid liquid now contains a base $C_9H_{19}ON$, which is formed from the oxime by formation of a ring with simultaneous displacement of one atom of hydrogen:



The citronellal oxime has consequently changed into a $\Delta^{8(9)}$-oxamino-3-menthene. If sodium nitrite is allowed to act on this base in the presence of oxalic acid in aqueous solution, the one atom of hydrogen of the NH·OH-group is replaced by NO, and a nitroso-oxamino-menthene is obtained as a crystallised compound melting at 52°. Under the influence of heat or dilute acids this compound is readily decomposed with liberation of nitrous oxide $N_2O$, by which there is

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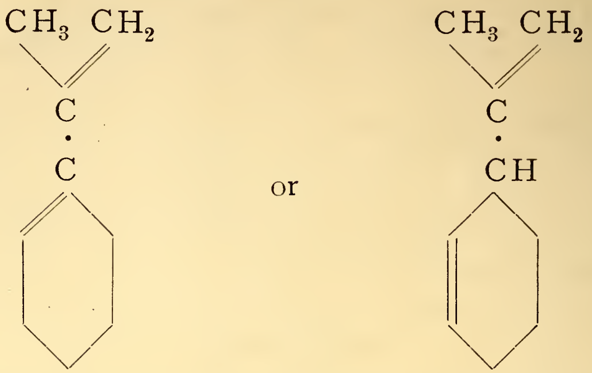
[1]) Berliner Berichte **36** (1903), 484.

formed, in addition to an optically inactive alcohol $C_{10}H_{20}O$ with a terpineol-like odour, a hydrocarbon $C_{10}H_{16}$, which in view of its origin must be considered as $\Delta^{2,\,8(9)}$-, or still more probably as $\Delta^{3,\,8(9)}$-menthadiene:

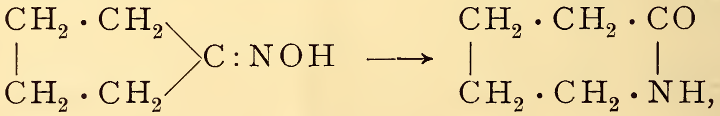


The hydrocarbon is dextrorotatory, like citronellal; it boils at 9 mm pressure between 75° and 80°, and has the specific gravity 0,8491. Its odour is said to remind of anise and star-anise, but at the same time also somewhat of fennel.

## Ketones.

Wallach[1]) has communicated a very interesting treatise on the conversion of cyclic ketones into alkamines and into non-oxygenous bases of nitrogenous cyclic systems.

The same investigator has already shown on a previous occasion, that the oximes of cyclic ketones, on conversion into the so-called isoximes, suffer a molecular rearrangement, with formation of compounds which may be considered as anhydrides of acid amides (lactams), and that in this manner it is possible to arrive partly at already known, and partly at new nitrogenous heterocyclic compounds[2]). Thus pentanone oxime is converted into $\alpha$-piperidone:



$$\begin{matrix} CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2 \end{matrix}\!\!\Big\rangle C:NOH \longrightarrow \begin{matrix} CH_2\cdot CH_2\cdot CO \\ |\qquad\qquad\quad | \\ CH_2\cdot CH_2\cdot NH, \end{matrix}$$

whilst from cyclohexanone and cycloheptanone oximes in a corresponding manner heterocyclic compounds with seven or eight members can be obtained.

These isoximes or lactams are now susceptible to direct reduction, preferably by the application of amyl alcohol and sodium, and it is thereby possible to arrive at non-oxygenous bases of nitrogenous cyclic

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[1]) Liebig's Annalen **324** (1902), 281.

[2]) Compare Report October **1900**, 74.

systems. At the same time, the reaction does not always pass off smoothly and uniformly, for the more the isoxime employed is inclined to ring-disruption (when, as is well known, fatty amido acids are formed), the smaller is the yield of non-oxygenous basic products. But moreover, there occur on reduction also oxygenous bases, i. e. alkamines, and that, in the case of higher cyclic systems, in considerable quantity. Whether with these only the reduction of the $CO$-group into a $CHOH$-group has taken place, or simultaneously also ring-disruption with formation of aliphatic amido alcohols, has not yet been definitely decided for all cases.

But in any case so much is certain, that this reduction supplies a means for obtaining the higher ring-homologues of piperidine, by which the doctrine of the nitrogenous ring-systems is enlarged in a welcome manner. For, next to the already known types tri- and tetramethyleneimine, as also the pentamethyleneimine or piperidine obtainable from $\alpha$-pyrrolidone, there are now also hexamethyleneimine $(CH_2)_6NH$ and heptamethyleneimine $(CH_2)_7NH$, of which the former can be obtained from cyclohexanoneisoxime, and the latter from the isoxime of suberone.

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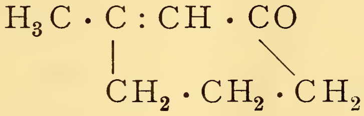
Just as dihydroisophorone or dihydroisophorol can be converted into $\alpha$-cyclogeraniolene and with the help of the latter into trimethyl cyclohexanone[1]), there can also be obtained (as Wallach has recently found[2]) from methyl-1-cyclohexanone-3 from pulegone, a cyclomethyl hexenone, which differs from Knoevenagel's well-known methyl cyclohexenone



either by the position of the ethylene linking, or by that of the carbonyl.

The alcohol formed by reduction from methyl hexanone yields, when heated with zinc chloride, a methyl cyclohexene (tetrahydrotoluene) which, like $\alpha$-cyclogeraniolene, forms a difficultly soluble nitrosate. On being heated with sodium methylate, the latter yields a liquid methyl cyclohexenoneoxime, which can be split up by dilute sulphuric acid. The cyclomethylhexenone thereby formed boils at 179° to 181°, and its semicarbazone melts at 207° to 208°; it therefore certainly differs from the ketone of the above-mentioned constitution.

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As was pointed out some few years ago by Rabe[3]), aceto-acetic ester, under the influence of sodium ethylate, is attached to $\alpha$, $\beta$-unsaturated

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[1]) Compare Report October **1902**, 86.

[2]) Berliner Berichte **35** (1902), 2822. — Nachrichten der Kgl. Ges. d. Wiss. zu Göttingen **1902**, 297.

[3]) Berliner Berichte **31** (1898), 1896.

esters, ketones etc. If the addition-product is saponified and carbon dioxide split off from the acid, there is not formed a 1,5-diketone, as might be expected, but (as was recently proved by Rabe and Weilinger[1]) with the condensation-product from aceto-acetic ester and carvone), an isomeric bicyclic ketone alcohol of the formula $C_{13}H_{20}O_2$, which on reduction with zinc and hydrochloric acid yielded a mixture of two optically active glycols. A product prepared years ago by Goldschmidt and Kisser[2]) by condensation of the above-mentioned bodies with hydrochloric acid, in which the isopropenyl-group of the carvone-rest is saturated with HCl, was also examined by Rabe and Weilinger[3]). They obtained on saponification with potassium hydrate, in addition to eucarvone, a body $C_{13}H_{20}O_2$ which is isomeric and possibly identic with the ketone alcohol mentioned above. When boiled with quinoline the condensation-product split up into acetone, aceto-acetic ester and carvacrol.

The physiological action of camphocarbonic acid and its esters has recently been examined by Gottlieb[4]), in continuation of the previous work by Kobert and Lapin. Whilst camphocarbonic acid itself, and also its salts, do not act on the heart and the nervous system, and pass through the body without change, the esters show in a varying degree of strength the typical spasm-provoking effect of camphor, though not quite so strongly as the latter. The effect of the amyl ester is the most powerful; it was less strong with the ethyl ester, and still weaker with the methyl ester. The physiological activity appears to be proportionate to the electrolytic dissociation of the ester; the strongly dissociated methyl ester has the least powerful action, as contrasted with the strongly acting but little dissociated amyl ester.

## Oxides.

From a trivalent alcohol of the terpene-series there can be formed, by splitting off water, a ketone (as with terpineol), or a double unsaturated alcohol, or an unsaturated oxide. The latter is the case, as Semmler[5]) has just reported, with the trivalent glycerine $C_{10}H_{20}O_3$, which is formed by oxidation in the cold of dihydrocarveol with a solution of potassium permanganate. Wallach[6]) had already allowed sulphuric acid to act on this compound, and had thus obtained a body $C_{10}H_{16}O$, which yielded two nitrogenous derivatives with hydroxylamine.

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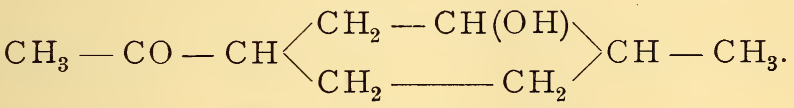
[1]) Berliner Berichte **36** (1903), 225, 227.
[2]) Berliner Berichte **20** (1887), 489.
[3]) Berliner Berichte **36** (1903), 234.
[4]) Berliner Berichte **35** (1902), 3518.
[5]) Berliner Berichte **36** (1903), 764.
[6]) Liebig's Annalen **277** (1893), 151, and **279** (1894), 386.

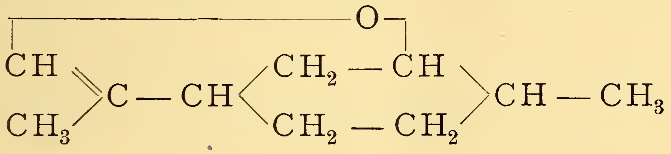
Semmler has taken up the study of these compounds which hitherto had not been examined further, and he has thereby found that the product obtained with sulphuric acid is an oxide, as it is not attacked by potassium and sodium at the boiling temperature. Its constants are: boiling point at 20 mm 95°, specific gravity 0,9647, index of refraction 1,4844, molecular refraction 45,2 (calculated 45,22 for the oxide $C_{10}H_{16}O$ with one double linking).

The dihydrocarvoxide (as the author designated this oxide) yields with bromine a fairly unstable dibromide of the melting point 55°; it is therefore unsaturated. On oxidation with a solution of potassium permanganate, an indifferent body $C_9H_{16}O_2$ is obtained which melts at 58° to 59°, and has the boiling point 144° to 145° (at 13 mm) and the specific gravity 1,0351 (at 20°). This is identic with the alcohol $C_9H_{16}O_2$ of the constitution



which Tiemann and Semmler[1]) had obtained direct from the dihydrocarveol-glycerine by oxidation.

From this the author deduces for the dihydrocarvoxide the formula



The reactions further described also agree with this formula.

If the oxide is submitted to the action of hydroxylamine in alcoholic solution, there is obtained the basic addition-product $C_{10}H_{19}NO_2$ of the melting point 113° to 114°, which dissolves readily in dilute acids, and which is reconverted by the latter with great facility into the oxide.

The hydrochloride of the base melts at 93°, and its benzoyl compound $C_{10}H_{18}NO_2(COC_6H_5)$ at 144°. From the formation of the latter the author concludes that a hydroxyl-group is present.

If the base is heated in a tube for half an hour with alcoholic potassa to 160°, an alcoholic acid $C_{10}H_{18}O_3$ is obtained in addition to nitril. This acid is monobasic, yields with carbanil a urethane, and can be oxidised into the ketonic acid $C_{10}H_{16}O_3$, whose semicarbazone melts at 178° to 179°. If the alcoholic acid is heated with bromine water in a melting tube, an isomeric cumic acid is

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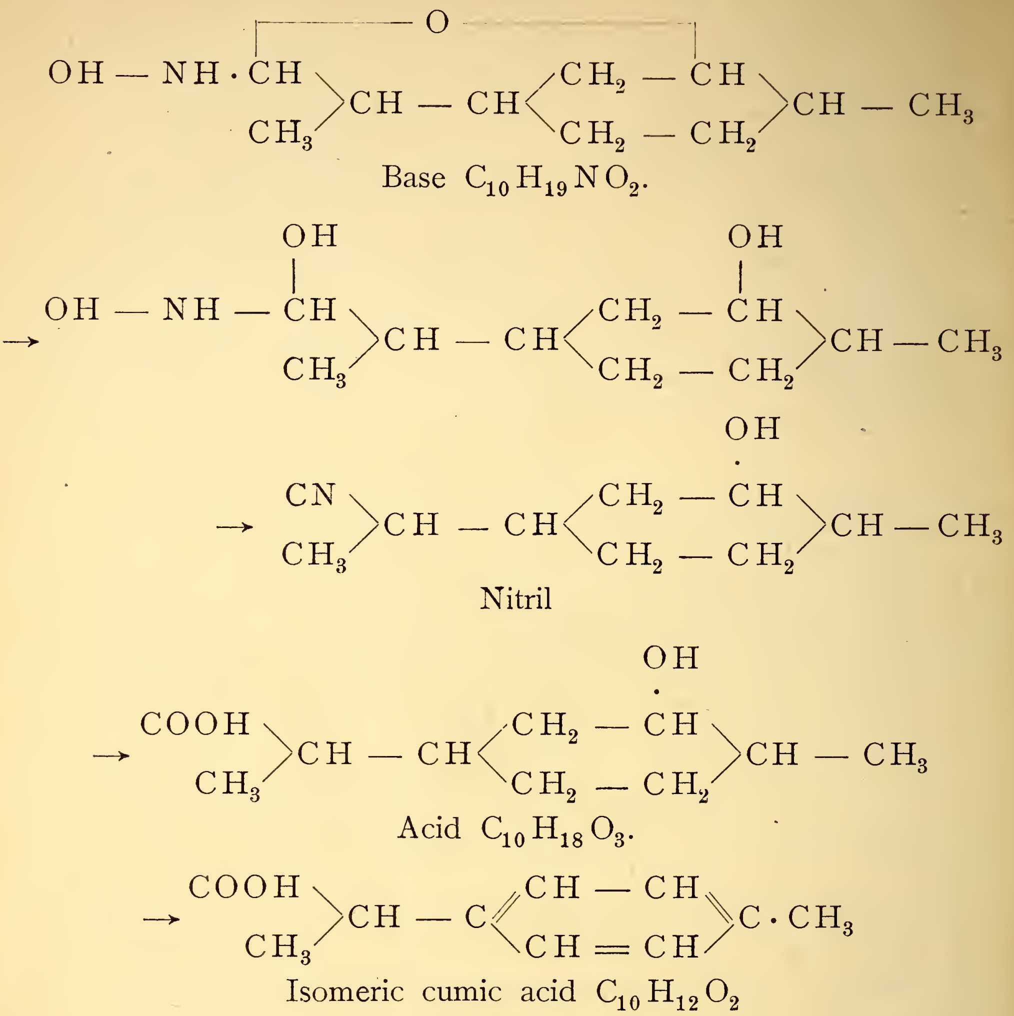
[1]) Berliner Berichte **28** (1895), 241.

formed, which contains the carboxyl-group in the side-chain. The formation of the acid is consequently as follows: —



Base $C_{10}H_{19}NO_2$.

Nitril

Acid $C_{10}H_{18}O_3$.

Isomeric cumic acid $C_{10}H_{12}O_2$

**Borneol** (Borneo camphor). This preparation, which many years ago we were the first to manufacture on a large scale, has gradually conquered an important market in the East, and, in proportion to the larger consumption, could be supplied at lower prices.

We produce it in very large quantities, and are always pleased to consider any special wishes with regard to the size of the crystals.

**Citral.** The prices of this body, which has been discovered by us, move in harmony with those of lemongrass oil; it is very doubtful whether they will ever return to their former level, as the demand for the above-mentioned crude material is not proportionate to the limited production, and offers have now been totally absent for some time.

There is, however, a prospect of fresh sources of supply being opened up, and a first consignment from that quarter has reached us some little time ago.

**Coumarin.** It seems as if the prices had now reached the lowest level, and that there is no inclination to cut the value still further. Those manufacturers who had looked for mountains of gold from this article, have probably committed a great error in estimating the turnover. Being at their wits' end, they now endeavour with American support to bring stability in the quotations.

Since the completion of our new factories we manufacture this article of the well-known exquisite quality on the largest scale.

**Eugenol.** The extensive manufacture of this preparation has been specially taken into consideration in our new premises. The price depends upon the quotations of cloves from time to time in force, and for this reason special arrangements will be made for contracts for large quantities.

**Geraniol.** With our vast installations we are in a position to supply a perfectly pure article in any quantity. The consumption would probably acquire larger dimensions if by chance the Indian geranium oil (palmarosa oil) were not now so cheap; this oil, as is well known, consists chiefly of geraniol, of which it contains 76 to 93 per cent.

**Mignonette (Reseda)-geraniol.** The demand for this interesting product has been so brisk, that our stock will hardly last until the new mignonette-harvest, which is gathered in August. We would earnestly request that any requirements may be specified without delay, so that the necessary quantities may be reserved.

**Heliotropin.** The situation has so far grown worse, that a manufacturer, whose chief merit is the ruination of this article, is unable to dispose of his stock, and now hawks it about at any price. The consumption of heliotropin has also been greatly overrated, and a senseless overproduction has taken place which now has an all the more depressing effect, as the sale of such perfumes cannot be forced, even at the cheapest prices.

At one time heliotropin was often considered poisonous. But, as will be seen from the communications in the Appendix to the present Report, piperonal is in man physiologically inactive. Its harmless character is proved by a case in which a chemist, for the purpose of suicide, took a dose of 50 cc of a concentrated alcoholic solution of piperonal (i. e. about 10 g piperonal). His condition was in no way affected even by this enormous dose.

On animals the effect is different. We would specially refer to the surprising results obtained in this connection which are quoted on pages 135 and 136.

**Menthol.** This article has also been carried along by the general upward movement of peppermint oil, and has been driven up to a level which has not been known for years. For crude Japanese crystals the movement was as follows: —

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Cheapest | quotation | in | July | 1902, | about | 12/- | per | lb. |
| average | ,, | ,, | August | ,, | ,, | 14/6 | ,, | ,, |
| ,, | ,, | ,, | September | ,, | ,, | 15/6 | ,, | ,, |
| ,, | ,, | ,, | October | ,, | ,, | 17/6 | ,, | ,, |
| ,, | ,, | ,, | November | ,, | ,, | 24/- | ,, | ,, |
| ,, | ,, | ,, | December | ,, | ,, | 25/- | ,, | ,, |
| ,, | ,, | ,, | January | 1903 | ,, | 24/- | ,, | ,, |
| ,, | ,, | ,, | February | ,, | ,, | 22/- | ,, | ,, |

These prices are no doubt high, but they are not by any means the highest which have ever been quoted, as many people believe. In 1883 crude menthol was quoted as high as 37/- per lb.

The upward movement has partly been caused by the numerous sales in blanc which were made in June and July for forward delivery, and for which in October to December either cover had to be found at high prices, or else large differences had to be paid.

In view of the constantly growing consumption of menthol for all kinds of toilet-preparations and pharmaceutical remedies, a decline of the prices to a very low level is no doubt out of the question; but it may be found impossible to maintain the present prices, which are still high, and we cannot recommend them for larger contracts for forward delivery.

The shipments of Japanese crude menthol from Japan since 1st August 1902 were: —

| | | | |
|---|---|---|---|
| To | Hongkong | 6900 | catties |
| ,, | San Francisco | 6120 | ,, |
| ,, | Hamburg | 4820 | ,, |
| ,, | London | 3510 | ,, |
| ,, | New York | 1845 | ,, |
| ,, | Seattle | 1575 | ,, |
| ,, | Tacoma | 1125 | ,, |
| ,, | Victoria | 450 | ,, |
| ,, | Havre | 135 | ,, |
| ,, | Bombay | 85 | ,, |
| ,, | Madras | 37 | ,, |
| ,, | Singapore | 30 | ,, |
| | Total | 26632 | catties, |
| | or about | 16000 | kilos. |

The high prices have brought many old speculative stocks to the light in Europe, which were frequently sold below the market-price.

On account of the slight solubility of menthol and peppermint oil in water, it is often necessary to have recourse to high-priced alcoholic solutions. Dr. Crésantignes[1]) therefore proposes to dissolve menthol first in tincture of quillaia, and to add this solution to the water in small portions. It is stated that in this manner clear and permanent menthol-mixtures can be obtained, for example: —

| | |
|---|---|
| Menthol. . . . . . . | 0,15 to 0,3 g |
| Tinct. quillaiae . . . . . . | 10,0 „ |
| Aq. qu. s. ad . . . . . . . . | 150,0 cc. |

The following prescription is given for a mouth-wash: —

| | |
|---|---|
| Menthol. . . . . . . | 0,1 to 0,2 g |
| Tinct. quillaiae . . . . . . | 20,0 „ |
| Solut. acid. boric. 1 per cent. | 1000,0 „ |

For internal use the mixtures may perhaps not be suitable, on account of the toxic properties of the quillaia-tincture.

**Safrol.** Nothing can as yet be noticed of the competition of the Japanese product, which some while ago was announced with such a great flourish; it appears that wise counsels have prevailed, and that the enterprise has been abandoned during the last few months, rather than let it come to a fiasco. The article is of too little importance than that its production, carried on as a separate industry, could be made remunerative. We push this article, and meet every competition where it is a question of a product of equal value.

**Amyl ester of Salicylic acid.** This preparation, of which we have taken up the manufacture some time ago, has found a large and varied application in the perfumery-industry. Lately it has also come into use for therapeutic purposes[2]). According to Doyen and Chanoz the ester is only slightly poisonous, and splits up in the liver into amyl alcohol and salicylic acid. Lyonett dressed rheumatic affections with 2 to 3 g of the ester, by means of cotton-wool and gutta-percha tissue. No inflammation was ever observed. He always found afterwards that the pain and swelling had abated, but never that the remedy was not tolerated. Salicylic acid can within a short time be detected in the urine. When administered internally good results are also obtained.

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[1]) Rep. de Pharm. **1903**, Nr. 1. According to Pharm. Ztg. **48** (1903), 78.

[2]) According to Pharm. Centralhalle **43** (1902), 637.

**Santalol.** This product, which, as is well known, was first introduced into commerce by us, finds a fairly large application, but it is already sold at prices which are directly unremunerative if the manufacture is carried on with care.

**Terpineol.** The enormous prices of American oil of turpentine have caused a hardening of the quotations of terpineol. In Austria the import-duty for this product has been raised to 1/6 d. per kilo, and as a consequence we now manufacture it at our Bodenbach works.

**Thymol.** The ridiculously cheap quotations of this article do not call for comment in order to characterise the situation which in this case also has been brought about by overproduction. At the same time, the price of the crude material is not correspondingly lower, and especially during the last few months rather firmer.

The following statistics show that the prices of thymol have never been as low as at this moment.

We quoted: —

on 1st April 1894: 18 marks per kilo
" " " 1895: 18 " " "
" " " 1896: 14 " " "
" " " 1897: 13,50 " " "
" " " 1898: 13,50 " " "
" " " 1899: 16 " " "
" " " 1900: 19 " " "
" " " 1901: 22 " " "
" " " 1902: 16 " " "
" " " 1903: 13 " " "

The prices of ajowan-seed (from which thymol is produced) usually depend on the sanitary conditions in the producing country, British India. They were always highest during epidemics of bubonic plague and cholera. If this factor is taken into account, the hygienic condition in India should at present be normal.

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Battandier1) reports on a new occurrence of thymol. He found that the essential oil of a plant which grows in the mountainous region of Algeria, *Origanum floribundum* Munby (*O. cinereum* de Nöe), when extracted with alkali, yields one-fourth of its volume to the latter. The separated phenol crystallises almost completely when a thymol crystal is brought into contact with it, and consequently consists chiefly of

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1) Journ. de pharm. et de chim. VI. **16** (1902), 536.

thymol; the small remnant of the oil which remains liquid appears to be carvacrol.

For practical purposes this new source of thymol is of no consequence, as the plant, although it is very rich in oil, is not found in large quantities.

**Vanillin.** The fall in the prices has made further progress since our last Report, in consequence of an increase in the production beyond all measure. There is no sensible reason for such far-going price-cutting, as it can only have the effect of bringing the article into bad repute. Unfortunately a certain doubt, that it may injuriously affect the quality, is not unwarranted, for products are met with in commerce, which in working up exhibit striking deviations from normal vanillin, and which have led to unpleasant experiences.

For this reason it is a bad plan to consider only the price when purchasing this article; on the contrary, the reliability of the manufacturer should first of all be taken into consideration. These inferior qualities are not always adulterated; they rather suffer from technical defects, which may possibly be due to a certain lack of cleanliness and care in the manufacture, or perhaps to the use of inferior solvents in the crystallisation. For the rest, according to human foresight the lowest selling price has probably now been reached, and the time may be near when the production of vanillin will be abandoned by many manufacturers as unremunerative.

**Schimmel & Co.**

In connection with the table for calculating from the ester numbers the percentages of alcohols of the formulæ $C_{10}H_{18}O$ and $C_{10}H_{20}O$, and of the acetates belonging thereto, which we published in our Report of October 1897, we have now drawn up a similar table for the alcohols $C_{15}H_{24}O$ (santalol) and $C_{15}H_{26}O$.

We have also provided a table for the calculation of geranyl tiglinate from the ester number, as in the case of geranium oils the ester-content is usually calculated on tiglinic acid.

With regard to the formulæ employed for the calculation, and to the use of the tables, we would refer to what we stated in the abovementioned Report, and also to the statements made by Gildemeister and Hoffmann in their work 'The Volatile Oils'¹).

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¹) page 202.

| | $C_{15}H_{24}O$ | | | $C_{15}H_{26}O$ | | | |
|---|---|---|---|---|---|---|---|
| Ester number | % Acetate | % Alcohol | % Alcohol in the orig. oil | % Acetate | % Alcohol | % Alcohol in the orig. oil | Ester number |
| 1 | 0,47 | 0,39 | 0,39 | 0,47 | 0,40 | 0,40 | 1 |
| 2 | 0,94 | 0,79 | 0,79 | 0,94 | 0,79 | 0,79 | 2 |
| 3 | 1,40 | 1,18 | 1,18 | 1,41 | 1,19 | 1,19 | 3 |
| 4 | 1,87 | 1,57 | 1,58 | 1,89 | 1,59 | 1,59 | 4 |
| 5 | 2,34 | 1,96 | 1,97 | 2,36 | 1,98 | 1,99 | 5 |
| 6 | 2,81 | 2,36 | 2,37 | 2,83 | 2,38 | 2,39 | 6 |
| 7 | 3,28 | 2,75 | 2,76 | 3,30 | 2,78 | 2,79 | 7 |
| 8 | 3,74 | 3,14 | 3,16 | 3,77 | 3,17 | 3,19 | 8 |
| 9 | 4,21 | 3,53 | 3,56 | 4,24 | 3,57 | 3,59 | 9 |
| 10 | 4,68 | 3,93 | 3,96 | 4,71 | 3,96 | 3,99 | 10 |
| 11 | 5,15 | 4,32 | 4,36 | 5,19 | 4,36 | 4,40 | 11 |
| 12 | 5,61 | 4,71 | 4,76 | 5,66 | 4,76 | 4,80 | 12 |
| 13 | 6,08 | 5,11 | 5,16 | 6,13 | 5,15 | 5,20 | 13 |
| 14 | 6,55 | 5,50 | 5,56 | 6,60 | 5,55 | 5,61 | 14 |
| 15 | 7,02 | 5,89 | 5,96 | 7,07 | 5,95 | 6,01 | 15 |
| 16 | 7,49 | 6,29 | 6,36 | 7,54 | 6,34 | 6,42 | 16 |
| 17 | 7,95 | 6,68 | 6,77 | 8,01 | 6,74 | 6,83 | 17 |
| 18 | 8,42 | 7,07 | 7,17 | 8,49 | 7,14 | 7,23 | 18 |
| 19 | 8,89 | 7,46 | 7,57 | 8,96 | 7,53 | 7,64 | 19 |
| 20 | 9,36 | 7,86 | 7,98 | 9,43 | 7,93 | 8,05 | 20 |
| 21 | 9,83 | 8,25 | 8,38 | 9,90 | 8,33 | 8,46 | 21 |
| 22 | 10,29 | 8,64 | 8,79 | 10,37 | 8,72 | 8,87 | 22 |
| 23 | 10,76 | 9,03 | 9,19 | 10,84 | 9,12 | 9,28 | 23 |
| 24 | 11,23 | 9,42 | 9,60 | 11,31 | 9,51 | 9,69 | 24 |
| 25 | 11,70 | 9,82 | 10,01 | 11,79 | 9,91 | 10,10 | 25 |
| 26 | 12,16 | 10,21 | 10,42 | 12,26 | 10,30 | 10,51 | 26 |
| 27 | 12,63 | 10,60 | 10,83 | 12,73 | 10,70 | 10,92 | 27 |
| 28 | 13,10 | 11,00 | 11,24 | 13,20 | 11,10 | 11,34 | 28 |
| 29 | 13,57 | 11,39 | 11,65 | 13,67 | 11,49 | 11,75 | 29 |
| 30 | 14,04 | 11,79 | 12,06 | 14,14 | 11,89 | 12,17 | 30 |
| 31 | 14,51 | 12,18 | 12,47 | 14,61 | 12,28 | 12,58 | 31 |
| 32 | 14,98 | 12,57 | 12,88 | 15,08 | 12,68 | 13,00 | 32 |
| 33 | 15,45 | 12,96 | 13,29 | 15,55 | 13,08 | 13,41 | 33 |
| 34 | 15,91 | 13,35 | 13,71 | 16,02 | 13,48 | 13,83 | 34 |
| 35 | 16,38 | 13,75 | 14,12 | 16,50 | 13,88 | 14,25 | 35 |
| 36 | 16,85 | 14,14 | 14,54 | 16,97 | 14,27 | 14,67 | 36 |
| 37 | 17,32 | 14,54 | 14,95 | 17,44 | 14,76 | 15,09 | 37 |
| 38 | 17,79 | 14,93 | 15,37 | 17,91 | 15,06 | 15,51 | 38 |
| 39 | 18,25 | 15,32 | 15,78 | 18,38 | 15,46 | 15,93 | 39 |
| 40 | 18,71 | 15,71 | 16,20 | 18,86 | 15,86 | 16,35 | 40 |

| $C_{15}H_{24}O$ | | | | $C_{15}H_{26}O$ | | | |
|---|---|---|---|---|---|---|---|
| Ester number | % Acetate | % Alcohol | % Alcohol in the orig. oil | % Acetate | % Alcohol | % Alcohol in the orig. oil | Ester number |
| 41 | 19,18 | 16,10 | 16,62 | 19,33 | 16,25 | 16,77 | 41 |
| 42 | 19,65 | 16,50 | 17,04 | 19,80 | 16,65 | 17,19 | 42 |
| 43 | 20,12 | 16,89 | 17,46 | 20,27 | 17,05 | 17,61 | 43 |
| 44 | 20,59 | 17,28 | 17,88 | 20,74 | 17,44 | 18,04 | 44 |
| 45 | 21,05 | 17,68 | 18,30 | 21,21 | 17,84 | 18,46 | 45 |
| 46 | 21,52 | 18,07 | 18,72 | 21,69 | 18,24 | 18,89 | 46 |
| 47 | 21,99 | 18,46 | 19,14 | 22,16 | 18,63 | 19,32 | 47 |
| 48 | 22,46 | 18,85 | 19,56 | 22,63 | 19,03 | 19,74 | 48 |
| 49 | 22,93 | 19,25 | 19,98 | 23,10 | 19,43 | 20,17 | 49 |
| 50 | 23,39 | 19,64 | 20,41 | 23,57 | 19,82 | 20,59 | 50 |
| 51 | 23,86 | 20,03 | 20,83 | 24,04 | 20,22 | 21,02 | 51 |
| 52 | 24,33 | 20,42 | 21,26 | 24,51 | 20,62 | 21,45 | 52 |
| 53 | 24,80 | 20,82 | 21,68 | 24,99 | 21,01 | 21,88 | 53 |
| 54 | 25,26 | 21,21 | 22,11 | 25,46 | 21,41 | 22,31 | 54 |
| 55 | 25,73 | 21,60 | 22,54 | 25,93 | 21,81 | 22,74 | 55 |
| 56 | 26,20 | 22,00 | 22,96 | 26,40 | 22,20 | 23,17 | 56 |
| 57 | 26,67 | 22,39 | 23,39 | 26,87 | 22,60 | 23,61 | 57 |
| 58 | 27,14 | 22,78 | 23,82 | 27,34 | 23,00 | 24,04 | 58 |
| 59 | 27,61 | 23,17 | 24,25 | 27,81 | 23,39 | 24,47 | 59 |
| 60 | 28,07 | 23,57 | 24,68 | 28,29 | 23,79 | 24,91 | 60 |
| 61 | 28,54 | 23,96 | 25,11 | 28,76 | 24,19 | 25,34 | 61 |
| 62 | 29,01 | 24,35 | 25,54 | 29,23 | 24,58 | 25,77 | 62 |
| 63 | 29,48 | 24,75 | 25,97 | 29,70 | 24,98 | 26,21 | 63 |
| 64 | 29,95 | 25,14 | 26,41 | 30,17 | 25,38 | 26,65 | 64 |
| 65 | 30,41 | 25,53 | 26,84 | 30,64 | 25,77 | 27,09 | 65 |
| 66 | 30,88 | 25,93 | 27,27 | 31,11 | 26,17 | 27,53 | 66 |
| 67 | 31,35 | 26,32 | 27,71 | 31,59 | 26,57 | 27,97 | 67 |
| 68 | 31,81 | 26,71 | 28,14 | 32,06 | 26,96 | 28,41 | 68 |
| 69 | 32,28 | 27,10 | 28,58 | 32,53 | 27,35 | 28,85 | 69 |
| 70 | 32,75 | 27,50 | 29,02 | 33,00 | 27,75 | 29,29 | 70 |
| 71 | 33,22 | 27,89 | 29,46 | 33,47 | 28,15 | 29,73 | 71 |
| 72 | 33,69 | 28,28 | 29,90 | 33,94 | 28,54 | 30,17 | 72 |
| 73 | 34,15 | 28,67 | 30,34 | 34,41 | 28,94 | 30,61 | 73 |
| 74 | 34,62 | 29,07 | 30,78 | 34,89 | 29,34 | 31,06 | 74 |
| 75 | 35,09 | 29,46 | 31,22 | 35,36 | 29,73 | 31,50 | 75 |
| 76 | 35,56 | 29,85 | 31,66 | 35,83 | 30,13 | 31,95 | 76 |
| 77 | 36,03 | 30,25 | 32,10 | 36,30 | 30,53 | 32,40 | 77 |
| 78 | 36,49 | 30,64 | 32,54 | 36,77 | 30,92 | 32,84 | 78 |
| 79 | 36,96 | 31,03 | 32,98 | 37,24 | 31,31 | 33,29 | 79 |
| 80 | 37,43 | 31,43 | 33,43 | 37,71 | 31,71 | 33,74 | 80 |

| $C_{15} H_{24} O$ | | | | $C_{15} H_{26} O$ | | | |
|---|---|---|---|---|---|---|---|
| Ester number | % Acetate | % Alcohol | % Alcohol in the orig. oil | % Acetate | % Alcohol | % Alcohol in the orig. oil | Ester number |
| 81 | 37,90 | 31,82 | 33,87 | 38,19 | 32,11 | 34,19 | 81 |
| 82 | 38,37 | 32,21 | 34,32 | 38,66 | 32,50 | 34,64 | 82 |
| 83 | 38,84 | 32,60 | 34,77 | 39,13 | 32,90 | 35,09 | 83 |
| 84 | 39,30 | 33,00 | 35,22 | 39,60 | 33,30 | 35,54 | 84 |
| 85 | 39,77 | 33,39 | 35,66 | 40,07 | 33,69 | 35,99 | 85 |
| 86 | 40,24 | 33,78 | 36,11 | 40,54 | 34,09 | 36,44 | 86 |
| 87 | 40,70 | 34,18 | 36,56 | 41,01 | 34,49 | 36,90 | 87 |
| 88 | 41,17 | 34,57 | 37,01 | 41,49 | 34,88 | 37,35 | 88 |
| 89 | 41,64 | 34,96 | 37,46 | 41,96 | 35,28 | 37,80 | 89 |
| 90 | 42,11 | 35,36 | 37,92 | 42,43 | 35,68 | 38,26 | 90 |
| 91 | 42,57 | 35,75 | 38,37 | 42,90 | 36,08 | 38,71 | 91 |
| 92 | 43,04 | 36,14 | 38,82 | 43,37 | 36,47 | 39,17 | 92 |
| 93 | 43,51 | 36,53 | 39,27 | 43,84 | 36,87 | 39,63 | 93 |
| 94 | 43,98 | 36,92 | 39,73 | 44,31 | 37,26 | 40,09 | 94 |
| 95 | 44,45 | 37,32 | 40,18 | 44,79 | 37,66 | 40,55 | 95 |
| 96 | 44,92 | 37,71 | 40,64 | 45,26 | 38,05 | 41,01 | 96 |
| 97 | 45,39 | 38,10 | 41,10 | 45,73 | 38,45 | 41,47 | 97 |
| 98 | 45,85 | 38,50 | 41,55 | 46,20 | 38,85 | 41,93 | 98 |
| 99 | 46,32 | 38,89 | 42,01 | 46,67 | 39,24 | 42,39 | 99 |
| 100 | 46,79 | 39,29 | 42,47 | 47,14 | 39,64 | 42,86 | 100 |
| 101 | 47,26 | 39,68 | 42,93 | 47,61 | 40,04 | 43,32 | 101 |
| 102 | 47,72 | 40,07 | 43,39 | 48,09 | 40,43 | 43,78 | 102 |
| 103 | 48,19 | 40,46 | 43,85 | 48,56 | 40,83 | 44,24 | 103 |
| 104 | 48,66 | 40,85 | 44,32 | 49,03 | 41,23 | 44,71 | 104 |
| 105 | 49,13 | 41,25 | 44,78 | 49,50 | 41,63 | 45,18 | 105 |
| 106 | 49,59 | 41,64 | 45,24 | 49,97 | 42,02 | 45,65 | 106 |
| 107 | 50,06 | 42,04 | 45,70 | 50,44 | 42,42 | 46,12 | 107 |
| 108 | 50,53 | 42,43 | 46,16 | 50,91 | 42,81 | 46,59 | 108 |
| 109 | 51,00 | 42,82 | 46,63 | 51,39 | 43,21 | 47,06 | 109 |
| 110 | 51,46 | 43,21 | 47,10 | 51,86 | 43,61 | 47,53 | 110 |
| 111 | 51,93 | 43,60 | 47,57 | 52,33 | 44,00 | 48,00 | 111 |
| 112 | 52,40 | 44,00 | 48,04 | 52,80 | 44,40 | 48,47 | 112 |
| 113 | 52,87 | 44,39 | 48,50 | 53,27 | 44,80 | 48,94 | 113 |
| 114 | 53,34 | 44,78 | 48,97 | 53,74 | 45,19 | 49,42 | 114 |
| 115 | 53,81 | 45,17 | 49,44 | 54,21 | 45,59 | 49,89 | 115 |
| 116 | 54,28 | 45,57 | 49,91 | 54,69 | 45,99 | 50,36 | 116 |
| 117 | 54,74 | 45,96 | 50,39 | 55,16 | 46,38 | 50,84 | 117 |
| 118 | 55,21 | 46,35 | 50,86 | 55,63 | 46,78 | 51,32 | 118 |
| 119 | 55,68 | 46,74 | 51,33 | 56,10 | 47,18 | 51,80 | 119 |
| 120 | 56,14 | 47,14 | 51,81 | 56,57 | 47,57 | 52,28 | 120 |

| $C_{15}H_{24}O$ | | | | $C_{15}H_{26}O$ | | | |
|---|---|---|---|---|---|---|---|
| Ester number | % Acetate | % Alcohol | % Alcohol in the orig. oil | % Acetate | % Alcohol | % Alcohol in the orig. oil | Ester number |
| 121 | 56,61 | 47,53 | 52,28 | 57,04 | 47,97 | 52,76 | 121 |
| 122 | 57,08 | 47,92 | 52,76 | 57,51 | 48,36 | 53,24 | 122 |
| 123 | 57,55 | 48,32 | 53,23 | 57,99 | 48,76 | 53,72 | 123 |
| 124 | 58,01 | 48,71 | 53,71 | 58,46 | 49,16 | 54,20 | 124 |
| 125 | 58,48 | 49,10 | 54,18 | 58,93 | 49,55 | 54,68 | 125 |
| 126 | 58,95 | 49,50 | 54,66 | 59,40 | 49,95 | 55,17 | 126 |
| 127 | 59,42 | 49,89 | 55,14 | 59,87 | 50,35 | 55,65 | 127 |
| 128 | 59,89 | 50,28 | 55,62 | 60,34 | 50,74 | 56,13 | 128 |
| 129 | 60,36 | 50,67 | 56,11 | 60,81 | 51,14 | 56,62 | 129 |
| 130 | 60,82 | 51,07 | 56,59 | 61,28 | 51,54 | 57,10 | 130 |
| 131 | 61,29 | 51,46 | 57,07 | 61,75 | 51,93 | 57,59 | 131 |
| 132 | 61,76 | 51,85 | 57,55 | 62,22 | 52,33 | 58,08 | 132 |
| 133 | 62,23 | 52,25 | 58,03 | 62,70 | 52,73 | 58,57 | 133 |
| 134 | 62,70 | 52,64 | 58,52 | 63,17 | 53,12 | 59,06 | 134 |
| 135 | 63,16 | 53,03 | 59,00 | 63,64 | 53,52 | 59,55 | 135 |
| 136 | 63,63 | 53,42 | 59,49 | 64,11 | 53,92 | 60,04 | 136 |
| 137 | 64,10 | 53,82 | 59,98 | 64,59 | 54,31 | 60,53 | 137 |
| 138 | 64,57 | 54,21 | 60,47 | 65,06 | 54,71 | 61,02 | 138 |
| 139 | 65,04 | 54,60 | 60,96 | 65,53 | 55,11 | 61,51 | 139 |
| 140 | 65,50 | 55,00 | 61,45 | 66,00 | 55,50 | 62,01 | 140 |
| 141 | 65,97 | 55,39 | 61,94 | 66,47 | 55,90 | 62,50 | 141 |
| 142 | 66,44 | 55,78 | 62,43 | 66,94 | 56,30 | 63,00 | 142 |
| 143 | 66,90 | 56,18 | 62,93 | 67,41 | 56,69 | 63,50 | 143 |
| 144 | 67,37 | 56,57 | 63,42 | 67,89 | 57,09 | 64,00 | 144 |
| 145 | 67,84 | 56,96 | 63,92 | 68,36 | 57,49 | 64,50 | 145 |
| 146 | 68,31 | 57,35 | 64,41 | 68,83 | 57,88 | 65,00 | 146 |
| 147 | 68,78 | 57,75 | 64,91 | 69,30 | 58,28 | 65,50 | 147 |
| 148 | 69,25 | 58,14 | 65,40 | 69,77 | 58,68 | 66,00 | 148 |
| 149 | 69,72 | 58,53 | 65,90 | 70,24 | 59,07 | 66,50 | 149 |
| 150 | 70,18 | 58,93 | 66,40 | 70,71 | 59,46 | 67,00 | 150 |
| 151 | 70,65 | 59,32 | 66,90 | 71,19 | 59,86 | 67,51 | 151 |
| 152 | 71,12 | 59,71 | 67,40 | 71,66 | 60,26 | 68,01 | 152 |
| 153 | 71,58 | 60,10 | 67,90 | 72,13 | 60,65 | 68,52 | 153 |
| 154 | 72,05 | 60,50 | 68,40 | 72,60 | 61,05 | 69,02 | 154 |
| 155 | 72,52 | 60,89 | 68,90 | 73,07 | 61,45 | 69,53 | 155 |
| 156 | 72,99 | 61,28 | 69,41 | 73,54 | 61,84 | 70,04 | 156 |
| 157 | 73,46 | 61,68 | 69,91 | 74,01 | 62,24 | 70,55 | 157 |
| 158 | 73,92 | 62,07 | 70,42 | 74,49 | 62,64 | 71,06 | 158 |
| 159 | 74,39 | 62,46 | 70,92 | 74,96 | 63,03 | 71,57 | 159 |
| 160 | 74,86 | 62,86 | 71,43 | 75,43 | 63,43 | 72,08 | 160 |

| | $C_{15}H_{24}O$ | | | $C_{15}H_{26}O$ | | | |
|---|---|---|---|---|---|---|---|
| Ester number | % Acetate | % Alcohol | % Alcohol in the orig. oil | % Acetate | % Alcohol | % Alcohol in the orig. oil | Ester number |
| 161 | 75,33 | 63,25 | 71,93 | 75,90 | 63,83 | 72,59 | 161 |
| 162 | 75,80 | 63,64 | 72,44 | 76,37 | 64,22 | 73,10 | 162 |
| 163 | 76,26 | 64,03 | 72,95 | 76,84 | 64,62 | 73,62 | 163 |
| 164 | 76,73 | 64,42 | 73,46 | 77,31 | 65,02 | 74,13 | 164 |
| 165 | 77,20 | 64,82 | 73,97 | 77,78 | 65,41 | 74,65 | 165 |
| 166 | 77,67 | 65,21 | 74,49 | 78,26 | 65,81 | 75,16 | 166 |
| 167 | 78,14 | 65,60 | 75,00 | 78,73 | 66,21 | 75,68 | 167 |
| 168 | 78,60 | 66,00 | 75,52 | 79,20 | 66,60 | 76,20 | 168 |
| 169 | 79,07 | 66,39 | 76,03 | 79,67 | 67,00 | 76,72 | 169 |
| 170 | 79,54 | 66,79 | 76,55 | 80,14 | 67,39 | 77,24 | 170 |
| 171 | 80,01 | 67,18 | 77,06 | 80,61 | 67,79 | 77,76 | 171 |
| 172 | 80,48 | 67,57 | 77,58 | 81,08 | 68,19 | 78,28 | 172 |
| 173 | 80,94 | 67,96 | 78,10 | 81,56 | 68,58 | 78,81 | 173 |
| 174 | 81,41 | 68,35 | 78,62 | 82,03 | 68,98 | 79,33 | 174 |
| 175 | 81,88 | 68,75 | 79,14 | 82,50 | 69,38 | 79,85 | 175 |
| 176 | 82,35 | 69,14 | 79,66 | 82,97 | 69,77 | 80,38 | 176 |
| 177 | 82,81 | 69,54 | 80,18 | 83,44 | 70,17 | 80,91 | 177 |
| 178 | 83,28 | 69,93 | 80,70 | 83,91 | 70,57 | 81,43 | 178 |
| 179 | 83,75 | 70,32 | 81,23 | 84,38 | 70,96 | 81,96 | 179 |
| 180 | 84,21 | 70,71 | 81,75 | 84,86 | 71,36 | 82,49 | 180 |
| 181 | 84,68 | 71,10 | 82,28 | 85,33 | 71,76 | 83,02 | 181 |
| 182 | 85,15 | 71,50 | 82,80 | 85,80 | 72,15 | 83,55 | 182 |
| 183 | 85,62 | 71,89 | 83,33 | 86,27 | 72,55 | 84,09 | 183 |
| 184 | 86,09 | 72,28 | 83,86 | 86,74 | 72,95 | 84,62 | 184 |
| 185 | 86,56 | 72,68 | 84,39 | 87,21 | 73,34 | 85,15 | 185 |
| 186 | 87,03 | 73,07 | 84,92 | 87,68 | 73,74 | 85,69 | 186 |
| 187 | 87,49 | 73,46 | 85,45 | 88,16 | 74,14 | 86,22 | 187 |
| 188 | 87,96 | 73,86 | 85,98 | 88,63 | 74,53 | 86,76 | 188 |
| 189 | 88,43 | 74,25 | 86,51 | 89,10 | 74,93 | 87,30 | 189 |
| 190 | 88,89 | 74,64 | 87,05 | 89,57 | 75,32 | 87,84 | 190 |
| 191 | 89,36 | 75,03 | 87,58 | 90,04 | 75,72 | 88,38 | 191 |
| 192 | 89,83 | 75,42 | 88,12 | 90,51 | 76,12 | 88,92 | 192 |
| 193 | 90,30 | 75,82 | 88,65 | 90,98 | 76,51 | 89,46 | 193 |
| 194 | 90,77 | 76,21 | 89,19 | 91,46 | 76,91 | 90,00 | 194 |
| 195 | 91,24 | 76,60 | 89,73 | 91,93 | 77,31 | 90,54 | 195 |
| 196 | 91,70 | 77,00 | 90,27 | 92,40 | 77,70 | 91,09 | 196 |
| 197 | 92,17 | 77,39 | 90,81 | 92,87 | 78,10 | 91,64 | 197 |
| 198 | 92,64 | 77,78 | 91,35 | 93,34 | 78,50 | 92,18 | 198 |
| 199 | 93,11 | 78,17 | 91,89 | 93,81 | 78,89 | 92,73 | 199 |
| 200 | 93,57 | 78,57 | 92,44 | 94,28 | 79,29 | 93,28 | 200 |

| $C_{15}H_{24}O$ | | | | $C_{15}H_{26}O$ | | | |
|---|---|---|---|---|---|---|---|
| Ester number | % Acetate | % Alcohol | % Alcohol in the orig. oil | % Acetate | % Alcohol | % Alcohol in the orig. oil | Ester number |
| 201 | 94,04 | 78,96 | 92,98 | 94,76 | 79,68 | 93,83 | 201 |
| 202 | 94,51 | 79,35 | 93,53 | 95,23 | 80,08 | 94,38 | 202 |
| 203 | 94,98 | 79,75 | 94,07 | 95,70 | 80,48 | 94,93 | 203 |
| 204 | 95,44 | 80,14 | 94,62 | 96,17 | 80,87 | 95,48 | 204 |
| 205 | 95,91 | 80,53 | 95,17 | 96,64 | 81,26 | 96,03 | 205 |
| 206 | 96,38 | 80,92 | 95,72 | 97,11 | 81,66 | 96,59 | 206 |
| 207 | 96,85 | 81,32 | 96,27 | 97,58 | 82,06 | 97,14 | 207 |
| 208 | 97,32 | 81,71 | 96,82 | 98,05 | 82,45 | 97,70 | 208 |
| 209 | 97,79 | 82,10 | 97,37 | 98,52 | 82,85 | 98,25 | 209 |
| 210 | 98,25 | 82,50 | 97,92 | 99,00 | 83,25 | 98,81 | 210 |
| 211 | 98,72 | 82,89 | 98,48 | 99,47 | 83,64 | 99,37 | 211 |
| 212 | 99,19 | 83,28 | 99,03 | 99,94 | 84,04 | 99,93 | 212 |
| 213 | 99,66 | 83,67 | 99,59 | 100,41 | 84,44 | 100,49 | 213 |
| 214 | 100,12 | 84,07 | 100,14 | | | | 214 |

## Geranyl tiglinate: $C_4H_7CO_2C_{10}H_{17}$.

| Ester number | % Ester | Ester number | % Ester | Ester number | % Ester | Ester number | % Ester | Ester number | % Ester |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0,42 | 21 | 8,85 | 41 | 17,28 | 61 | 25,71 | 81 | 34,13 |
| 2 | 0,84 | 22 | 9,27 | 42 | 17,70 | 62 | 26,13 | 82 | 34,55 |
| 3 | 1,26 | 23 | 9,69 | 43 | 18,12 | 63 | 26,55 | 83 | 34,98 |
| 4 | 1,69 | 24 | 10,11 | 44 | 18,54 | 64 | 26,97 | 84 | 35,40 |
| 5 | 2,11 | 25 | 10,54 | 45 | 18,96 | 65 | 27,39 | 85 | 35,82 |
| 6 | 2,53 | 26 | 10,96 | 46 | 19,38 | 66 | 27,81 | 86 | 36,24 |
| 7 | 2,95 | 27 | 11,38 | 47 | 19,80 | 67 | 28,23 | 87 | 36,66 |
| 8 | 3,37 | 28 | 11,80 | 48 | 20,23 | 68 | 28,65 | 88 | 37,09 |
| 9 | 3,79 | 29 | 12,22 | 49 | 20,65 | 69 | 29,08 | 89 | 37,51 |
| 10 | 4,21 | 30 | 12,64 | 50 | 21,07 | 70 | 29,50 | 90 | 37,93 |
| 11 | 4,63 | 31 | 13,06 | 51 | 21,49 | 71 | 29,92 | 91 | 38,35 |
| 12 | 5,05 | 32 | 13,49 | 52 | 21,91 | 72 | 30,34 | 92 | 38,77 |
| 13 | 5,47 | 33 | 13,91 | 53 | 22,33 | 73 | 30,76 | 93 | 39,19 |
| 14 | 5,90 | 34 | 14,33 | 54 | 22,75 | 74 | 31,18 | 94 | 39,62 |
| 15 | 6,32 | 35 | 14,75 | 55 | 23,18 | 75 | 31,61 | 95 | 40,04 |
| 16 | 6,74 | 36 | 15,17 | 56 | 23,60 | 76 | 32,03 | 96 | 40,46 |
| 17 | 7,16 | 37 | 15,59 | 57 | 24,02 | 77 | 32,45 | 97 | 40,88 |
| 18 | 7,58 | 38 | 16,01 | 58 | 24,44 | 78 | 32,87 | 98 | 41,30 |
| 19 | 8,01 | 39 | 16,44 | 59 | 24,87 | 79 | 33,29 | 99 | 41,72 |
| 20 | 8,43 | 40 | 16,86 | 60 | 25,29 | 80 | 33,71 | 100 | 42,14 |

**From the Institute for Pharmacology and Physiological Chemistry at Rostock i. M.**

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# Contributions

to

# the knowledge of the pharmacological and physiologico-chemical behaviour of some volatile substances

by

**Hans Kleist.**

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1. Anthranilic acid as a sodium salt.
2. Acetyl compound of methyl ester of anthranilic acid.
3. Methyl ester of methyl anthranilic acid as a sulphate salt.
4. Acetyl compound of methyl ester of methyl anthranilic acid.
5. Piperonal.

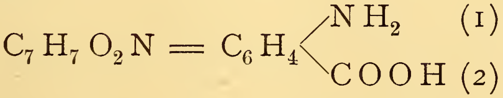
The number of plants containing volatile oils is enormous, and the variety of purposes for which these plants and their oils have been employed medicinally from time immemorial, in the most diverse countries, is also not inconsiderable. It should be the object of scientific pharmacology to ascertain to which constituents of the essential oils (which are mostly of very mixed compositions) the particular effects must be attributed. This question can only be solved in one way, and that a very difficult one; that is to say, by decomposing the oils into their constituents, and by testing each individual constituent for its physiologico-chemical and pharmacological behaviour. The decomposition of the oils is a subject to which a few individual chemists have applied themselves for many years, notably among them Wallach, and also Messrs. Schimmel & Co.; but the examination of the action of the constituents isolated from those oils is a long way behind. May the following pages form a small contribution towards the solution of this task.

I am indebted to the kindness of Professor Rudolf Kobert for having had placed at my disposal anthranilic acid and a few of its esters, and further piperonal, for the examination of their pharmacological properties, and of the fate of these bodies in the animal organism.

With the exception of piperonal, I have found in the literature on the subject no particulars on the physiologico-chemical and pharmacological behaviour of these substances.

## Anthranilic acid and some of its esters.

Anthranilic acid



$$C_7H_7O_2N = C_6H_4 \left\langle \begin{array}{ll} NH_2 & (1) \\ COOH & (2) \end{array} \right.$$

is orthoamido benzoic acid. Its melting point lies at 144° to 145°. The acid, which can be sublimed, is on distillation split up into aniline and $CO_2$. In water and alcohol it is readily soluble; the aqueous solution shows a blue opalescence, and has a slightly sweet taste. Anthranilic acid crystallises in leaflets or trimetrical crystals. Salts of platinum and gold are reduced already in the cold by anthranilic acid, also potassium permanganate; potassium chromate and bichromate, and salts of copper and silver, on the other hand, are not reduced even when the mixture is heated, the last-named salt not even when ammonia is added. If to an aqueous solution of anthranilic acid potassium ferricyanide and ferric chloride are added, a blue precipitate is formed. The sodium salt forms brownish-yellow laminæ which are very readily soluble in water. In an aqueous solution, when potassium-bismuth iodide is added, a yellow-red precipitate is formed.

Anthranilic acid is not apparently present in essential oils; but as derivatives of the acid are found in certain oils, it was necessary that a scientific investigation of these esters should be preceded by an examination of anthranilic acid itself.

For the experiments on animals sodium anthranilate was always selected.

Experiment No. 1. A frog weighing 44 g (for all the experiments with anthranilic acid and its esters the eatable frog, *Rana esculenta*, was employed) received 0,05 g sodium anthranilate dissolved in water. At the injection-spot the green and black pigment of the skin became almost immediately discoloured in a fairly sharply defined area of about 1 cm diameter; the skin assumed here a dirty yellow hue, which became tinged with red in consequence of the rapidly supervening hyperæmia. The passage of the sodium salt in the lymphatic vessel towards the zone of the pelvis was also marked by a slight discoloration of the pigment. In the course of the day the natural colours again became more pronounced, and after 24 hours the previously discoloured regions of the skin had again assumed their normal appearance. The same or corresponding symptoms after injection of sodium anthranilate, were subsequently not again observed, neither with the same frog, nor with others. For the rest, this dose of sodium salt had no apparent effect on the organism.

Experiment No. 2. The same frog was given 0,2 g sodium anthranilate. After 4 hours the animal felt very exhausted, and upon being stimulated mechanically, it crawled about slowly and with difficulty. The dorsal position was tolerated. After 5 hours, in the dorsal position, very slight tonic spasms, and slow irregular and inco-ordinated movements of the trunk, head, and extremities occurred. After 6 hours these inco-ordinated movements were only extremely feeble, the reflex-action scarcely noticeable. After 22 hours the animal was apparently dead, but by a small fenestra cut in the breast it was seen that the heart was still beating. After 44 hours the animal was found to be dead.

Experiment No. 3. A frog weighing 60 g, was given 0,1 g sodium anthranilate. No consequent symptoms were observed.

Experiment No. 4. A frog weighing 38 g received an injection of 0,15 g sodium anthranilate. After 5 hours the animal reacted little when stimulated; inco-ordinated and tonic movements were indicated. After 10 hours it was no longer possible to obtain reflex. Death supervened after about 40 hours. The section showed a medium degree of hyperæmia of the gastro-intestinal tract, and of the mesentery. The mucous membrane of the mouth was not affected by the hyperæmia.

Experiment No. 5. 0,15 g sodium anthranilate was subcutaneously given to a frog weighing 45 g. After 3 hours the frog only made a few and futile efforts to change from the dorsal to the abdominal position. The movements became increasingly feebler, the reflex had almost disappeared after $3^1/_2$ hours. At the trunk, but especially at the extremities, slight symptoms of stimulation occurred, which manifested themselves in faint inco-ordinated movements. Once there occured even opisthotonos, lasting a few seconds. After 5 hours no reaction took place, and after 18 hours it was found that rigor mortis had set in.

Section: The stomach, which was in a highly hyperaemic condition, contained blood-stained mucus; the mesentery showed slight, the mucosa of the cavity of the mouth and of the gastro-intestinal canal but very little hyperaemia; the rectum alone was more strongly injected. The nerves and muscles reacted normally on electric stimulation.

Experiment No. 6. A frog weighing 50 g, which was in a somewhat enfeebled condition owing to previous experiments, received subcutaneously 0,1 g sodium anthranilate. After one hour the animal was already greatly exhausted. Death occured after 4 hours.

Section: The mesentery was not hyperaemic. The alimentary canal, with the exception of the mucus membrane of the mouth, was slightly injected. The stomach contained blood-stained mucus.

Experiment No. 7. A medium-sized frog was given 0,1 g sodium anthranilate. No symptoms whatever occurred, not even the slightest.

Experiment No. 8. A frog weighing 58 g was injected on each of two consecutive days with 0,15 g sodium anthranilate, and on the third day with 0,2 g. The injections were also tolerated without consequent symptoms.

Experiments No. 9 and 10. One frog of 68 g received 0,2 g, and another of 60 g 0,15 g sodium anthranilate. No consequent symptoms whatever occurred.

Experiment No. 11. A frog weighing 69 g was given 0,4 g sodium anthranilate. After 4 hours isolated inco-ordinated movements were still observed; the reflex actions had completely disappeared, the action of the heart had become considerably slower. After $4^3/_4$ hours 0,000075 g nitrate of strychnine was injected. After 6 hours (i. e. $1^1/_4$ hours after the strychnine injection) convulsions and slight spasms of the extremities, of short duration, occurred on stimulation. No strychnine-action could be observed on the musculature of the trunk. After 18 hours the animal was found dead.

It follows from the foregoing that anthranilic acid paralyses the central nervous system of the frog. The tonic spasms (which, however, were only slight) observed before the occurrence of absolute paralysis, are no doubt due to a less intense and transitory stimulation of the muscles or peripheral nerves. The ataxic movements, however, are probably due to the comparatively early paralysis of centripetal ducts, and the loss of controlling sensations thereby caused, with comparatively well-preserved motor-power. Strychnine in large doses, although it allows again a slight flicker of the reflex-action which had already disappeared, is not capable of completely removing the paralysing effect of anthranilic acid, or to prevent death. The fatal dose amounts to about 3,0 g per kilogram weight of the frog.

The urine of 24 hours of several frogs which had received an injection of anthranilic acid, was collected. After addition of potassium-bismuth iodide, a strong precipitate of a yellow-red colour was formed. The urine was now filtered, the residue on the filter collected, and decomposed with potash liquor;

it was then again filtered, and the filtrate exactly neutralised with sulphuric acid. After evaporating this neutral filtrate, it was repeatedly extracted with alcohol, the alcohol again driven off, and the small residue acidified with acetic acid, and precipitated with acetate of copper. In order to remove the copper from the liquid thus obtained, it was treated with sulphuretted hydrogen, and filtered. The filtrate had a faint yellowish colour, with a slight blue fluorescence. The melting point could not be determined, as the quantity remaining after slowly evaporating the water was too small. But the fluorescence could only have been caused by anthranilic acid.

If the fatal dose of anthranilic acid in frogs is not less than 3,0 g per kilogram, a more powerful toxic effect of the substance on warm-blooded animals may hardly be expected.

Experiment No. 12. A rabbit was injected with 1,0 g sodium anthranilate, without occurrence of any symptoms whatever. The quantity of urine obtained in 24 hours was 30 cc; it had an alkaline reaction, and contained neither sugar nor albumin. No aniline could be detected in the urine by means of chloride of lime. The urine was next added with alkali in order to test it for hippuric acid; it was evaporated to the consistency of syrup, the residue repeatedly extracted with cold alcohol, the alcoholic extract evaporated, decomposed with hydrochloric acid, and repeatedly shaken with acetic ether. In order to isolate benzoic acid, which possibly might be present, the residue, after driving off the acetic ether, was extracted with petroleum ether. But not even traces of benzoic acid could be detected. The residue from the acetic ether was dissolved in alcohol, when immediately a beautiful blue fluorescence appeared, which could only be due to the presence of anthranilic acid. One half of the solution was poured off, the alcohol evaporated, and the residue taken up with water. When potassium-bismuth iodide was added, a yellow-red precipitate was formed, but the pure anthranilic acid could not again be obtained.

In the remaining half of the alcoholic solution some crystals floated at the bottom of the vessel, which could only be dissolved with difficulty in cold alcohol, and not at all in ether. By means of ether they could very readily be freed from the greasy matter which still adhered to them. In hot water the crystals dissolved. After slowly evaporating the water, there could be detected with the microscope, firstly small rhombic prisms, secondly crystals arranged in druse-like form. The yield was too small for making any determinations whatever. Anorganic constituents were not present in the crystals.

Experiment No. 13. Even 5,0 g sodium anthranilate, injected subcutaneously in a medium-sized rabbit, had no effect. The urine collected in 48 hours had an alkaline reaction, and did not reduce a solution of copper with the application of heat. The fermentation test gave negative results. In about 15 cc urine submitted to the phenylglucosazone test, the precipitate contained only a few star-shaped crystals, quite isolated and badly formed, although the urine had been cooled very slowly on a water bath. They, however, proved that the urine contained traces of sugar.

Small traces of albumin could also be detected by means of Esbach's reagent, and the underlaying test with nitric acid.

The urine was rendered still somewhat more alkaline with soda, evaporated to the consistency of syrup, repeatedly extracted with alcohol, the alcohol extract evaporated, the residue decomposed with hydrochloric acid, and repeatedly shaken with acetic ether. The acetic ether showed intense fluorescence. As the fluorescence sufficed for the detection of anthranilic acid, the production of the acid in the pure state was not proceeded with. After driving off the acetic ether, the residue was taken up with water, rendered alkaline with soda, filtered, and acidified with an excess of hydrochloric acid. But no crystals as in the previous experiment could be obtained.

The residue of the evaporated urine was finally acidified with hydrochloric acid, once more evaporated, and treated with alcohol and acetic ether. The fluorescence of the latter was but very faint. This time also no crystals could be obtained.

Experiment No. 14. 2,0 g sodium anthranilate given subcutaneously to the same rabbit, caused no separation either of albumin or of sugar. The results of the examination of the urine were the same as in experiment No. 13.

Experiment No. 15. A medium-sized dog was treated subcutaneously with 2,0 g sodium anthranilate. No action. In the urine of 48 hours neither sugar nor albumin were present. The urine rendered alkaline with soda was evaporated to a syrupy consistency, and tested for hippuric acid. There remained a residue which only dissolved in cold water when soda liquor was added. After the solution had been acidified with an excess of hydrochloric acid, the substance was again precipitated. The residue collected from the filter after filtration was repeatedly purified in this manner. The substance has an acid character, and forms salts with bases; like hippuric acid, it dissolves with great difficulty in cold water and in ether, more readily in cold alcohol and acetic ether and hot water, and very rapidly in hot alcohol and hot acetic ether. The crystals of this acid wholly resemble those of hippuric acid, but it is not in this case a question of the last-named acid, whose melting point lies at 188°. The melting point of this acid lies between 315 and 318°. By means of potassium, potassium ferricyanide, and ferric chloride, the presence of nitrogen could be detected.

Experiment No. 16. The same dog received an injection of 4,0 g sodium anthranilate. The urine of 48 hours, which showed a slight fluorescence, had an alkaline reaction, contained no albumin, and reduced a solution of copper already in the cold. As this reduction in the cold could doubtless only have been caused by sugar, it was remarkable that the fermentation-test had a negative result. For purposes of control two fermentation tubes were now prepared with a solution of sugar of equal percentage. To one of these 0,05 g sodium anthranilate was added, and so much tartaric acid, that the liquid had a slightly acid reaction. After 6 hours the fermentation-process had in the one tube come to an end, whilst in the other tube, to which the substance had been added, no carbon dioxide had as yet evolved. Only after 24 hours a quantity of carbon dioxide had been formed which was less than half that in the other tube. Further fermentation did not, however, take place in the following 24 hours. Anthranilic acid or its salt, consequently, acts on the yeast, and retards, and therefore curtails, the process of fermentation considerably.

The presence of sugar in the urine was definitely proved by the phenylglucosazone test. Many and well-developed crystals of the characteristic form were obtained.

From the presence of sugar, and the negative result of the fermentation test, it may be concluded that the urine contained anthranilic acid, and that in such abundance, that it was capable of acting on the yeast.

The urine was now treated in the same manner as in experiment No. 13. The alcohol, and also the acetic ether, showed a beautiful blue fluorescence. But the acid which I obtained in experiment No. 15, could not be produced.

Experiment No. 17. A small dog, weighing about 16 pounds, was subcutaneously injected with 5,0 g sodium anthranilate. After 24 hours the animal was attacked by diarrhœa, and on the second day it took absolutely no food. On the third day it had completely recovered.

The urine collected in 48 hours was alkaline, showed a blue fluorescence, contained no albumin, and reduced solution of copper in the cold. The fermentation-test was negative; the phenylglucosazone-test yielded positive results.

In spite of the most careful examination (compare experiment No. 13) the acid obtained in the first experiment on the dog, could not now be produced.

Experiment No. 18. I personally took per os 2,0 g sodium anthranilate, viz., twice 1,0 g with an interval of 2 hours. Half an hour after each administration a slight attack of perspiration occurred without increase of temperature. About 3 hours after the last dose a slight but yet troublesome salivation was noticeable. Apart from a slight feeling of discomfort in the abdomen, which occurred 12 to 15 hours after administration, disturbances on the part of the gastro-intestinal canal remained absent. The stools were normal. The urine, collected in 48 hours, had an acid reaction; it showed an extremely intense fluorescence, contained no albumin, and reduced copper solution. The fermentation-test had negative, and the phenylglucosazone-test positive results. When soda was added, the fluorescence disappeared. No attempt was made to isolate anthranilic acid. No hippuric, benzoic, or any other organic acids whatever could be obtained from the urine which was treated in the same manner as described in experiment No. 13.

These experiments show that warm-blooded animals tolerate without lasting injury the injection, or administration per os, of anthranilic acid in considerable doses. In the worst case, diarrhœa and salivation occur. The substance is found back in the urine in an unchanged condition, and can already be recognized without chemical examination by the fluorescence. In addition to the substance, sugar is found in the urine of man and dog; in that of the rabbit, however, sugar is either not found at all, or, if very large doses have been given, only traces are present. The sugar can be detected either forthwith by means of the phenylglucosazone-test, or less readily by the fermentation-test, as our substance, like many other reducing bodies, impairs the fermenting power of the yeast.

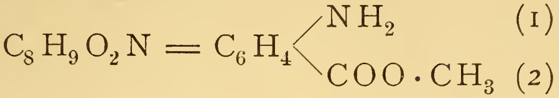
It was not possible to detect any action of anthranilic acid on bacteria.

One cc of a 3 per cent. solution of sodium anthranilate was added to cultures of each *Bacterium coli*, *Staphylococcus albus* and *Bacillus subtilis*, which had been inoculated in about 4 cc peptone-water. When the substance had been in contact with the bacteria for 48 hours at a constant temperature of 34°, the cultures were inoculated into alkaline peptone-agar. Their growth was vigorous and showed no difference from that of control-cultures which had not been treated with anthranilic acid. It follows that sodium anthranilate, in a 0,06 per cent. solution, during 48 hours' action, does not exert any demonstrable influence on *Bacterium coli*, *Staphylococcus albus*, and *Bacillus subtilis*.

It was also impossible to prove any influence of the sodium salt of anthranilic acid on hæmachrome and on the red blood corpuscles.

## Acetyl compound of methyl ester of anthranilic acid.

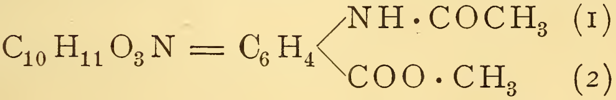
Methyl ester of anthranilic acid



$$C_8H_9O_2N = C_6H_4\left\langle\begin{matrix} NH_2 & (1) \\ COO\cdot CH_3 & (2)\end{matrix}\right.$$

was discovered in the year 1894, in the laboratory of Messrs. Schimmel & Co., as a constituent of oil of orange flowers (neroli oil). It plays an important part in the formation of the aroma of the orange-flower. The proportion of methyl anthranilate in oil of orange-flowers is about 0,6 per cent. The melting point of this compound lies at 25,5°. The solutions show a beautiful blue fluorescence. In the undiluted state the full odour is disagreeable, and only when it has been diluted in due proportion, it reminds of the odour of orange flowers. When a solution of methyl ester of anthranilic acid in water is submitted to destillation, the ester passes over into the receiver. The ester has basic properties.

The acetyl compound of methyl ester of anthranilic acid:



$$C_{10}H_{11}O_3N = C_6H_4\left\langle\begin{matrix} NH\cdot COCH_3 & (1) \\ COO\cdot CH_3 & (2)\end{matrix}\right.$$

represents a loose flocculent white powder free from odour and taste, which can be sublimed. In cold or hot water it dissolves with difficulty; in alcohol, ether, and concentrated hydrochloric acid it is readily soluble. Its solutions show no fluorescence. From water the acetyl compound crystallises in delicate needles. It does not reduce solutions of salts of copper, silver, gold or platinum, or of potassium chromate and permanganate. With platinum chloride it forms a double salt, which crystallises out in beautiful, long needles. When boiled for several hours in concentrated hydrochloric acid, it splits up into methyl anthranilate and acetic acid.

The physiological action of the acetyl compound of methyl ester of anthranilic acid on the animal organism is also slight.

Experiment No. 1. A frog weighing 52 g received 0,1 g methyl ester of acetyl anthranilic acid in emulsion with olive oil. After 45 minutes the animal in dorsal position (without being able to turn over on its abdomen) still made fairly strong movements as if swimming, but subsequently only a few inco-ordinate movements. After 1 1/2 hours the frog lay quietly; the reflex-action was much reduced, and after 4 hours only indicated. The heart continued its normal action for several hours longer. After 18 hours the frog was found dead.

Section: The cavity of the mouth slightly injected. The stomach was filled with a glutinous green mucus; the intestine also contained some greenish mucus. The stomach and mesentery were strongly injected; the intestine had a dark-red appearance, in consequence of hyperæmia. No blood extravasation was present in the alimentary tract. When stimulated electrically, the muscles and nerves reacted normally.

Experiment No. 2. A frog of 40 g weight received 0,05 g methyl ester of acetyl anthranilic acid in emulsion with olive oil. Only after 2 hours the dorsal position was tolerated, and the reflex-actions commenced to grow more feeble. After 18 hours reflex-action could no longer be produced. The heart beat slowly and faintly. After 28 hours, on stimulation, the first faint reflex-actions again became noticeable; in the course of the day they grew stronger. After 3 times 24 hours the frog had so far recovered that it no longer tolerated the dorsal position.

Experiment No. 3. A frog weighing 28 g (which appeared to be somewhat exhausted already before the experiment) received a subcutaneous injection of 0,04 g of the acetyl compound. After $^3/_4$ hour the dorsal position was tolerated without the slightest resisting movements. The reflex-action was still good, but disappeared completely already after $2^1/_2$ hours. The action of the heart after 16 hours was scarcely perceptible. Death occurred after about 70 hours.

Section: Cavity of the mouth, and also the mesentery, moderately injected. The stomach and intestine were strongly hyperæmic, but without extravasation of blood.

Experiment No. 4. A frog wheighing 30 g received an injection of 0,04 g methyl ester of acetyl anthranilic acid. An hour later the frog was still perfectly healthy, but after 2 hours it was no longer able to turn over on the abdomen. The reflex-action even after $3^3/_4$ hours was still normal. In the dorsal position some faint swimming movements were made. Respiration was superficial, but had not become slower. The reflex-action gradually decreased, and ceased after 38 hours. Death occurred after 4 × 24 hours.

Section: The cavity of the mouth, and the stomach and intestine, were slightly injected. A completely-filled gallcyst of 1,4 cm diameter, whose walls were also slightly injected, was situated on the liver.

Experiment No. 5. A frog weighing 31 g was injected with 0,02 g of the acetyl compound. After 45 minutes the animal felt somewhat feeble, and after $2^1/_2$ hours no longer resisted the dorsal position. In that position it made some inco-ordinate movements. Slight swimming movements in the dorsal position were made after $3^3/_4$ hours. At this time the respiration became slower and more superficial, but it became again normal after 21 hours. Recovery progressed but slowly. After 3 × 24 hours the frog was found in a sitting posture, and appeared to be healthy, but, when placed in the dorsal position, it could not turn over on its abdomen in spite of all efforts. During the whole time the action of the heart had remained good, and the reflex-action had not diminished.

Experiment No. 6. The same dose was given to a frog of 27 g weight. After 45 minutes it could only turn over with difficulty from the dorsal to the abdominal position. Reflex-action had disappeared already after 2 hours. The action of the heart which grew increasingly feeble, again became stronger after 18 hours. When stimulated, a slight reaction also became again noticeable. After 3 × 24 hours the frog, like the one in experiment No. 5, appeared to be in a healthy state when in the abdominal position. When turned on its back, it suddenly breathed very rapidly and deeply. The extremities, especially those in front, thereby showed slight clonic and tonic spasms. A complete recovery only occurred after 4 × 24 hours (from the time of injection).

Experiment No. 7. A frog weighing 42 g received a dose of 0,1 g of the substance. When after $^3/_4$ hour the reflex-action had ceased, it made some isolated inco-ordinate movements. After 18 hours it was found dead.

Experiment No. 8. The same dose was given to a frog weighing 63 g. 45 minutes later, when it was absolutely without reaction, an injection was made with 0,00006 g strychnine nitrate. The action of the strychnine became apparent after 30 minutes by slight twitchings after stimulution. Tetanus did not occur. When 5 hours after the first injection (i. e. of the acetyl compound) the action of the strychnine had again almost disappeared, another injection was made with 0,000025 g strychnine. After this injection also only convulsions occurred, but no tetanus. 18 hours after injection of the ester the frog was found dead.

It appears from these experiments, that the action of the acetyl compound of methyl ester of anthranilic acid is similar to that of anthranilic acid. After a few inco-ordinate movements, paralysis of the central nervous system occurs, which is not completely removed even by large doses of strychnine. The fatal dose, of which the quantity does not appear to be affected by strychnine, amounts to about 1,0 g per kilogram weight of the frog.

While the frogs were being dissected (experiments No. 1, 3 and 4), an intense and penetrating odour of orange flowers was emitted from the portions of the body. The urine of the frogs which survived the injection, possessed the same characteristic aromatic odour. From the ether, with which a few cc urine of the frogs was repeatedly extracted, no crystals of methyl ester of acetyl anthranilic acid could be obtained. The compound consequently is split up completely in the organism of the frog into acetic acid and methyl anthranilate, the presence of which is revealed by its peculiar aromatic odour.

Experiments No. 9 and 10. On rabbits and dogs (of medium size) doses of 1,0 g methyl ester of acetyl anthranilic acid, in oil emulsion, had no effect. Sugar and albumin were not detected in the urine. On account of the strong odour proper to the urine, an aromatic odour like orange-flowers could not be determined with certainty.

As methyl ester of anthranilic acid, as a primary aromatic base, forms azo-dyes, this property can be made use of for purposes of demonstration. The dye has a yellow-red colour, is insoluble in water, but dissolves in concentrated sulphuric acid with a deep violet colour. The insolubility of the dye in water permits a quantitative estimation of methyl ester of anthranilic acid in solutions and in essential oils. For this purpose a definite quantity of the diazotised solution of methyl ester of anthranilic acid is titrated with an alkaline solution of $\beta$-naphthol, when the dye thereby produced is precipitated. The litmus test shows whether the reaction is completed.

In accordance with Erdmann's method [comp. Berliner Berichte 35 (1902) 24] 0,5 g $\beta$-naphthol, purified by crystallisation from hot water, was dissolved in 0,5 cc soda liquor and 150 cc water with the addition of 15 g sodium carbonate.

A portion of the urine obtained from the rabbits was acidified with hydrochloric acid, and diazotised at a low temperature with a 5 per cent. solution of nitrite. When, after a few minutes, free nitrous acid could be detected by means of potassium iodide and starch paper, a measured quantity of the $\beta$-naphthol solution was titrated with this urine. After a few minutes a dark-red colouring-matter appeared, which, however, was not precipitated, but, on the contrary, dissolved immediately. It is quite possible that the solubility of the azo-dye was due to the presence of ammonia. Although this method therefore also proved useless for the quantitative estimation of methyl ester of anthranilic acid, it had yet demonstrated, that the acetyl compound is not again separated out as such, but, on the contrary, in the animal organism passes over into the methyl ester, with loss of the acetyl-group.

The other portion of the urine of the rabbits was slightly acidified with hydrochloric acid, carefully and slowly evaporated to the consistency of syrup, extracted with alcohol, the alcohol again driven off, and the residue dissolved in a fews drops concentrated hydrochloric acid and a small quantity of water. After adding alcohol, small crystals, glittering in the liquid, were precipitated. Examined under the microscope, they were found to be small lancet-shaped laminæ, of which the majority possessed a fine serrated edge. As soon as the solution was heated, the crystals dissolved again. It was probably a question of hydrochloric methyl ester of anthranilic acid, which was precipitated from the aqueous solution when alcohol was added. After again slowly evaporating the alcohol and water, a white mass remained which was interspersed with greasy constituents. These could be readily removed from the white salt by means of alcohol. The presence of free methyl ester of anthranilic acid could be recognised by a slight blue fluorescence of the alcohol. The residue was dissolved in a weak solution of soda, and extracted with ether. The ether showed a strong blue fluorescence. After driving off the ether, there remained no crystals of the acetyl compound, but a thin oily film with an offensive odour was found to adhere to the glass. The small contents of the vessel were washed out with 1 to 2 cc dilute hydrochloric acid, and diazotised with sodium nitrite, and with this solution a solution of $\beta$-naphthol was titrated. As was to be expected, the azo-dye was now obtained insoluble.

With the urine of the dogs the diazo-reaction also gave positive results. But, as in the case of the urine from rabbits, the dye immediately dissolved. A portion of the urine was submitted to distillation. The distillate in the receiver had an extremely strong ammonia-like odour. As in the distillation of a solution of methyl ester of anthranilic acid the ester also passes over into the receiver, it was clear that in the distillate of the dog's urine it should be possible to detect methyl ester. And as a matter of fact, in the diazo-test the same red dye occurred again, which immediately dissolved in the liquid.

The other portion of the urine of the dog was acidified with sulphuric acid, evaporated to one-fourth its volume, next rendered again strongly alkaline with soda liquor, and a few times extracted with ether. The ether showed a strong blue fluorescence. Crystals of methyl ester of acetyl anthranilic acid could not be obtained from the ether; that is to say, the acetyl compound had been completely decomposed.

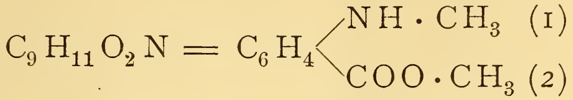
It follows that doses of 1,0g of the acetyl compound of methyl ester of anthranilic acid are tolerated by rabbits and dogs without any apparent or demonstrable disturbance. The acetyl-group is completely split off in the animal organism, and the methyl ester of anthranilic acid can be detected in the urine by means of the diazo-reaction after having been isolated by extraction with alcohol.

On bacteria the acetyl compound had no influence, as was shown by experiments carried out in the same manner as with sodium anthranilate (compare page 116). The developing capacity of *Bacterium coli, Staphylococcus albus* and *Bacillus* *subtilis*, was in no way impaired after 48 hours' action of a 0,8 per cent solution of the substance.

The acetyl compound also exerts does not act hæmachrome and red blood corpuscles.

## Methyl ester of methyl anthranilic acid.

Methyl ester of methyl anthranilic acid:



$$C_9H_{11}O_2N = C_6H_4\left\langle\begin{array}{l}NH\cdot CH_3\ \ (1)\\ COO\cdot CH_3\ (2)\end{array}\right.$$

is an oily liquid with a sweetish, penetrating, aromatic odour which to some extent reminds of the odour of oranges. This ester, whose melting point lies between 18,5° and 19,5°, occurs regularly in oil of mandarins, and also (as has recently been determined in the laboratory of Messrs. Schimmel & Co.) in oil of rue. In water it is only sparingly soluble, but in alcohol and ether it dissolves in every proportion. Its solutions also show a magnificent blue fluorescence. As it possesses basic properties, it forms salts with acids. The preparation placed at my disposal was the sulphate of methyl ester of methyl anthranilic acid. It is readily soluble in water, but is then for the greater part decomposed into free sulphuric acid and methyl ester of methyl anthranilic acid. For this reason the essential oil floats on the fluorescent water which turns litmus paper red. After adding soda liquor, the sulphuric acid combined with the dissolved ester salt is now also abstracted from the latter, and the oil which is then finely divided in the water, gives it a milky appearance.

Solutions of gold, silver and platinum are reduced by the ester salt, but not copper solution. Potassium chromate and bichromate are only reduced in the acid solution of the salt.

When potassium permanganate is added to an aqueous solution of sulphate, there appears at first a yellow-green hue, which almost immediately changes into deep blue-black. After a few minutes this colour also disappears, to make room for a delicate bright-red hue. This red solution has at first an intense dirty slaty-blue fluorescence, but after a few hours this appearance vanishes completely. While gradually manganese dioxide is precipitated and deposited at the bottom, the liquid acquires a reddish-brown shade.

If a sulphate solution is selected which has been neutralised or rendered alkaline with soda, there occurs, after potassium permanganate is added, only a green hue, and after a few hours manganese dioxide is precipitated whilst the liquid acquires a dirty turbidity.

With potassium ferricyanide and ferric chloride, the sulphate (and consequently methyl ester of methyl anthranilic acid) forms a blue precipitate. This reaction is so delicate that even in 0,000000000001 $= \frac{1}{10^{12}}$ g of the sulphate, methyl ester of methyl anthranilic acid could be detected.

When mercuric iodide is added to a sulphate solution, no precipitate is formed. But after prolonged standing bright-yellow prisms crystallise out. Of some few of these prisms the angles are truncated.

With potassium-bismuth iodide the sulphate forms a red precipitate, from which in a few days magnificent red prisms separate out.

In an acid and highly concentrated solution of the salt, a white, delicately violet-coloured precipitate is formed when phosphotungstic acid is added.

If to a sulphate solution a concentrated solution of iodine and potassium iodide, or the so-called Florence-solution, be added, a thick, brown precipitate is formed; this precipitate, after several hours, crystallises out in the form of brown, sharp needles, which arrange themselves in the form of stars or in druse-form. These also form a blue precipitate with red prussiate of potassium and ferric chloride.

The physiological effect of methyl ester of methyl anthranilic acid in the animal organism is unimportant, like that of the other substances already discussed.

For the following experiments, an aqueous and exactly neutralised solution of the sulphate was always selected.

Experiment No. 1. A large strong frog received a subcutaneous injection of 0,05 g of the salt. The animal gradually became more and more feeble; after $1^1/_2$ hours, it made at first only faint and fruitless efforts to change from the dorsal to the abdominal position, but subsequently, when in the dorsal position, it made powerful swimming movements with the hind legs. The reflex-action was scarcely diminished; respiration and action of the heart were not impaired. After 4 hours the first symptoms of recovery became apparent.

Experiment No. 2. The same frog, after 24 hours, when it had completely recovered, received 0,075 g. The same action was observed.

Experiment No. 3. A frog weighing 52 g received 0,07 g. After an hour the animal was already very weak. The reflex-action of the anterior extremities ceased after 2 hours, that of the hind legs had slightly diminished. The action of the heart remained constantly good. After 20 hours the animal had recovered.

Experiment No. 4. A frog weighing 65 g received 0,075 g. After one hour feebleness occurred which increased up to the third hour. At this time slight disturbances of the co-ordination were also observed. For the rest, the symptoms and the course were the same as in experiment No. 1.

Experiment No. 5. The same frog, two hours after an injection of 0,1 g, was very exhausted; the reflex-action diminished more and more, was only very feeble after $2^1/_2$ hours, and had completely ceased after 16 hours. Not until after 43 hours some slight reflex-action of the extremities could again be excited by stimulation. The action of the heart had throughout this time remained good and strong. After 54 hours the animal had recovered.

Experiment No. 6. A frog weighing 26 g received 0,15 g of the substance. After 10 minutes the animal had already ceased to react, and the action of the heart could no longer be observed. After 9 hours rigor mortis had set in.

Section: The skin was normal, the cavity of the mouth slightly red; the stomach, which contained a glutinous, glassy mucus, was strongly injected. The other organs were in no way abnormal. The nerves and muscles responded normally to electric stimulation.

Experiment No. 7. A frog weighing 45 g received a dose of 0,2 g. The animal, which ceased to react already after a few minutes, was injected after 15 minutes with 0,00005 g strychnine nitrate. This only caused convulsive movements, but no tetanus. The action of the heart still continued for a comparatively long time, although it was scarcely perceptible. After 20 hours the animal was found dead and rigid.

The section gave the same results as in experiment No. 6.

Methyl ester of methyl anthranilic acid administered to frogs paralyses the central nervous system, and its toxic action is not appreciably influenced by strychnine. The fatal dose of the sulphate of the ester is about 4,0 g per kilogram weight of the frog.

Experiments Nos. 8 and 9. Doses of 0,5 g and 1,4 g of sulphate of methyl ester of methyl anthranilic acid (subcutaneously) had no perceptible effect to rabbits.

Experiment No. 10. A medium-sized dog also tolerated 2,1 g very well.

It should be mentioned, however, that both in the dog and in the rabbit, during the 24 hours after injection, slight catarrhal symptoms of the superior respiratory passages occurred.

The urine of both the rabbit and the dog contained neither albumin nor sugar.

The urine of the rabbit, which possessed the aromatic odour of methyl ester of methyl anthranilic acid, after having been acidified with sulphuric acid, was reduced to about one fourth its volume, then rendered decidedly alkaline by soda liquor, and extracted with ether. The ether showed an intense blue fluorescence. After adding a few cc water, the ether was slowly driven off. There remained on the water numerous small drops of oil coloured brown-black by dirty matter. Attempts to remove the adhering dirt from the oil drops did not succeed. With potassium ferricyanide and ferric chloride the drops formed a strong blue precipitate. As soon as a few drops concentrated sulphuric acid were added to the water, the oil dissolved in the latter. In the presence of Florence-solution a brown precipitate was formed, which changed into crystals of druse-like formation. A solution of potassium permanganate was quickly discoloured, without the occurrence of the previously described hues.

The aromatic odour of methyl ester of methyl anthranilic acid in the urine of rabbits; the fluorescence of the ether; the intense Berlin-blue reaction of the oil drops; the precipitate and the crystals from the Florence-solution; the difficult solubility of the oil in the presence of acids; all these facts prove that it can only have been a question of methyl ester of methyl anthranilic acid. The fact that potassium permanganate was discoloured without the occurrence of those hues, was possibly due to contamination of the ester.

From the urine of the dog the oil-drops could also be obtained in the same manner. They showed the same behaviour.

Finally, in the urine of the frogs the presence of the ester could be demonstrated by means of iron. The urine was strongly shaken with ether. After driving off the latter, and treating the scarcely visible fatty residue with potassium ferricyanide and ferric chloride, the blue colouring matter was precipitated.

It follows from the foregoing that methyl ester of methyl anthranilic acid is tolerated by warm-blooded animals in comparatively large doses without injurious effect, and without the occurrence of any apparent disturbances in the organism whatever.

The substance therefore again passes out of the animal organism as such. But the ester is separated out not only by the kidneys, but also by the superior respiratory passages. This conclusion at least is justified by the catarrhal symptoms occurring in the dog and the rabbit after the injections.

In spite of its low physiological action, methyl ester of methyl anthranilic acid possesses the properties of a bactericide.

The experiments with this substance made for the purpose of determining the intensity of the action on bacteria, were carried out in this manner, that to a measured quantity of peptone-water into which the bacteria had been inoculated, 24 hours after the inoculation was added one cc of an aqueous solution containing a definite percentage of the sulphate of methyl ester of methyl anthranilic acid.

When the ester had acted for 24 hours, the micro-organisms were again inoculated into alkaline peptone-agar. The temperature of the incubator in which the bacteria were placed, was kept throughout at 34°.

The aqueous solutions of the ester were freshly prepared for each experiment, and not only acid solutions were employed, but also such which had been exactly neutralised by soda. This was done not so much with the view of removing the small quantity of free sulphuric acid (which, as a matter of fact, could not exert any influence on the bacteria selected), as for this reason, that possibly the action of pure methyl ester of methyl anthranilic acid might differ from that of the ester combined with sulphuric acid.

The experiments were made at first with *Bacterium coli, Staphylococcus albus* and *Bacillus subtilis*. But as the development of the last-named was not retarded even in a 0,15 per cent. solution of the ester, only the two first-named micro-organisms were employed in the subsequent experiments. The results, which were frequently checked, are given in the following tables.

## Bacterium coli.

| In acid solution of the sulphate of methyl ester of methyl anthranilic acid. | | In solution of sulphate of methyl ester of methyl anthranilic acid, rendered alkaline with soda. |
|---|---|---|
| After 24 hours' action of the solution on the bacteria, the cultures were inoculated into alkaline peptone-agar. 24 hours after this inoculation the agar tubes were: | The percentage of the substance in the solution acting on the cultures was: | After 24 hours' action of the solution on the bacteria, the cultures were inoculated into alkaline peptone-agar. 24 hours after this inoculation the agar tubes were: |
| sterile and remained so. | 0,08 % | sterile and remained so. |
| sterile | 0,06 % | sterile |
| sterile | 0,05 % | sterile |
| found to contain from 1 to 4 small colonies. | 0,04 % | found to contain sparsely developed colonies. |
| found to contain sparsely and badly developed colonies. | 0,03 % | crowded with well-developed colonies. |
| crowded with well-developed colonies. | 0,02 % | |

## Staphylococcus albus.

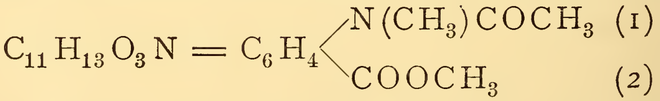
| In acid solution of the sulphate of methyl ester of methyl anthranilic acid. | | In solution of sulphate of methyl ester of methyl anthranilic acid, rendered alkaline with soda. |
|---|---|---|
| After 24 hours' action of the solution on the cocci, the cultures were inoculated into alkaline peptone-agar. 24 hours after this inoculation the agar tubes were: | The percentage of the substance in the solution acting on the cultures was: | After 24 hours' action of the solution on the cocci, the cultures were inoculated into alkaline peptone-agar. 24 hours after this inoculation the agar tubes were: |
| sterile and remained so. | 0,1 % | crowded with strongly-developed colonies. |
| sterile | 0,08 % | do. |
| sterile | 0,06 % | do. |
| found to contain strongly-developed colonies. | 0,05 % | do. |

These two tables do not show any pronounced difference in the results. The bactericidal action of methyl ester of methyl anthranilic acid within 24 hours asserts itself in the case of *Bacterium coli* already in a 0,05 per cent., and in that of *Staphylococcus albus* in a 0,06 per cent. solution of the sulphate, whilst the action of the solutions which have been neutralised with soda is less powerful. This difference in the action of the two solutions is not very great in the case of *Bacterium coli*, but yet noticeable; in that of *Staphylococcus albus*, however, it is very marked. In order to destroy this micro-organism in 24 hours, a 0,06 per cent. acid solution, or a neutralised solution of 0,15 per cent. is required. It would appear that the free sulphuric acid, which in such dilution as in these experiments does not impair or weaken, but rather favours the development both of *Bacterium coli* and of *Staphylococcus albus*, in the presence of the ester still enhances the bactericidal effect of the latter.

Hæmachrome and red blood corpuscles are not attacked either by methyl ester of methyl anthranilic acid, or by a neutralised solution of its sulphate. But an acid sulphate solution immediately causes the formation of methæmoglobin, with lixiviation of the red blood corpuscles, an action which of course does not result from the presence of the ester, but from that of the sulphuric acid.

## Acetyl compound of methyl ester of methyl anthranilic acid.

The acetyl compound of methyl ester of methyl anthranilic acid



$$C_{11}H_{13}O_3N = C_6H_4 \left\langle \begin{array}{ll} N(CH_3)COCH_3 & (1) \\ COOCH_3 & (2) \end{array} \right.$$

is a yellow oily substance, which has a bitter and slightly pungent taste, and which solidifies at 15°. In the undiluted state this body has a faint, offensive odour, and only when it is strongly diluted it acquires a penetrating aromatic sweetish odour which distantly reminds of the odour of orange-flowers. In alcohol, ether, and water the oil is soluble in every proportion. The substance shows no fluorescence.

It does not reduce solutions of copper, nor of gold, platinum, silver, potassium chromate, and potassium permanganate.

When Florence-solution is added to an aqueous solution of this substance, a brown precipitate is formed, which after several hours crystallises out in the form of hexagonal light-brown laminæ and rhombic prisms. In transmitted light the prisms are partly light-brown, partly black coloured.

If to an aqueous solution of methyl ester of acetyl methyl anthranilic acid, after the addition of Florence-solution, soda liquor is added, the precipitate dissolves with a bright-yellow colour, and is not formed again even when an excess of hydrochloric acid is added. On the other hand, there is formed, either immediately, or, in case of insufficient concentration, in the course of 24 hours, an abundant precipitate of delicate sharp needles, which in transmitted light have a greenish-blue, and in reflected light a green-black colour. In hot water and in dilute soda liquor they dissolve immediately, but are again precipitated after the addition of hydrochloric acid.

With potassium ferricyanide and ferric chloride the acetyl compound does not form a blue precipitate.

A short time ago the makers succeeded in producing the acetyl compound of methyl ester of methyl anthranilic acid in crystalline form, instead of the amorphous mass hitherto obtained. The preparation placed at my disposal consisted of small crystals, which liquefied into an oil on being slightly heated. Treated with Florence-solution they formed a precipitate only when a small quantity of hydrochloric acid was added, but this precipitate did not crystallise out. After adding soda and hydrochloric acid the above-mentioned crystalline needles were precipitated.

For the following experiments on animals with the acetyl compound of methyl ester of methyl anthranilic acid, the form in which the compound was used was always that of aqueous solutions of the first consignment, except in those cases where the remarks show that either the pure substance was employed, or else aqueous solutions of the second consignment.

Experiment No. 1. A frog weighing 53 g received 0,0458 g. After 25 minutes it reacted but little. The action of the heart remained good. After 18 hours the frog was found to be again quite healthy.

Experiment No. 2. A frog weighing 60 g received 0,06 g. After 30 minutes the reflex-action was only feeble. Complete absence of reaction was observed after 4 hours, but the heart acted powerfully. After 24 hours the animal had made fair progress towards recovery.

Experiment No. 3. A frog weighing 60 g, 15 minutes after injection of 0,09 g, tolerated already the dorsal position; reflex-action was only faintly indicated, and ceased completely shortly afterwards. The action of the heart diminished gradually, and was subsequently hardly perceptible. The first slight reflex-action was again obtained after three times 24 hours; it increased a little in the course of the fourth day, but had again ceased after 104 hours (after injection). On the abdomen, and especially on the lower part of the throat and mouth, and also on the axillary and inguinal regions, and the lower part of the upper thigh, there appeared on the third day a few papillæ varying in size from that of a poppy-seed to a millet-grain, and having a reddish-yellow colour. After five times 24 hours the frog was found dead, but not rigid.

Section: The abdominal wall, stomach and intestine were strongly injected. The injected condition of the intestine diminished towards the cloaca.

A portion of the skin on which the papillæ were situated, after being hardened, was placed in paraffin, and stained. When examined under the microscope, it was found that at the places where the papillæ were situated, the layer of epithelium was raised. The contents of these vesicles consisted of a few detached epithelial cells which were partly already whithout nucleus, and a small quantity of detritus. At a few isolated parts of the skin which under the microscope did not externally show any change, the epithelium was also already raised.

Experiment No. 4. A middle-sized frog received the same dose. After one hour the animal was absolutely without reaction. Death occurred after about 36 hours.

The section showed the same results as in experiment No. 3, except that the abdominal wall was not hyperæmic.

Experiment No. 5. A medium-sized frog received 0,1 g. After $^1/_2$ hour the animal had lost all power of reaction; the action of the heart had diminished and become slower. After 24 hours the frog was found dead.

Section: The intestine showed general hyperæmia especially well-marked in certain circumscribed spots. The stomach which was also in a strongly injected condition, contained blood-stained mucus. The skin showed no peculiarities.

When the undiluted substance was injected, it acted already after a few minutes.

Experiment No. 6. A frog weighing 25 g received an injection of 0,14 g of the methyl ester of acetyl methyl anthranilic acid which I had received with the second consignment. After 10 minutes the animal had ceased to react. On electric stimulation the muscles and nerves reacted in a normal manner. The action of the heart was slow and feeble. After 15 minutes an injection was made of 0,00005 g strychnine nitrate; this produced no convulsions, but only slight twitching in response to stimulation. After 20 hours the frog was found rigid.

Section: The skin was normal, the cavity of the mouth slightly red; the stomach and intestine were strongly hyperæmic. The latter contained blood-stained mucus in addition to fæcal matter.

It must appear remarkable that in other frogs the formation of vesicles on the skin did not occur, either when smaller doses were given than in experiment No. 3, or in the case of equal or larger doses; and that, in fact, the abdominal wall of those animals was not even hyperæmic. At first the view was not wholly unwarranted, that possibly, in consequence of secretion of the substance through the skin, irritation of the latter by the essential oil might have occurred, followed by the formation of vesicles. This view, however, had to be abandoned, when it was subsequently found that the acetyl-group is split off in the body of the frog, and only the methyl ester of methyl anthranilic acid is excreted. But the same action on the skin was not observed in the case of methyl ester of methyl anthranilic acid (compare page 122).

Moreover, I do not believe that the acetyl compound alone is capable of producing such comparatively powerful changes, without acting in an equally strong manner in the interior of the organism, especially on the intestine and stomach. The occurrence of the vesicles on the side of the abdomen rather points to some external local cause.

The frog survived by $3^1/_2$ days the one (experiment No. 4) which had received the same dose of 0,09 g, and by 4 days the other one (experiment No. 5) which had received 0,1 g. The action, therefore, was considerably less powerful. It is probable that shortly after the injection a few drops of the acetyl compound had again flown out of the puncture canal, and as the plate on which the frog was placed, was not kept very damp, those drops could exert a caustic action on the abdomen of the animal.

The acetyl compound of methyl ester of methyl anthranilic acid, like the other substances already discussed, paralyses the central nervous system of the frog, but this toxic effect occurs comparatively rapidly, in any case at a considerably earlier period than with the other substances. Strychnine administered after poisoning with the acetyl compound, also induces a slight revival of the extinguished reflex-actions, but for the rest does not possess any antidotal properties. The fatal dose of the acetyl compound of methyl ester of methyl anthranilic acid amounts to 1,5 g per kilogram weight of the frog.

Before discussing the examination of the urine of the frogs, I will deal with the experiments made with this acetyl compound on warm-blooded animals.

Experiment No. 7. A guinea pig, weighing 500 g, received 0,55 g subcutaneously. After a few minutes it made some ataxic movements, fell down on its side, and fell asleep. The reflexes of the hind legs were much reduced, and had completely disappeared after 3 hours; those of the anterior extremities still remained indicated for a long time. Occasionally the animal, in the dorsal position, spontaneously made some slow walking-movements with the front legs; at the hind legs there occurred only short single twitches at intervals of from 1 to 15 minutes. The respiration gradually became slower and very superficial; the frequency of the pulsations of the heart also became reduced, but the energy of the contractions, as far as it could be judged after the puncture was made, still remained normal. After $5^1/_2$ hours the corneal-reflex also ceased. During somnolence about 2 cc alkaline, milky urine could be pressed out of the bladder. After 19 hours the animal was found dead and rigid.

Section: At the injection-spot a briny œdema had occurred. Hyperæmia could not be detected in any of the organs. The intestine was moderately filled with formed fæcal matter. Kidneys, liver, lung and heart showed no peculiarities.

Experiment No. 8. A small rabbit received subcutaneously 0,5 cc of the undiluted acetyl compound of methyl ester of methyl anthranilic acid. After a few minutes it made inco-ordinate movements, fell down, and fell asleep. The power of reaction of the hind legs was much reduced. Respiration and pulsation were neither slower nor more feeble. After lying down for half an hour, it turned over a few times as if about to wake up. In the course of 5 hours it had completely recovered, and took food.

Experiment No. 9. A full-grown medium-sized rabbit received 0,55 g subcutaneously. The animal soon became feeble, and after half an hour sat down quietly. When laid on the back, it regained its feet only slowly. The reflex-actions, respiration, and pulsation were not reduced. After 3 hours it had recovered fairly well.

This rabbit died suddenly 5 weeks afterwards. The internal organs, with the exception of the stomach, were found to be normal. But at the pylorus several ulcers were found, varying in size from a pin's head to the size of a lentil, and of a black-brown colour. A piece of the stomach was embedded in paraffin and stained. Examined under the microscope, it was found that the ulcers did not penetrate into the submucosa, but that only the mucous membrane was ulcerated. It was a remarkable fact that blood or blood-pigment could not be detected microscopically at the transverse sections.

It may be assumed that these ulcers were connected with the sudden death of the animal, but it is doubtful whether there exists any connection between the injection of the acetyl compound of methyl ester of anthranilic acid, and the presence of the ulcers in the stomach.

Experiment No. 10. A small dog weighing about 5 kilograms received a subcutaneous injection of 1 cc of the pure undiluted substance. The animal remained healthy.

Experiments No. 11 and 12. The same dog remained in good health after being injected with 1,2 g of the substance in dilution, and 1,8 cc of the undiluted substance.

All the specimens of urine formed with Florence-solution a brown precipitate, which, however, did not crystallise out. After adding soda liquor and an excess of hydrochloric acid, the characteristic needles were never precipitated, neither immediately, nor subsequently.

The urine of the guinea pig, which possessed an aromatic odour, was repeatedly treated with Florence-solution, and each time extracted with ether in which the precipitate dissolved. After driving off the ether, the residue was heated on a water bath until iodine was no longer sublimed, and it was then absorbed with a small quantity of water. After one week a few druses had crystallised out, which with potassium ferricyanide and ferric chloride formed a blue precipitate. They resembled the crystals mentioned on page 123.

The urine of the two rabbits had a strong characteristic odour and was free from albumin, but after adding soda liquor it possessed a very powerful reducing-action on copper sulphate, even when the temperature was but slightly raised. At first bright-yellow protoxide hydrate was formed, then red protoxide of copper. Salts of silver and of gold were also reduced.

As the presence of sugar was suspected, a portion of the urine of the rabbit which had received 0,55 g of the acetyl compound of methyl ester of methyl anthranilic acid (comp. experiment No. 9), was fermented with yeast. The sugar test gave positive results, the quantity of sugar found being 0,6 per cent.

The remaining portion of the urine was treated in the same manner as that of the guinea pig. After one week small druses and verruciform and fascicular crystals were found on the bottom of the vessel.

The urine of the other rabbit was treated with sulphuric acid until it had a pronounced acid reaction; it was then evaporated to the consistency of syrup, again rendered alkaline, and extracted with ether. The ethereal extract showed a blue fluorescence. After adding a few cc water, the ether was driven off, and there were then floating on the water a few oil-drops of a yellowish colour. One of these was removed with a spatula, the spatula round the oil-drop carefully cleaned, and then placed in a solution of potassium ferricyanide and ferric chloride. The solution assumed an intense blue colour. The other oil-drops, after treatment with Florence-solution, produced beautiful fascicular crystals.

The urine of the dogs contained neither albumin nor sugar. The ethereal extract of the urine which had first been acidified with sulphuric acid, and after concentrating had been rendered alkaline with soda liquor, also showed a blue fluorescence, but only slightly. After driving off the ether, only a few small oil-drops floated on the water which had been added, and these formed a strong blue precipitate with iron.

Experiment No. 13. A medium-sized rabbit received a subcutaneous injection of 1,0 g of a solution of methyl ester of acetyl methyl anthranilic acid from the second consignment. After half an hour the animal became sleepy, and extended the fore legs. When placed in the dorsal position it turned over with difficulty. Pulsation, respiration and reflex-action remained normal. After 4 hours the animal had to some extent recovered.

The urine secreted in 48 hours had an alkaline reaction, contained no albumin, reduced copper solution, and gave a positive phenylglucosazone-test. By means of the fermentation-test it was found to contain 1,1 per cent. sugar. The urine was now acidified with sulphuric acid, slowly evaporated almost to dryness, again rendered alkaline with soda, and extracted with alcohol. After driving off the alcohol, the residue was extracted with ether. The latter showed an intense blue fluorescence. When the ether, after adding a small quantity of water, had again been driven off, there floated on the water numerous small and most minute drops of oil which showed all the reactions of methyl ester of methyl anthranilic acid.

Experiment No. 14. A medium-sized dog received a subcutaneous injection of 3,0 g of a solution of the substance received with the second consignment. This dose did not give rise to any symptoms. The urine of 48 hours measured only 30 cc. It had an alkaline reaction, and contained neither albumin nor sugar. The urine was treated in the same manner as in the last experiment. Fluorescence of the ether could not be observed with certainty. After driving off the ether, no oil-drops floated on the added water. Although this liquid produced an intense blue precipitate with potassium ferricyanide and ferric chloride, the reduction of metal salts was only slight.

Finally, the urine of the frogs which had received an injection of the acetyl compound, formed with Florence-solution a precipitate, from which, however, no crystalline needles were precipitated when soda and hydrochloric acid were added, a proof that the acetyl compound was not present in the urine.

As the presence of methyl ester of methyl anthranilic acid was suspected, the small residue of an ethereal extract of the carefully evaporated urine was treated with potassium ferricyanide and ferric chloride. A strong blue precipitate confirmed the supposition.

As is shown by the experiments on warm-blooded animals, the acetyl compound of methyl ester of methyl anthranilic acid appears to be fairly indifferent for the organism of the dog, as doses of even 3,0 g were tolerated by a medium-sized animal without the slightest demonstrable injuries to the organs, and without general disturbances. Nor was the appetite reduced. No sugar was excreted by the organism.

With the guinea pig and the rabbit the conditions are different. After the introduction of moderate doses, the substance causes in these animals at first slight disturbances of the co-ordination, but soon afterwards they become stupefied. The narcotic effect is, however, not prolonged. After stronger doses the central nervous system becomes paralysed. For guinea pigs the fatal dose is 1,0 g per kilogram weight. Apart from these nervous symptoms, the substance produces in the rabbit a considerable excretion of sugar, which can be readily detected by the fermentation- and phenylglucosazone-tests.

The acetyl compound of methyl ester of methyl anthranilic acid is not stable in the organism of frogs, guinea pigs, rabbits and dogs, but is excreted as methyl ester of methyl anthranilic acid after the acetyl-group has been split off.

On micro-organisms the acetyl compound of methyl ester of methyl anthranilic acid has no influence. The development of *Bacterium coli, Staphylococcus albus,* and *Bacillus subtilis* — the cultures had been inoculated into about 4 cc peptone-water — was in no way impaired by the addition of 1 cc of a 3 per cent. solution acting for 3 days.

The question now presented itself, whether per contra the bacteria had exerted any action on the substance. Such action, in view of the composition of the substance, and of the results of the experiments on animals, could, naturally, only have consisted of the splitting off of the acetyl group.

When the bacteria had been in contact for 4 days with the acetyl compound of methyl ester of methyl anthranilic acid, the cultures were submitted to the following examination.

## Culture of Bacterium coli.

1. To one part peptone-water were added, after acidification with one drop dilute sulphuric acid, a few drops of a solution of potassium permanganate. Although it was at once discoloured, the various hues observed with the solution of the pure sulphate of methyl ester of methyl anthranilic acid did not occur. Nor could a dirty-blue fluorescence of the peptone-water be recognised.

2. A small quantity of Florence-solution was added to one part peptone-water. Although a stronger precipitate was formed, no crystallisation took place even after several week's standing.

3. Another part was slowly evaporated, extracted with ether, and the ether driven off. The residue, treated with potassium ferricyanide and ferric chloride, formed only a very slight blue precipitate.

As a check, about 4 cc peptone-water which had also been charged with *Bacterium coli*, but to which no acetyl compound had been added, was evaporated to dryness and extracted with ether. The residue in this case also formed only a slight blue precipitate.

### Culture of Staphylococcus albus.

The examination was conducted in the same manner as with *Bacterium coli*, and led to the same results.

### Culture of Bacillus subtilis.

1. A portion of the peptone-water, after acidification, discoloured a solution of potassium permanganate. The change of colours was here also absent, but a dirty-blue fluorescence could be observed, which, however, was but very faint.

2. The precipitate formed after adding Florence-solution, did not crystallise out.

3. The residue from the ethereal extract of peptone-water, when treated with iron, formed a strong blue precipitate. But an equally strong precipitate was obtained from a pure peptone-water culture of *Bacillus subtilis*.

It follows that *Bacterium coli* and *Staphylococcus albus* have no influence on the acetyl compound of methyl ester of methyl anthranilic acid. Such a result was to be expected in the case of these two micro-organisms, for if the acetyl-group had split off from only one-twelfth part of the substance, the micro-organisms would have been destroyed. The slight blue reaction at any rate does not yet prove the presence of free methyl ester of methyl anthranilic acid.

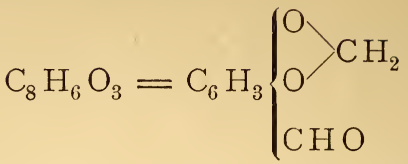
*Bacillus subtilis*, which is fairly indifferent towards free methyl ester of methyl anthranilic acid (compare page 124) appears, contrary to the other two micro-organisms, to split off a small part of the acetyl group. This conclusion at least would seem justified by the slight dirty-blue fluorescence of peptone-water after adding potassium permanganate.

Neither blood corpuscles nor hæmachrome undergo any change by the action of the acetyl compound of methyl ester of methyl anthranilic acid.

## Piperonal.

Of the six possible dioxybenzaldehydes $C_6H_3(OH)_2 \cdot CHO$, of which three isomers have been obtained by means of chloroform-reaction from the three dioxybenzenes (pyrocatechol, resorcinol, and hydroquinone), $[H_2O + CHCl_3 + C_6H_4(OH)_2 = C_6H_3(OH)_2 \cdot CHO + 3\,HCl]$ protocatechuic aldehyde is worthy of notice, as it is the substance from which piperonal and vanillin are derived — two bodies which have recently acquired great importance.

Piperonal, also called heliotropin:



$$C_8H_6O_3 = C_6H_3\left\{\begin{array}{l} \left.\begin{array}{l} O \\ O \end{array}\right\rangle CH_2 \\ CHO \end{array}\right.$$

is methylene ether of protocatechuic aldehyde. It is found regularly in oil of spiræa, i. e. the oil of *Spiraea Ulmaria*, and in many kinds of vanilla.

Piperonal is produced on a large scale by treating piperic acid, or — and now almost exclusively — safrol and isosafrol with oxidising agents. It forms inch-long lustrous crystals (from water), is soluble in 500 to 600 parts cold water, readily in alcohol, in every proportion in ether and hot alcohol. The melting point lies at 37°, the boiling point at 263°. It behaves generally as benzaldehyde. It is a remarkable fact that it does not give the characteristic reduction of salts of copper, gold, etc. by aldehydes. On oxidation it forms the corresponding piperonylic acid.

Piperonal plays an important part in the perfumery industry. It possesses a penetrating, coumarin-like odour, which strongly reminds of the actual perfume of the heliotrope flower. It is used in the manufacture of extraits, sachets, and soaps. When exposed to the sun, the crystals acquire a yellowish-brown colour, and lose the perfume completely.

According to the experiments made by Dr. Ricardo Frignani (comp. New York Medical Record), heliotropin possesses antipyretic and antiseptic properties. The antipyretic action is not very energetic, but in many cases sufficient. It is best administered in doses of 15 grains 3 to 4 times daily, but larger doses are also tolerated quite well. Its antiseptic action is stronger, and as it is harmless even in doses of $^1/_2$ to 1 drachm, it deserves a high place among similar remedies.

According to O. Wimmer, "Further experimental examinations respecting piperonal. Thesis (Liebreich) Berlin", piperonal checks the action of pepsin and pancreas, the fermentation of lactic acid, putrescence, but not the action of yeast. It reduces the temperature of animals in a normal or feverish condition (also clinical observation).

More detailed examinations of the behaviour of piperonal in the animal body have been made by Dr. A. Heffter. In the organism of the rabbit (4,0 g were injected), piperonal was converted into the allied piperonylic acid, which could be precipitated from the alcoholic extract of the urine be means of hydrochloric acid. It was remarkable that here no combination had taken place with glycocoll, as this is the case with all aromatic monocarboxylic acids, if they contain not more than one hydroxyl-group.

The author therefore administered to himself 5,0 g piperonylic acid, and obtained from the urine two acids, of which one was the unchanged piperonylic acid, but the other piperonyluric acid $C_6H_3(O_2CH_2)CONHCH_2 \cdot COOH$. This represents colourless, bright, broad prisms of the melting point 178°; in cold water it dissolves with difficulty, but in hot water and in alcohol it is readily soluble. When boiled with hydrochloric acid it is split up into its components, of which one was recognised as piperonylic acid. Dr. Heffter adds in a note "As this and some other experiments showed, piperonal is physiologically quite free from action. The following particulars for which I am indebted to a medical friend show that it is also harmless to man. A chemist intending to commit suicide, swallowed 50 cc of a concentrated alcoholic solution of piperonal, i. e. about 10 g. His health was in no way affected by it."

Now a chemical substance may undoubtedly be almost completely indifferent in the animal body, and need not show, even in large doses, a toxic effect, or one of pharmaco-dynamic value. The chemical changes which take place in the organism may be very slight, and may qualitatively and quantitatively be so little beyond the normal, that functional disturbances do not occur at all. On the other hand, every animal reacts upon a poison in a varying degree, and in a different manner, according to its chemical organisation. In dogs and rabbits I could certainly not observe any subsequent symptoms, even with doses of 5,0 or 4,0 g respectively. 8,0 g piperonal administered to a medium-sized dog per os caused severe stomach complaints, so that after $1\frac{1}{2}$ hours the animal began to vomit with severe vomiturition, in consequence of which probably almost the whole of the administered substance was ejected from the stomach.

But the experiments made with frogs showed surprising results.

Experiment No. 1. Two frogs weighing 30 and 31 g respectively, received each an injection into the lymphatic vessels of the back, of 0,08 g piperonal in emulsion with acacia. Paralysis occurred almost immediately; the anterior extremities responded little to mechanical stimulation, whilst the reflex-action of the posterior extremities had ceased. Respiration and pulsation became more feeble, and ceased after half an hour. The section showed, that the emulsion was completely resorbed. Muscles and nerves reacted normally on electric stimulation. The disappearance of the reflex-action must therefore have been due to paralysis of the central nervous system, whilst many substances of the group of essential oils exert an action which paralyses the nerves peripherally, in the manner of curare.

Experiment No. 2. Two frogs weighing 30 and 32 g, each received 0,04 g piperonal in acacia-emulsion. After a few minutes paralysis occurred already, so that the dorsal position was tolerated. After 24 hours the animals had completely recovered.

An injection of 0,05 g piperonal showed the same symptoms.

Experiment No. 3. Two frogs received 0,075 g piperonal each, in emulsion. Again paralysis of the extremities supervened very rapidly; the reflex-action was very feeble. One of the frogs, weighing 31 g, expired after 5 hours; the other one, weighing 40,5 g, survived.

Experiment No. 4. Two frogs, 39 and 41 g respectively, each received 0,1 g piperonal in emulsion. The symptoms were the same as before. Both frogs recovered.

Experiment No. 5. Two frogs weighing 41 and 47 g, each received 0,12 g piperonal. Both animals became very ill, and only commenced to recover after 12 hours.

Piperonal therefore paralyses in frogs the central nervous system. In subcutaneous injections the action is extremely rapid. The fatal dose amounts to about 2,5 g per kilogram weight of the frog.

As piperonal in frogs has especially the effect of paralysing the centra of the nervous system, the morbid symptoms produced by piperonal should be allayed, or possibly their complete disappearance be effected, by means of agents which stimulate the same nerves.

Experiment No. 6. A small frog received 0,17 g piperonal, which for this animal was almost double the fatal dose. As the piperonal emulsified in acacia, in spite of the finest possible trituration, frequently clogged the small tubes of the syringes, an oil-emulsion was employed in the two following experiments. The oil was heated to 38 to 40°, then violently agitated, and rapidly cooled to the temperature of the room. The piperonal suspended in the oil remained, even at this low temperature, for a few minutes in a molten state.

In the body of the frog the piperonal commenced to act only after 20 minutes, and not until after $1^1/_2$ hours had the reflex-action almost completely disappeared.

Occasionally very slight twitchings could be observed, which occurred simultaneously at all the extremities. After an hour 0,00005 g strychnine nitrate was injected. An hour after the strychnine-injection the first slight twitchings showed themselves on stimulation, and reached their maximum intensity after 2 hours. Convulsions or tetanus did not occur. A control-frog received only 0,00005 g strychnine nitrate. After $1^1/_2$ hours it was suffering from the most severe tetanus. After 20 hours the frog was only slightly indisposed, but it was still so exhausted that it tolerated the dorsal position. It had only recovered completely after 30 hours.

Experiment No. 7. A small frog received 0,00005 g strychnine nitrate. After $1^1/_4$ hours, when suffering most severely from tetanus, 0,16 g piperonal in oil was injected. An hour after the injection only slight convulsions, but no tetanus, occurred. These convulsions also changed in the course of an hour into slight twitches. Like the other frog which had received first an injection of piperonal and subsequently one of strychnine, this one, after 20 hours, was also only somewhat exhausted, and after 30 hours had completely recovered.

Strychine, therefore, is for frogs a remedy which completely counteracts the paralysing action of piperonal, even when the latter is administered in double the fatal dose. Per contra, piperonal is an excellent antidote against strychnine poisoning.

In order to ascertain in what form piperonal is excreted from the body of the frog, the urine of several frogs which had received a piperonal-injection, was collected. This urine, which had no aromatic odour, was slowly evaporated almost to dryness; after acidifying with hydrochloric acid it was extracted with alcohol, and the alcohol driven off. There remained as a residue small crystalls which were insoluble in cold water, but readily dissolved in alcohol and ether. These properties, and also the melting point and the capacity of subliming, proved that it was a question of piperonylic acid. The melting point no doubt lay at 223°, that is 4° lower than that of pure piperonylic acid. But this small error is of no further importance, as already slight contaminations reduce the melting point by many degrees. The remainder of the piperonylic acid was once more purified by subliming, but the quantity was too small for the determination of the melting point.

It follows that, as in the organism of the rabbit and the dog, piperonal in the body of the frog is converted into the allied piperonylic acid; it can be identified as such by its capacity of subliming, and by the determination of the melting point. Piperonyluric acid is not present in the urine of the frog.

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# SEMI-ANNUAL REPORT

OF

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# Contents.

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## List of abbreviations.

$d$ = specific gravity at 15°, unless otherwise stated.
$d_{20^\circ}$ = specific gravity at 20°.
$d\frac{20^\circ}{4^\circ}$ = specific gravity at 20°, compared with water at 4°.
$\alpha_{D_{15^\circ}}$ = optical rotation, at 15°, in a 100 mm tube.
$[\alpha]_D$ = specific rotation.
$n_{D_{15^\circ}}$ = index of refraction at 15°.
n = normal.
$\frac{n}{2}\left(\frac{n}{10}\right)$ = semi-normal or deci-normal (titrated solutions).
g = gramme; cc = cubic centimeter; mm = millimeter.

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Temperatures are uniformly stated in **centigrade** degrees (°).

**Miltitz** near Leipzig, October/November 1903.

The sketch of the economic condition of Germany presented in our Report of last April gives on the whole still a true picture of the present situation. No changes of any importance can be recorded, and in fact may not be expected until the negotiations concerning the new commercial treaties have been brought to an end.

So long as this question has not been settled, a certain check will be put to the spirit of commercial enterprise. It is greatly to be desired that the negotiations may now soon commence and be concluded, and that practical men representing every important branch of Industry may take part in them. Nothing has a more restraining effect on commercial intercourse than a long-continued period of uncertainty, which to remove is the urgent wish of the whole commercial community.

In our Industry a brisk activity has prevailed also during the summer, and the export-statistics of the first half-year of 1903 are favourable. The statistics for 1902, which have now also been published, show a considerable increase both in the imports and the exports.

The total exports of essential oils from Germany amounted

in 1898 to 287 100 kilos, value 2 871 000 marks
„ 1899 „ 351 000 „ „ 3 862 000 „
„ 1900 „ 380 000 „ „ 4 634 000 „
„ 1901 „ 388 000 „ „ 4 658 000 „
„ 1902 „ 424 700 „ „ 5 683 000 „

The total imports, on the other hand, were

in 1899, 416 000 kilos, value 5 938 000 marks
„ 1900, 421 000 „ „ 5 631 000 „
„ 1901, 417 000 „ „ 5 192 000 „
„ 1902, 408 886 „ „ 6 309 000 „

The value of the export of German perfumes and toilet-soaps in 1902 again shows high figures. It is made up as follows: —

| | | | | | |
|---|---|---|---|---|---|
| Soap in tablets, including scented soap . . . . | 4 423 100 | kilos, | value | 6 192 000 | marks |
| Fatty oils, scented . . . | 22 200 | „ | „ | 244 000 | „ |
| Scents, not containing alcohol . . . . . . . . | 123 000 | „ | „ | 12 000 | „ |
| Liquid perfumes containing alcohol or ether, including hair-washes, dentifrices, and mouth-washes . . | 1 424 100 | „ | „ | 6 950 000 | „ |
| All other perfumes not otherwise enumerated . . . | 577 000 | „ | „ | 2 164 000 | „ |
| Soap and perfumes insufficiently specified . . . | 1 600 | „ | „ | 8 000 | „ |
| Total in 1902: | 6 571 000 | kilos, | value | 15 570 000 | marks. |

| | | | | |
|---|---|---|---|---|
| against in | 1901, | value | 15 678 000 | marks |
| „ | 1900, | „ | 15 048 000 | „ |
| „ | 1899, | „ | 15 415 000 | „ |
| „ | 1898, | „ | 12 972 000 | „ |
| „ | 1897, | „ | 11 714 000 | „ |
| „ | 1896, | „ | 12 549 000 | „ |

With regard to the export of toilet-soaps and perfumes from France, only the figures for 1900 are available, and then only the quantities, and not the values. For this reason no accurate comparisons are possible. The exports were: —

| | | |
|---|---|---|
| Soaps . . . . . . . | 2 609 644 | kilos |
| Perfumes, alcoholic . . | 2 315 055 | „ |
| Perfumes, non-alcoholic | 3 044 014 | „ |
| Total: | 7 968 713 | kilos. |

If the value of the German export is, on the average, taken in round figures as 2,50 marks per kilo, an estimated unit-price of the French products of perfumery at double that figure will not be far from the mark, because as a rule more articles of a high selling-price are exported from France. On this basis the value of the French export of 1900 may be taken as roughly 40 000 000 marks, against say 15 000 000 marks for Germany.

The export of essential oils from France has in the last few years declined slightly. It amounted to

| | | | | | | |
|---|---|---|---|---|---|---|
| 540885 | kilos, | value | 16064650 | francs | in | 1897 |
| 540513 | „ | „ | 16366645 | „ | „ | 1898 |
| 440800 | „ | „ | 13169000 | „ | „ | 1899 |
| 498000 | „ | „ | 15214406 | „ | „ | 1900 |

There has again been a very brisk trade this year with the United States of America, where the consumption of essential oils increases from year to year. The manufacture of toilet-soaps and perfumes in that country is in a very flourishing condition. In 1902 the following quantities of essential oils were imported: —

| | | | | | |
|---|---|---|---|---|---|
| Oil of bitter almonds . . | 8370 | pounds, | value | 10520 | $ |
| „ „ anise . . . . . . | 79810 | „ | „ | 93520 | „ |
| „ „ the *Aurantiaceae* . | 99886 | „ | „ | 166651 | „ |
| „ „ lemon . . . . . | 391485 | „ | „ | 282092 | „ |
| „ „ caraway . . . . | 114206 | „ | „ | 13582 | „ |
| „ „ cinnamon . . . | 83558 | „ | „ | 49436 | „ |
| „ „ citronella . . . | 643033 | „ | „ | 118430 | „ |
| „ „ fusel . . . . . . | 2606979 | „ | „ | 137006 | „ |
| „ „ lavender and spike | 124075 | „ | „ | 114691 | „ |
| „ „ neroli . . . . . | 7761 | „ | „ | 64963 | „ |
| „ „ orange . . . . . | 79160 | „ | „ | 104159 | „ |
| „ „ rosemary . . . | 38414 | „ | „ | 18019 | „ |
| „ „ rose . . . . . . | 58759 | „ | „ | 257530 | „ |
| „ „ thyme . . . . . | 40080 | „ | „ | 25944 | „ |
| Other essential oils . . | 185855 | „ | „ | 307728 | „ |

In most countries across the seas, the economic situation is about the same as at the time of our April Report. A matter of great importance for the trade with the Far East, is the opening of postal communication by the Transiberian railway via Port Arthur, which has already led to a saving of several days as compared with the transmission by sea, and which will reduce the time still further when a regular express-service has also been established on the Asiatic portion of the route.

The sale of our products in Germany and Austria has been normal. The movement against the abuse of alcohol has brought the manufacture of so-called non-alcoholic beverages to the front, — a question whose solution is not at all simple. Our trade with the other civilised countries of Europe was very animated, the more so as it was supported by favourable conditions in the prices of a few of the most important articles of this branch.

The abnormal weather-conditions which prevailed during the summer in various countries producing vegetable and other raw materials for our industry, have only in a few individual cases exerted an unfavourable influence; most of the products which come under consideration have thriven well.

We have again added as an Appendix to this Report the following interesting work: —

On the pharmaco-therapeutics of the *Aethereo-oleosa,*

by

Professor Dr. R. Kobert,

Director of the Institute for Pharmacology and Physiological Chemistry,
University of Rostock.

We are greatly indebted to Professor Kobert for thus adding to the value of our Reports.

**Almond oil, bitter.** In the peculiar situation created for this article by the artificial products free from chlorine, only those can fully guarantee a pure natural product who manufacture it themselves. There are no certain means for detecting an admixture of benzaldehyde, free from chlorine. In harmony with this state of affairs, the quotations for "genuine" oil also differ from each other, and if there is a case where cheap offers should not be an inducement for buying, it is with this oil. Whoever requires a cheap oil should buy the reliable genuine distillate, and cheapen it himself by a proportionate admixture of benzaldehyde free from chlorine, instead of purchasing from the second hand, for the sake of a difference in the price of a few shillings per lb., an oil which does not carry the slightest guarantee. Quite recently an oil was again submitted to our testing-laboratory, which showed a powerful chlorine-reaction, in spite of the fact that it was sold as genuine oil. Here it was therefore not even considered necessary to supply an oil free from chlorine, and a product of the most common quality, having a value of 3 marks per kilo, had been substituted.

Apricot-kernels form the principal raw material for oil of bitter almonds, and there is every justification for this, as the essential oil does not differ in any way from that made from bitter almonds, and provides a decidedly cheaper substitute.

**Almond Oil, pressed from apricot-kernels.** The apricot-harvest in Syria has given a good result. The yield is estimated at about 4000 bales of 100 kilos, or say 400 000 kilos, and moderate prices are anticipated. Owing to firm purchases we are in a position to make contracts for large quantities of this oil at exceptionally low prices, and we shall be pleased to quote on receipt of enquiries.

Mersina, Mogador and Salonica kernels come cheaper than the Syrian quality, but they are not worked up by us. The Californian kernels no doubt yield a large quantity of oil, but the latter has a peculiar flavour which is not admired. In view of the enormous growth in the shipment of Californian apricot-preserves, the production of kernels may possibly be capable of a considerable increase. At this moment we estimate it at about 80000 kilos per annum.

**Oil of Ambrette-seeds.** It was feared that the natural phenomena in Martinique would have led to a scarcity in ambrette-seeds, but this has not been the case. On the contrary, there has never before been such a large supply on the market as at present. Sample-parcels from the Comores have recently also been introduced into commerce.

As the consumption is comparatively small, every new source of supply may affect the value.

Liquid oil of ambrette-seeds, which we were the first to introduce into commerce, is in great demand. It can be worked up to greater advantage than the ordinary concrete oil.

**Anise Oil.** Up to the time of going to press we have learnt the following with regard to the harvest in the various countries where anise is cultivated: —

In Russia about the same quantity of anise has been cultivated as last year, but the result is decidedly worse. Heavy rains in May produced such a large growth of weeds in the fields, that these threatened to choke the seed which had just come up. By energetic weeding, however, the danger was averted. The fields recovered, and promised a good crop. But unfortunately the wet weather was followed in June and July, during the flowering season, by continued drought and hot winds, causing enormous damage which could not possibly be made good. The early seed has suffered most, the late seed somewhat less, but the latter also has not escaped.

Quantitatively the crop is estimated at little more than half that of last year, and as regards quality this year's seed leaves also much to be desired. It has a dark colour, is small-grained, contains much earth, and, with regard to the yield of oil, falls also considerably behind the 1902 seed.

The quantity of seed brought to the first market, which was held at Krassnoje on September 11th, was, in accordance with the prevailing conditions, infinitesimal, and amounted only to about one-tenth of last year's quantity. The prices ruled very high, but in view of the inferior quality, there was not much inclination to buy.

In Roumelia the cultivation of anise is constantly increasing, and this may ultimately have some effect on the general market-quotations of this article. The Roumelian seed is of a very uniform grain and very pure. Its aroma is exquisite. In view of the cheap prices, this year's harvest must have given a good result.

We have not yet received more detailed reports on the results of this year's harvest in Spain, whose product excels all others in point of quality. The price paid for this variety is so high, owing to its beautiful appearance and the incomparable purity, that it cannot come under consideration for the oil-manufacture.

If the production of anethol depended on one single variety of anise, there is no doubt that the price of this important product would have to be raised. But this is, fortunately, not the case and we are in a position to offer our anethol, the quality of which is unsurpassed, still at moderate terms. As is well known, we were the first to take up the manufacture of anethol.

**Apopin Oil.** On this hitherto unknown oil, a treatise has appeared in Japanese language¹) which we have had translated, and of which we give here a somewhat abridged but partly literal reproduction. It is entitled: "On the constituents of an essential oil of Formosa", "apopin oil", or "Shu-yu", by K. Keimazu, translated by T. Kumagai.

In Formosa an essential oil is produced, whose odour greatly resembles that of camphor, and which the natives call "Shu-yu". When Professor Schimoyama undertook a scientific journey in that district, he found that the name "Shu-yu" (evil-smelling oil) was not very appropriate, and he gave to the oil the name "apopin oil", *Oleum apopinense,* in view of the producing district Aupin. This oil is produced in Central Formosa, and also in the North Eastern districts, the quantity, as I have been told, being about 4 to 5 million kin per annum. But as the production of this essential oil is entirely in the hands of the natives, it was up to now impossible to obtain more definite data as to the quantity, and there is also some uncertainty as to the plant itself. As the collection of preparations at the University only possesses one specimen of the plant, it is difficult to compare it with other camphor trees and to come to a decision. There appears, however, to be no doubt that the plant which yields apopin belongs to the *lauraceae.* As the natives mix this "Shu-yu" with oil of camphor, and place it on the market as camphor oil, the Formosan Government has recently taken stronger measures by exercising more strict control over the cutting of the trees and the destillation of the oil.

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¹) Journal of the Pharmaceutical Society of Japan No. 253, March 1903.

## I. Fractional destillation of "Shu-yu".

Apopin oil represents a colourless, clear oil, which turns brown on exposure to the air. Its specific gravity ascertained with the pycnometer, is 0,9279, at 15° C. When examined with the polarisation apparatus according to Wild, this oil shows, in a tube of 100 mm, a rotation of 17° 19′ to 17° 06′ to the right. In the fractional distillation of 1000 parts by weight of the oil, the following fractions were obtained:

| | | |
|---|---|---|
| I. | up to 180° | 29 parts |
| II. | 180°—190° | 63 „ |
| III. | 190°—195° | 109 „ |
| IV. | 195°—200° | 209 „ |
| V. | 200°—205° | 213 „ |
| VI. | 205°—210° | 151 „ |
| VII. | 210°—215° | 107 „ |
| VIII. | over 215° | 79 „ |
| IX. | Loss and $H_2O$ | 40 „ |

## II. Detection of Camphor.

Fractions IV, V, and VI were repeatedly submitted to fractional distillation, until white crystals separated out in the receiver, which, after drying on tiles, showed the melting point of camphor 176°. For further identification the oxime was produced according to Auwers' process. It crystallised from alcohol in beautiful rhombic crystals, and had the melting point 117°—118°. The alcoholic solution of the oxime turned the polarised light to the left, whilst camphor turns it to the right. From this it follows that the camphor isolated by me from "Shu-yu", is identic with the *lauraceae* camphor of Japan.

## III. Detection of Eugenol.

By extracting the portions of the oil boiling above 215° (fraction VIII) with 5 per cent. potash liquor, a tar-like product separated out, which had the odour of eugenol, but also possessed an additional empyreumatic odour. In order to demonstrate the presence of eugenol, the benzoyl compound was prepared by Schotten-Baumann's method; this melted, after purification, at 69°, the melting point of benzoyl eugenol.

## IV. Detection of safrol.

The oil freed from eugenol was repeatedly shaken with water, dried, and then submitted to repeated distillation. The distillate of 225°—235° was shaken in the "ice-cream" apparatus, when a pasty mass was obtained. It was collected on a filter, pressed on a tile, and again submitted to distillation. The fraction passing over between

230° to 233°, which had the characteristic safrol-odour, was collected; it showed the specific gravity 1,10. The substance obtained in this manner crystallises without cooling it to —25°; the melting point lies between 8° and 10°. It should, however, be mentioned, that the substance obtained after only one single distillation does not by any means possess the tendency of crystallising at a low temperature; on the other hand, the parts which have once crystallised appear to be readily capable of recrystallisation.

In order to identify this substance with safrol, isosafrol was prepared by Eykman's method, and by oxidising the latter, piperonal of the melting point 37° was obtained.

When the safrol was oxidised with potassium permanganate according to Tiemann, homopiperonylic acid melting at 127° to 128° was obtained.

## V. Detection of cineol.

Fractions, I, II, and III were combined and distilled. The portions passing over at 174° to 179° were three times submitted to fractional distillation, when finally a fraction of 175° to 177° was obtained; specific gravity = 0,9024.

A small quantity of this substance was placed on a watch-glass, and while gently heated some iodol added, when pretty crystals were obtained which, after re-crystallisation from alcohol, showed the melting point 120°. The body therefore represented the double-compound of cineol with iodol. In order to supply a further proof of the presence of cineol, the hydrobromide compound of cineol was prepared, whose melting point lay at 53° to 54°. Although the melting point of cineol hydrobromide is given in literature as 56°, I believe that my substance was as a matter of fact, cineol hydrobromide.

## VI. Detection of dipentene.

As already mentioned, pure cineol possesses the specific gravity 0,9267, the portion identified by me as cineol showed the specific gravity 0,9024. This important difference in the data must, I think, be attributed to the fact that in the fraction under consideration a terpene was present (viz., limonene or dipentene, which both possess the specific gravity 0,844) which passes over with cineol at the same temperature. In order to detect the presence of this compound, the tetrabromide was produced.

According to Wallach, it is prepared by dissolving the terpene in glacial acetic acid and adding bromine; but this method necessitates an absolutely anhydrous substance, so that the experiments made by this process were all unsuccessful.

Finally I employed Baeyer-Villiger's method.

20 grams of the substance were dissolved in 20 grams amyl alcohol and 80 cc. ether added to this solution; it was then strongly cooled in ice, and bromine added in drops until the bromine-coloration remained. Thereupon the solution was poured into a crystallising dish and put away. Although the authors state that when the ether is evaporated the bromide is precipitated in granular crystals, I was only able after about a week to detect on the bottom of the dish some small white crystals which increased in quantity on prolonged standing. These were then collected, washed with ether, and recrystallised from alcohol. The melting point of this compound lay at 124° to 125°, and therefore proved the identity with dipentene.

### Final observations.

In this manner I was able to detect in "Shu-yu", and isolate from it, as ketone, camphor: as oxide, cineol; as phenol ethers, safrol and eugenol; as terpene, dipentene. The object I had in view of detecting pinene in the fractions which I had obtained, could unfortunately not be accomplished on account of loss caused by the method of examination. But as a matter of fact, the portion 195° to 202° contains a more or less large quantity of this body. If in this portion camphor and terpene formed a mixture, a gradual rise in the temperature should become apparent after repeated distillation, (an occurrence which I was unable to observe), or other constituents should be present. For this reason I made experiments with reference to linalool, which were unsuccessful; this fraction showed in the polarisation-apparatus a dextrorotation of $4^\circ\ 48'$ in a tube of 100 mm; specific gravity = 0,9056, at 15°.

Although the study of "Shu-yu" with regard to its constituents is still incomplete, I was forced to discontinue the examination on account of lack of material. I hope, however, that other chemists will deal with this interesting subject, and I await their results. Finally, I would express my warmest thanks to Professor Shimoyama for his friendly advice.

**Bay Oil.** From the Director of the Botanical Gardens of Victoria (Cameroons) we received an oil distilled from the green leaves of *Pimenta acris*, which entirely resembles West Indian bay oil in its properties, as will be seen from the following data: $d_{15^\circ} = 0{,}9753$; $\alpha_D = -3^\circ$; phenol-content: 64 per cent.; soluble in 90 per cent. alcohol, at first clear, with opalescence if more than one volume alcohol is added; this opalescence remains even when the oil is strongly diluted. As the oil also possesses a pleasant, powerful aroma, it might possibly become a competitor of the West Indian distillate. *Pimenta acris* is said to thrive well in the Cameroons, and the cultivation on a large scale might therefore be found remunerative. It remains, however, an open question, whether it is more expedient only to ship the bay leaves from the Cameroons, or to take up the distillation of the leaves on the spot.

**Camphor Oil.** In the "Deutsche Japan-Post" of July 18th we find the following particulars concerning the Camphor Monopoly Act which for a long time has excited the people's minds: —

> When the Japanese Government in 1899 introduced the camphor-monopoly in Formosa, it drew up an estimate of the income to be derived from it, basing its calculations on the average quantity of camphor produced in Formosa during the last few years. But it soon became clear that this calculation was deceptive, for the monopoly had brought about such an increase in the prices of camphor, that the camphor-production in Old Japan, which for many years had been on the decline, received a strong impulse. The export of camphor from Old Japan grew to wholly unexpected dimensions; it rose from 24000 piculs, value 1,2 million yen, in 1898, to 42000 piculs, value 3,9 millions yen, in 1901, — an increase in three years of 75 per cent. in quantity and 225 per cent. in value.
>
> As, however, the demand for camphor on the world's market is, as a matter of fact, but limited, the increase in the production in Old Japan was naturally bound to influence the sale of Formosa camphor considerably, and for this reason the profit of the Formosa Government from the monopoly fell very much below the expectations.
>
> In order to remove this evil, the Governor-General of Formosa had already urged for many years that the camphor-monopoly should also be extended to Old Japan. He finally succeeded in enlisting the sympathies of the Cabinet for this plan, and in the Session just closed the Japanese Parliament has now adopted a bill to this effect, which it had rejected only last year.
>
> The Act which has thus come into existence has been published in the Japanese Official Gazette of the 17th June. Its title is "Crude Camphor and Camphor Oil Monopoly Act" and it comes into force on October 1st of this year. The various camphor-regulations, etc., issued up to now for Formosa, are cancelled by this Act, and the camphor-question has now been settled on a uniform basis for the whole of Japan.
>
> According to the new law the production of, and trade in, camphor in Japan will be carried on as follows: —
>
> Producers of crude camphor and camphor oil will require a licence for carrying on their trade, which can at any time be revoked in case they should commit acts contrary to the law. They must keep exact accounts of the manufacture, and submit to a most stringent control on the part of the monopoly-officials. They must deliver their camphor-products to the Japanese Government, and will receive against this a compensation which is left to the discretion of the Government. The amount of compensation is, however, published in advance. The producers are not allowed to refine crude camphor; this is the exclusive right of the State.
>
> The Government now sells the camphor which it has acquired, mostly at a fixed price, in exceptional cases also by auction. The selling-price is of course so calculated, that it covers all expenses of storage, transport, loss of weight (which in the case of camphor, as is well known, is a matter of great importance), refining, etc., and that moreover a very considerable profit is left for the Government.

The export of camphor is only allowed from ports indicated by the Government. The Government has also the right to restrict the production, when a disparity between supply and demand is to be feared. In the case of unrest in the native districts of Formosa, the camphor-production there may be entirely prohibited.

The crude camphor and camphor oil which at the time the Act comes into force are in possession of the camphor-producers or merchants in Old Japan, must also be delivered up to the Japanese Government.

Contraventions of the law are punished with heavy fines and with confiscation of the camphor which has been adulterated, or fraudulently held back, etc.

The above are the more important regulations of the Act, which will no doubt shortly be supplemented by detailed working-instructions.

It remains to be seen to whom the Japanese Government will entrust the exploitation of the monopoly. At present it appears to be somewhat in a dilemma. Many weighty voices have been heard against a new agreement with the old proprietors, but on the other hand, not many applicants will be found willing to accept the considerable risk connected with such an enormous enterprise. Up to this moment nothing is known on this point.

It is as yet too early to express an opinion as to how the prices of camphor and camphor oil will shape themselves under the new conditions.

With regard to the manufacture of artificial camphor, which is known to have been called into existence in America, we have heard nothing further since our last Report. This venture, therefore, does not seem to have as yet come into operation.

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We have been induced by repeated requests on the part of our clients to have the flash-point of light and heavy camphor oils determined in an officially tested apparatus. The results were as follows: —

| | Light camphor oil | Heavy camphor oil |
|---|---|---|
| Height of the barometer . . | 750 mm | 750 mm |
| Temperature at commencement | 18° | 18° |
| Flash-point . . . . . . . . | 55° | — |

As the flash-point of heavy camphor oil could not be ascertained with Abel's apparatus, the oil was heated, for the purpose of firing, by means of an oil-bath, and the flash-point tested in the same manner from degree to degree. An actual firing with explosive extinction of the ignition flame could not be observed, but the oil developed vapours commencing at 160°, which could be fired by applying the ignition flame.

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The fact that terpineol is present in camphor oil has been proved by us many years ago¹). At that time we confined ourselves for its

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¹) Report April 1888, 9; Report April 1889, 8.

detection to the reaction products which portions of oil yield boiling between 215° and 220°. It is well known that the oil contains considerable quantities of camphor and safrol, i. e. two bodies whose boiling points lie so close to that of terpineol, that it is not possible to bring about a separation of this alcohol in a state which is at least to some extent pure, even if the fractional distillation is repeated over and over again. We have now succeeded in isolating terpineol from oil of camphor in the pure state, and that as a solid product, by removing in the first place the camphor as much as possible from the mixture of the three bodies. For this purpose, 600 grams of a camphor oil fraction whose boiling point was below that of safrol, were fractioned twice to three times *in vacuo*, and the portions boiling between 98° and 103° (10 mm pressure) thus obtained treated in alcoholic solution with hydroxylamine. After driving off the alcohol, the oil which had not reacted was separated by means of steam from the camphor oxime which had been formed. By repeated rectification of the oil at atmospheric pressure we obtained fractions boiling at 216° to 218°, 218° to 219°, and 219° to 221°, of which particularly the last two, when kept in a freezing mixture, formed viscid oils, and congealed in crystal-form when inoculated with a terpineol crystal. The crystals, recrystallised from dilute alcohol, melted at 34° to 35°. The physical constants were as follows: $d_{15^\circ} = 0{,}9391$; $\alpha_{D21^\circ} = -2^\circ 45'$ (20 mm); boiling point 99° to 100° (9 to 10 mm pressure). The isolated terpineol was therefore l-terpineol of the melting point 35°. The mother liquors of the crystallised body served for the production of the phenyl urethane of the melting point 112°, and also of the nitroso-chloride. The piperidine derivative of the latter melted at 158° to 159°.

The final proof of the presence of terpineol in camphor oil having now been supplied, we have taken pains to demonstrate once more the presence of camphene[1]). In 1894 this terpene had already been detected in our laboratory in oil of camphor[2]), but, as the presence of large quantities of pinene renders the detection of camphene difficult, the result obtained by us was not quite free from objection. A separation of these two hydrocarbons by fractional distillation is not possible, but this time, when working up the first runnings of a very large quantity of camphor oil, we were able by long-continued fractional distillation to separate two principal portions, of which the one consisted chiefly of pinene, whilst the other contained large quantities of camphene.

The portion boiling between 155° and 157° was chiefly pinene; $\alpha_D + 25^\circ 35'$; $d_{15^\circ} = 0{,}865$. The nitroso chloride obtained from it,

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[1]) This examination was made in our laboratory by Mr. Zadig, of Malmö.

[2]) Report April **1894**, 69; Journ. f. prakt. Chemie II. **49** (1894), 19.

when treated with benzylamine, yielded pinene nitrolbenzylamine melting at 123°.

As camphene boils at a slightly higher temperature than pinene, the fraction boiling between 161° and 164° was employed for the detection of this terpene. The fraction had the following constants: $d_{15^\circ} = 0{,}8678$; $\alpha_D + 26^\circ\ 5'$. One part of this fraction was heated for 2 to 3 hours to 60°—70° with 3 parts glacial acetic acid and a few drops 50 per cent. sulphuric acid, and the mixture then poured into water. The oil separating off contained isobornyl acetate, which was already evident by the odour of the reaction-mixture. In order to enrich this ester, the separated oil sufficiently washed with soda and water was fractionated *in vacuo.* The fraction richest in ester then yielded on saponification with alcoholic potassa, solid isoborneol of the melting point 210°. From 440 grams of the camphor fraction 23 grams isoborneol were obtained. For the further detection a part of the isorborneol was again converted into camphene by means of zinc chloride in benzene solution. This melted at 50°. Another part of the isoborneol, when oxidised with chromic acid in glacial acetic acid, yielded camphor of the melting point 176°; $(\alpha)_D$ in alcoholic solution $+ 3^\circ\ 23'$. The oxime produced from it melted at 118°, and was lævorotatory. The fraction 161° to 164° of camphor oil behaves consequently as a pinene fraction containing camphene. It was further possible to detect in the fractions boiling about 170° (by means of Hirschsohn's iodol-cineol reaction), cineol, which had already been detected earlier by the hydrobromic acid method.

**Oil of Carana Elemi Resin.** A. Tschirch and A. Saal[1]) communicate an examination of carana elemi resin from *Protium carana* (Humb.) L. March. The resin collected in 1887 by A. Gaillard near San Fernando de Atabapo in Venezuela, had a greenish-yellow colour and reminded of the odour of fennel, dill, and lemon oil. It dissolves in warm alcohol and also in the other usual solvents, such as ether, chloroform, benzene, etc. By successive extraction of the ethereal solution of the resin with ammonium carbonate and soda solution, several acids were isolated, viz. isocareleminic acid $C_{40}H_{56}O_4$, melting at 75°; careleminic acid $C_{40}H_{56}O_4$, m. p. 215°; and carelemic acid $C_{57}H_{36}O_4$, m. p. 120°. There were also obtained: a product, caramyrin $C_{30}H_{50}O$, $\alpha_D \pm 0^\circ$, m. p. 175°, identic with amyrin which is derived from other elemi-varieties, and which by means of benzoyl chloride could be split up into an $\alpha$- and a $\beta$-amyrin of different melting points, and an essential oil to which the resin owes its odour. This oil boils chiefly from 170° to 172°. No further data of its properties are given.

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[1]) Arch. d. Pharmacie **241** (1903), 149.

**Caraway Oil.** According to the reports received from a confidential source, the caraway-harvest in Holland has suffered rather much from the bad weather, as only a part has been gathered in the dry state. It is said that about 7,500 acres have been under cultivation which, at a yield of 12 bales per acre, would give a total result of 90000 bales. The old stocks were estimated in the middle of July at 30000 bales; there will consequently be no lack of caraway. The sample truck-loads of new seed which have been received show an excellent quality. The price has so far remained without change at a low level, so that there are no grounds for an alteration in the prices of the oil.

Up to the present no offers of Swedish caraway have come in. As a rule this seed is not ready for shipment until November. The price for the East Prussian article is still too high.

**Cassia Oil.** Nothing of any consequence whatever can be reported on this important subject. The prices have slowly risen during the last months, and there is reason to think that they will still run somewhat higher in the future. The present value may still be characterised as a low one, and taken advantage of for laying in an abundant supply.

Our stock consists exclusively of direct-imported goods containing 80 to 85 per cent. aldehyde.

**Oil of Cassie-flowers.** We have already on various occasions reported on the essential oil of cassie-flowers¹). The examinations which hitherto have been made more particularly with the oil obtained from the flowers of *Acacia farnesiana,* have also been extended to other oils of this species which are important for purposes of perfumery; in the first instance we have occupied ourselves with the essential oil of *Acacia cavenia* Hook. et Arn. This oil, which is prepared in the South of France by extracting the flowers with petroleum ether, is, like all flower-extracts, not a pure essential oil, but a salve-like mass consisting chiefly of as yet unknown odourless vegetable waxes and other extractive matter, and only for a small part of oil which can be driven off with steam.

The flower-extract from *Acacia cavenia* known in the trade as "Cassie Romaine", which served for the examination, was supplied by Mr. Jean Gras of Cannes.

In order to obtain the essential oil, we distilled 1,6 kilos of the mass with steam, when a brown oil with a strong cassie-like odour was obtained, of which the bulk could be dissolved in dilute caustic

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¹) Report April **1899**, 58; April **1901**, 18; April **1903**, 17. The physical constants of the pure essential oil of *Acacia farnesiana* obtained from cassie pomade, are as follows: $d_{15^\circ} = 1{,}0475$; $\alpha_D \pm 0^\circ$; $n_{D_{20^\circ}} = 1{,}51331$.

soda. The part soluble in the lye amounted to 94 grams, and consisted of 73 grams eugenol, and 21 grams salicylic acid of the melting point 156°. The portion of the oil remaining after the treatment with soda, after further steam distillation and rectification *in vacuo*, amounted to 103 grams.

Apart from salicylic acid, which in this oil, like in that of *Acacia farnesiana*, occurs in any case chiefly as methyl ester of salicylic acid, only a small quantiy of a liquid, as yet unknown, acid was detected.

The eugenol, identified more closely by its benzoyl compound melting at 69° to 70°, and also by conversion into methyl eugenol and oxidation of the latter into veratric acid, had the following constants: Boiling point 253° to 254°, at 747 mm; $d_{15^\circ} = 1{,}0702$; $n_{D19^\circ} = 1{,}54205$.

Isoeugenol, which we had previously detected in ylang-ylang oil¹), was not present. The portions of the oil not dissolved in soda liquor, distilled at 3 to 4 mm pressure from 20° to over 115°. In the lowest boiling fractions there were present hydrocarbons with an odour like petroleum ether, which undoubtedly originated from the petroleum ether employed for the extraction. Terpenes could not be detected in them. On further fractionating the oil was split up into the following four principal fractions:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| fraction | a) | 40° | to | 70° | = | 3 | grams |
| „ | b) | 70° | to | 80° | = | 42,5 | „ |
| „ | c) | 75° | to | 95° | = | 16 | „ |
| „ | d) | 95° | to | 105° | = | 34 | „ |

Fraction a, which had a distinct odour of benzaldehyde, yielded on treatment with semicarbazide the benzaldehyde semicarbazone melting at 214°.

Fraction b consisted chiefly of benzyl alcohol, which was separated from it by means of the phthalic anhydride method. The benzyl alcohol thus obtained showed the following constants: boiling point 206° to 207°, at 754 mm; $d_{15^\circ} = 1{,}0457$; $n_{D20^\circ} = 1{,}53723$. The phenyl urethane produced from it melted at 77°.

0,1237 g yielded 0,3355 g $CO_2$ and 0,0684 g $H_2O$.

| Calculated for $C_{14}H_{13}O_2N$: | Found: |
|---|---|
| C = 74,00 per cent. | 73,97 per cent. |
| H = 5,73 „ „ | 6,14 „ „ |

The hitherto unknown benzyl phthalic ester acid which is also suitable for the identification of benzyl alcohol, melts at 106° to 107°. It is readily soluble in chloroform, alcohol, and ether, and crystallises from benzene in beautiful prisms. In the portions of fraction b which do not react with phthalic anhydride, linalool and decylic aldehyde

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¹) Report October **1901**, 53.

appear to be present, but these two bodies could not be detected with sufficient certainty.

Fraction c, when treated with phthalic anhydride, yielded an alcoholic mixture in which geraniol was present in preponderating quantity. In addition to this, benzyl alcohol could also be detected. The geraniol was converted into the diphenyl urethane[1]) melting at 81°, and the latter analysed.

0,1315 g of the substance yielded 0,3800 g $CO_2$ and 0,0920 g $H_2O$.

| Calculated for $C_{23}H_{27}O_2N$: | Found: |
|---|---|
| C = 79,05 per cent. | 78,80 per cent. |
| H = 7,75 „ „ | 7,77 „ „ |

This proves the presence of geraniol in oil of cassie flowers.

The fraction from which the geraniol had been removed reacted with bisulphite liquor, and yielded a small quantity of an aldehyde which on oxidation with dilute solution of potassium permanganate was converted into anisic acid (melting point 180°). This aldehyde proved to be anisic aldehyde, and it was found in larger quantity in the higher-boiling fractions. The analysis of the silver salt produced from the anisic acid gave the following results:

0,1658 g yielded 0,0688 g Ag
0,1272 „ „ 0,1720 „ $CO_2$ and 0,0355 g $H_2O$

| Calculated for $C_8H_7O_3Ag$: | Found: |
|---|---|
| C = 37,06 per cent. | 36,88 per cent. |
| H = 2,70 „ „ | 3,10 „ „ |
| Ag = 41,70 „ „ | 41,50 „ „ |

On examining fraction d, there were found, in addition to eugenol which was removed by treatment with soda liquor, as principal constituents eugenol methyl ether and anisic aldehyde; there were also proofs of the presence of a violet-ketone, perhaps ionone or irone. In order to obtain first of all the anisic aldehyde and other aldehydes and ketones, the fraction was treated with semicarbazide. The semicarbazide-compound of anisic aldehyde thus obtained melted after recrystallisation from alcohol at 203° to 204°. The analysis gave the following values:

I. 0,1736 g of the substance yielded 0,3564 g $CO_2$ and 0,0944 g $H_2O$
II. 0,1622 „ „ „ „ „ 0,3326 „ $CO_2$ „ 0,0866 „ $H_2O$

| Calculated for $C_9H_{11}O_2N_3$: | Found: | |
|---|---|---|
| | I. | II. |
| C = 55,99 per cent. | 55,99 | 55,92 per cent. |
| H = 5,70 „ „ | 6,04 | 5,93 „ „ |

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[1]) Erdmann and Huth, Journ. für prakt. Chemie II. **53** (1896) 45.

The anisic aldehyde regenerated from the semicarbazone yielded on oxidation anisic acid. Apart from anisic aldehyde, which up to now had not yet been met with in any flower oil[1]), no other aldehydes and ketones could be detected with certainty with the available material, but the pronounced violet odour of the higher fractions points to the presence in the oil of ionone or irone, or a similar violet-ketone. This is all the more probable, as we have made the same observation with the essential oil of *Acacia farnesiana.* We are now engaged on a further examination of this ketone.

The bulk of the remaining oil, after separating the anisic aldehyde, distilled from 245° to 255°, and proved to be eugenol methyl ether. On oxidation with potassium permanganate it yielded veratric acid of the melting point 178°. The silver salt of the latter was analysed:

0,2692 g contained 0,1004 g Ag = 37,30 per cent. Ag
Calculated for $C_9H_9O_4Ag$ = 37,37 " " "

From the methoxyl-determination of the acid the following value can be calculated:

0,1582 g acid yielded 0,3904 g Ag I = 32,55 per cent. $OCH_3$
Calculated for $C_9H_{10}O_4$ = 34,06 " "

The examination of the essential oil of *Acacia cavenia* (which is still continued) proves therefore that the oil has the following composition: about 50 per cent. phenols, chiefly eugenol; about 8 per cent. methyl ester of salicylic acid, and about 42 per cent. non-phenols. In the latter the following compounds were detected:

Benzyl alcohol (about 20 per cent.), geraniol, anisic aldehyde, eugenol methyl ether, linalool (?), decylic aldehyde (?), violet-ketone (ionone, irone) (?).

**Oil of Chamomile.** Both distillates are in stock in fresh quality. The blue oil of the common chamomile has remained at the same price, whilst the distillate of the Roman chamomile can be quoted a little lower.

**Oil of Chamomile, Roman.** Up to the present it was an open question whether tiglinic acid, which had previously been detected by various chemists in the oil of Roman chamomile, had to be regarded as an original constituent of the oil, or whether the detection of this acid must be attributed to a conversion of the angelic acid which occurs in this oil in considerable quantity. E. E. Blaise[2]) now has been able to prove that tiglinic acid is not a constituent of the oil.

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[1]) In addition to the well-known hawthorn, *Crataegus oxyacantha* L., the flowers of *Viburnum Tinus* (Laurustinus) and also of *Erica arborea* have in a remarkable degree the odour of anisic aldehyde.

[2]) Bull. soc. chim. III **29** (1903), 327.

According to this author the saponification of 500 grams of oil, at ordinary temperature, produced 190 grams crude acid; of this 90 grams were angelic acid, 25 grams isobutyric acid, and considerable quantities polymerised methacrylic acid which remained as a residue, in the form of a colourless powder, on distillation of the acids. The neutral products of the saponification formed 25 grams isoamyl alcohol, 80 grams active hexyl alcohol, 33 grams anthemol, and (contrary to Koebig's[1]) observations, who believed to have recognised isobutyl alcohol as a constituent of the oil) 30 grams normal butyl alcohol. The latter was identified by the boiling point, and by its phenyl urethane melting at 55° to 56°.

**Cinnamon Oil, Ceylon.** The value of this important article has undergone a sharp decline since cinnamon-chips have been offered at prices which have never been known before. This appears to be due to continuous overproduction, of which the effect is still increased by the fact that large parcels are shipped to Europe and are finally sold there at absurd prices. It is not believed that this state of affairs can continue for any length of time, as cinnamon is an article beloved by speculators, and it may therefore not be out of place to make use of the present cheap prices in order to secure the requirements for a long time to come. The following statistics of the prices of the oil may be given in support of the above advice: —

| | | | |
|---|---|---|---|
| Value on October | 1st 1894 | 58 | marks per kilo |
| " " " | 1st 1895 | 70 | " " " |
| " " " | 1st 1896 | 70 | " " " |
| " " " | 1st 1897 | 75 | " " " |
| " " " | 1st 1898 | 72 | " " " |
| " " " | 1st 1899 | 76 | " " " |
| " " " | 1st 1900 | 76 | " " " |
| " " " | 1st 1901 | 68 | " " " |
| " " " | 1st 1902 | 62 | " " " |
| " " " | 1st 1903 | 50 | " " " |

Years ago, before we first of all commenced the distillation in Europe, when only exported oil was met with in commerce, the value of the latter was fairly stable, about 300 marks per kilo. Since 1873, when we first took up the distillation of Ceylon cinnamon oil, it fluctuated between 200 and 320 marks, according to the price of the raw material. From a product of luxury it has now become one of the most important articles of consumption of this branch.

At these low prices, the artificial Ceylon cinnamon oil (German Patent No. 134789) can of course hardly take a prominent place.

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[1]) Liebigs Annalen **195** (1879), 97.

**Oil of Cinnamon leaves.** It appears that important stocks of this Ceylon product have accumulated in Europe and America, as the shipments this year up to the beginning of August have fallen from 66536 ounces in the same period to only half, i. e. 33435 ounces. We are informed that the present value is unremunerative for the manufacturers. A smaller production will have to be reckoned upon.

**Oil of Cinnamomum pedatinervium.** E. Goulding[1]) has published an examination of the essential oil from the bark of a tree[2]) indigenous to the Fiji Islands (*Cinnamomum pedatinervium*). The pulverised bark yielded on distillation with steam 0,92 per cent. of a yellowish-brown oil with a pleasant spicy odour. The oil is optically active $[\alpha]_D = -4^\circ 96'$; $n_{D15^\circ} = 1{,}4963$; in a refrigerating mixture it did not solidify. At ordinary pressure it distilled from 180° to 255°. The saponification number was 4,4 = 1,5 per cent. ester, calculated for linalyl acetate. After acetylising the oil, the saponification number had risen to 115,8, which proves that the oil contains about 30,75 per cent. free alcohols of the formula $C_{10}H_{18}O$. From the result of a methoxyl-determination, the content of 1,16 per cent. $OCH_3$ could be calculated.

The chemical examination of the oil showed that the principal constituent (about 50 per cent.) is safrol; there were further detected: about 30 per cent. linalool, 10 to 20 per cent. unknown terpenes, 1 per cent. eugenol, and about 3 per cent. eugenol methyl ether (?).

The terpene fraction distilled from 167° to 172°; it had the specific gravity 0,8659 at 15°, the specific rotatory power $[\alpha]_D - 17{,}72^\circ$, and yielded a liquid dibromide.

From the linalool fraction citral was obtained by oxidation with chromic acid; this was proved by the conversion into $\alpha$-citryl-$\beta$-naphthocinchoninic acid. The eugenol obtained by extraction with dilute caustic soda-lye yielded the benzoyl compound melting at 70°. The presence of safrol was proved by oxidation of the corresponding fraction into piperonal and piperonylic acid, and also by isolating the safrol-$\alpha$-nitrosite (melting at 129° to 130°) according to Angeli and Rimini's method[3]).

**Citronella Oil.** In the Official Report of the Royal Botanic Garden in Ceylon it is explicitly stated that the citronella-oil industry is still in a very depressed condition, and shows a decrease of about 15 per cent. in the year 1902. The continual adulteration of this

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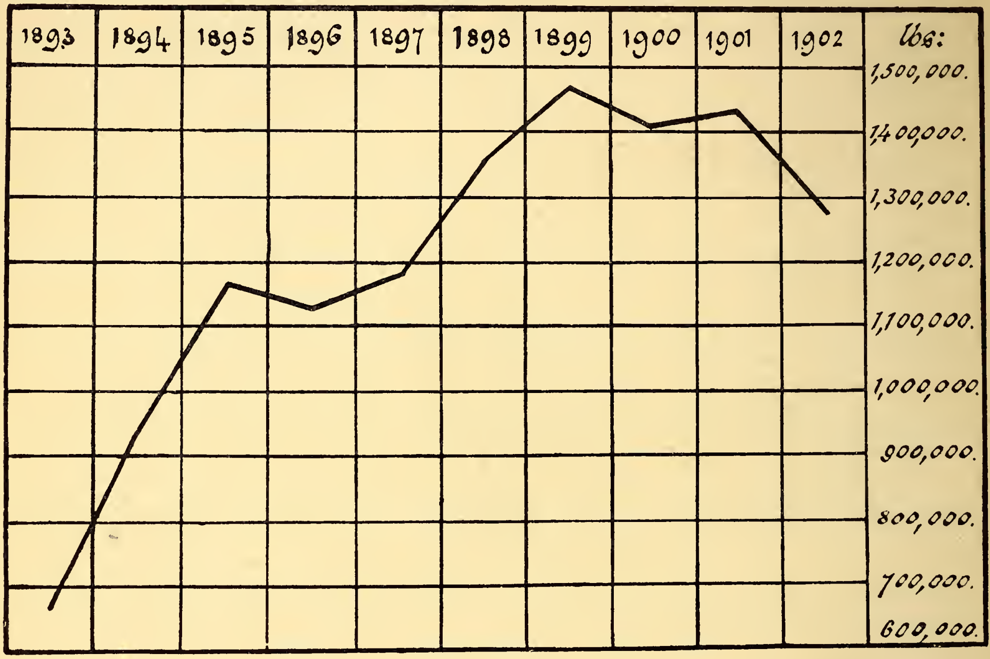
[1]) The constituents of the volatile oil of the bark of *Cinnamomum pedatinervium* of Fiji. Thesis, London 1903.

[2]) The tree has been described by Berthold Seemann in his Flora Vitiensis, p. 202.

[3]) Gazz. chim. ital. 25 II. (1895), 200.

oil with kerosene and other cheap oils, which is difficult to detect, has influenced the value, and the present quotation of 9 d. per lb. renders the cultivation unremunerative. As long as this practice is continued, no hope can be entertained of an improvement in the price.

The following diagram, which shows the annual export during the last decade, is given in the said Report: —



According to this diagram, the annual export has steadily decreased since 1899, but the falling off in this year will be even more pronounced, for, according to the official returns, the citronella-oil export from Ceylon up to August 3rd of this year, i. e. in 7 months, amounts to only 569 875 lbs., made up as follows: —

| | | |
|---|---|---|
| To the United States . . . | 328 136 | lbs. |
| „ „ United Kingdom . . | 152 877 | „ |
| „ „ Germany . . . . . . | 47 920 | „ |
| „ „ China . . . . . . . | 22 272 | „ |
| „ „ Australia . . . . . | 9 377 | „ |
| „ „ India . . . . . . . | 5 972 | „ |
| „ „ Singapore . . . . . | 3 321 | „ |
| Total | 569 875 | lbs. |

The export for the year 1903 would consequently amount to scarcely 1 000 000 lbs.

In order to detect in a practical manner the remarkable increase in the adulteration of citronella oil, we have by means of inquiries been able to ascertain that not all exporters experience in the same degree the difficulty of obtaining oils which answer our test ("Schimmel's test"), but that in the severe competition in the purchase of the oil, the conditions are occasionally winked at in order to secure the parcel offered. A natural consequence is that the producers are spoilt by such tolerance.

One of the firms in the trade stated that our test, if correctly carried out, was quite sufficient to obtain a good oil; that the Galle native dealers know this perfectly well, and offer only unobjectionable qualities of oil to those purchasers who insist on the test being carried out correctly. For this reason we believe that if in the purchase of the oil the same care were again exercised as formerly, a normal quality of oil would soon be again the order of the day. The present state of affairs is most annoying for all who are connected with the citronella-oil trade.

The above-mentioned extensive adulteration of Ceylon citronella oil has recently led to the publication of a large number of communications[1]), which partly attempt to clear up the question of the character of the adulterant, and partly offer suggestions for remedying the evil. The general opinion is that on the one hand the rapid fall in the prices is the direct cause of the adulteration, and on the other, that the abnormally low prices without adulteration are quite impossible, as they cannot even cover the distillation-expenses. Under these circumstances the prevailing conditions have become absolutely untenable, so much so that the Government has been induced to take countermeasures. Thus, the question of the own cultivation of citronella-grass has been under consideration, in order to prove to the distillers that it is possible to supply a better quality of oil.

With regard to the adulterant, Parry maintains that resin-spirit is added to the oil, and he states inter alia that, clearly as a result of the publication of his notes, large quantities of resin-spirit have lately been exported from England to Ceylon, which are undoubtedly intended for dishonest purposes.

On the other hand, several persons well acquainted with the state of affairs in Ceylon declare that petroleum is the only adulterant which comes under consideration, and that mostly Russian petroleum (which can nowadays be readily obtained in Ceylon in any desired quantity) instead of the American oil which was at one time used. The differences between the two kinds of petroleum are believed to have led Parry to the erroneous view that it was a question of adulteration with resin-spirit.

This question is difficult to decide for this reason, that we have here to deal with bodies of very similar compositions, and that nothing

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[1]) The Chemist and Druggist **62** (1903), 630, 689, 985, 999.

definite is known about the quantities of resin-spirit imported in Ceylon, as in the custom's statistics resin-spiritis is included, along with a number of other oils, under the general designation of "oils, other".

On this occasion "Schimmel's test"[1] is blamed from various quarters as unreliable, it being said that pure oils occasionally do not pass the test, whilst other oils containing up to 15 per cent. petroleum make a clear solution with 80 per cent. alcohol.

We will not in this place discuss in how far these statements are correct, but we wish to point out that the solubility-test alone has naturally but a limited value, and will always give only general data, but that in such tests the ready practicability is one of the chief advantages. It is naturally impossible in such cases to prevent an occasional passing of adulterated oils. However this may be, the fact that the detection of the recent adulteration is in the first place due to "Schimmel's test", speaks volumes. The value of this test is fully admitted also by experts, and its retention recommended.

In addition to this, the specific gravity, and above all the geraniol and citronellal-content of the oil, are important factors. For this reason Parry and Bennett recommend to lay special value on these constants when examining citronella oil, and they give the following limits for Ceylon citronella oil, based on examinations of normal oils: $d_{15,5^\circ} = 0{,}900 — 0{,}915$; $\alpha_D = 0^\circ$ to $— 15^\circ$; total geraniol (geraniol and citronellal): above 58 per cent.

$d_{15,5^\circ}$ of the first 10% of the distillate (at 20 to 40 mm pressure *in vacuo*), not below 0,858.

$n_{D20^\circ}$ of the first 10% of the distillate (pressure as above) not below 1,4570.

Solubility: the oil must pass "Schimmel's test".

For the present we will leave it an open question in how far these requirements are justified, as we are expecting authentic samples from Ceylon, and numerous tests made by us with purposely adulterated citronella oils from Java led to a somewhat different result, and cannot therefore be included within the scope of these observations. We hope soon to be in possession of the material required for examination, and then to clear this matter up further.

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[1] According to our method of testing citronella oil, known as "Schimmel's test", the oil should make a clear solution with 1 to 2 vol. 80% alcohol at 20° C., which should remain clear even when 10 vol. alcohol of the same strength are added, or at most show a faint opalescence. Even after prolonged standing no drops of oil should separate from the solution. As regards the execution of the test we would point out, that turbid mixtures should only be shaken sparingly, as otherwise the oil becomes so finely suspended that insoluble parts only separate out after a very long time, which renders the observation more difficult. The time required for the observation should be about 12 hours, during which the temperature should be kept at about 20° C.

The examinations of a larger quantity of citronella oil, made by us with the view of ascertaining the character of the adulterant, are also approaching completion, and we expect soon to be able to communicate further details also on this point.

We find in the "Circular and Agricultural Journal", on page 81, that experiments have been made in the Royal Botanical Gardens of Ceylon, the principal producing country of citronella oil, with the cultivation of *Andropogon* species, in order to ascertain whether the cultivation of these grasses is also possible in the higher-lying districts of the island. The results obtained here with a few varieties of citronella-grass, which also grows wild there, have been successful, and justify the hope that it can be cultivated everywhere in Ceylon, even at altitudes up to 2,000 feet.

The cultivation, however, can only be remunerative if the present yield and price of citronella oil are raised; there is a prospect of this if the cultivation can be improved, and if the adulteration which is carried on with this oil in Ceylon on a large scale, can be suppressed. On this question of adulteration, which is of such importance for the citronella-oil trade, and to which we have now given our attention for years, the Director of the Royal Botanical Gardens will shortly issue a report. We are looking forward with great interest to the communications promised.

In the West Indian Islands the cultivation of different *Andropogon* species has now been attempted for some years, with a view of obtaining the essential oil of those plants. On several occasions we have already had before us samples of oils distilled there; they all differ from oils of other origin by a lower solubility in alcohol¹).

H. H. Cousins²) has recently reported on Andropogon oils which had been produced at the Hope Experiment Station in Jamaica. In the distillation of the fresh grass of *Andropogon citratus* D. C., one pound yielded one cc. of a golden-yellow oil of the specific gravity 0,8897 at 60° F., and the optical rotation — 1° 0′ in a 20 mm tube. The yield in the distillation of the citronella grass *Andropogon nardus* was nearly three times as much; here, 2,9 cc. oil were obtained from one pound fresh grass. The specific gravity of this oil was 0,8935 at 60° F., and the optical rotation + 17° 0′. As compared with the oils produced in Trinidad, the higher dextrorotatory power and lower specific gravity of the Jamaica oils are worthy of note.

**Oil of Cloves.** Up to the moment we are unfortunately still without any official report on the result of the last clove-harvest in Zanzibar and Pemba, and one has to rely exclusively on the information

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¹) Report April **1896**, 68; April **1902**, 48; October **1902**, 50; April **1903**, 49.

²) Jamaica. Bulletin of the Department of Agriculture Vol. 1 (March **1903**), 49.

received via Holland and England. According to the latter, a continuation of the upward movement in prices, which has now taken place without interruption for many months, is inevitable. Especially in Holland on the terminal market, the opinion is in favour of this article, and the greatest trouble is taken to explain the favourable situation by means of statistical comparisons. The particulars for the first six months of 1903 are as follows: —

| Stock of cloves in Holland on 1st July | 1903 | 1902 | 1901 | 1900 | 1899 |
|---|---|---|---|---|---|
| Bales | 38920 | 57039 | 67423 | 83251 | 81043 |
| Import from Jan. 1st to July 1st „ | 5000 | 4300 | 2700 | 17500 | 49000 |
| Deliveries „ „ „ „ | 14100 | 8800 | 10900 | 7000 | 4000 |

The total stocks of cloves on the three principal markets of the world were: —

| 1st September | 1903 | 1902 | 1901 | 1900 | 1899 | |
|---|---|---|---|---|---|---|
| Holland | 31865 | 51456 | 62960 | 74842 | 79373 | |
| London | 17130 | 16034 | 16310 | 21557 | 33516 | |
| New York | 9000 | 11000 | 13900 | 14700 | 16700 | |
| | 57995 | 78490 | 93170 | 111099 | 129589 | bales. |

According to these figures the situation is undoubtedly favourable, and the prices have advanced in proportion.

The movements in the prices on the principal markets since April are: —

in Hamburg from 72 marks to 135 marks per 100 kilos
„ Holland „ $19^{1}/_{2}$ florins to 40 florins per 50 kilos
„ London „ $3^{3}/_{4}$ d. to $7^{3}/_{4}$ d. per lb.

which is equal to an increase of 100 per cent.

In the quotations of oil of cloves a corresponding increase has now also occurred, and all those who have taken advantage of the low prices to lay in an abundant supply are to be congratulated. The opportunity is now past.

The demand for clove oil during the last few months was exceptionally strong, and could only be met by overwork.

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From the hand of E. C. Spurge[1]) a work has recently appeared, in which he submits to a comparative study the methods in use for determining the eugenol content (according to Umney[2]), Thoms, and

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[1]) Pharmaceutical Journal **70** (1903), 701, 757.

[2]) Umney originally employed 10 per cent. aqueous potash-lye, when, however, the results obtained were much too high. We modified the method thus, that we used 3 to 5 per cent. aqueous soda-solution. Hereafter the expression "Umney's method" means the method modified as above. For the rest it is immaterial whether soda- or potash-lye of equal percentage is used.

Verley-Boelsing), and at the same time endeavours to establish to what cause the difference in the results obtained by the various methods must be attributed. It is said to be solely due to the content of eugenol acetate in the oils of cloves, which, contrary to Erdmann's observations[1]), according to Spurge amounts to 7 to 17 per cent. The examinations made by Spurge have proved that with Umney's method the whole of the eugenol acetate contained in the oil of cloves is saponified quantitatively, and is consequently included in the estimation as eugenol, whereas in Thoms' method a partial saponification takes place, and in Verley-Boelsing's process only the free eugenol is determined.

Spurge further states that he has found in mixtures of eugenol and clove oil terpene, that the correction indicated by Thoms is incorrect, and gives results which are too low by about 4 per cent.[2]). If, in spite of this, the results obtained with oil of cloves according to Thoms agree well with those after Verley-Boelsing's method, this equalisation of errors must be attributed exactly to the partial saponification of the eugenol acetate which takes place in Thoms' process.

In order to obtain comparable results by Umney's and Verley-Boelsing's methods, Spurge proposes to determine the percentage of eugenol acetate by the saponification of the oil of cloves in question, and to deduct the resulting acetyl rest[3]) from the eugenol-content found by Umney's method, or to add the eugenol-content ascertained from the saponification, to the result obtained according to Verley-Boelsing. These corrections, especially in the last-named case, are all the more important, as for the proper valuation of clove oil the eugenol present in the form of ester is also of importance.

Spurge draws the conclusion that neither of the existing methods of eugenol-determination gives absolutely correct figures, but that in this respect preference should be given to Verley-Boelsing's method over the two others. He admits that the uncorrected modified method of Umney is also sufficiently exact to be used occasionally with advantage.

Spurge endeavours to prove the correctness of the results obtained also by the fact that he calculates the specific gravities of the clove

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[1]) Journ. f. prakt. Chemie II. **56** (1897), 143.

[2]) In examinations made by us years ago with mixtures of eugenol and the sesquiterpene of clove oil, the results differed only by 1 per cent. Comp. Report April **1892**, 28.

[3]) Spurge gives the following formula for the direct estimation of the percentage of acetyl: $\%$ acetyl $= \frac{a \cdot 2{,}1}{s}$; a = the cc. semi-normal liquor used for saponification; s = the quantity of clove oil used (in grams).

oil examined by him from the specific gravities of the components estimated quantitatively, and places them against the values determined by scale[1]). But Spurge leaves here out of account that both the values obtained for eugenol by Verley-Boelsing's method, and those for eugenol acetate obtained by saponification, represent percentages by weight, whilst Spurge deals with them as if they were percentages by volume. A re-calculation shows that the values calculated in the correct manner still more closely approach those determined by balance than Spurge mentions.

In our last Report (page 27) we have expressed ourselves in detail on the question of the determination of eugenol in clove oil, and it is therefore sufficient to refer here in a general way to the statements made by us at the time. We are of opinion that the uncorrected but modified method of Umney gives results of a sufficiently satisfactory character, and on account of its ready feasibility should be preferred in practice over other methods, as the latter also leave something to be desired in the exactness of their results.

We can confirm Spurge where he says that by Umney's method esterified eugenol is also determined in addition to the free eugenol; but the experiments made by us with mixtures of eugenol, eugenol-acetate, and caryophyllene, have shewn that a quantitative saponification of eugenol acetate only occurs in the mixtures of high percentage (above 90 per cent. eugenol), whilst with a lower content of free eugenol a corresponding smaller quantity of eugenol acetate is saponified. This is shown most clearly in the following table:

| | Eugenol | Eugenol Acetate | Caryophyllene | Eugenol-determination with 3 % NaOH |
|---|---|---|---|---|
| I. | 96 % | 2 % | 2 % | 98 % |
| II. | 92 % | 4 % | 4 % | 96 % |
| III. | 80 % | 10 % | 10 % | 87 % |
| IV. | 40 % | 10 % | 50 % | 42 %. |

The different behaviour of the richer mixtures as compared with those less rich in free eugenol, can be explained in this manner, that the eugenol sodium formed, dissolves in the first place a definite quantity of eugenol acetate, and that the portion of the ester present in the solution is then saponified by the soda liquor.

As clove oils contain but rarely less than 80 per cent. free eugenol, it is sufficient for practical purposes to assume that in Umney's method the free as well as the total esterified eugenol are estimated,

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[1]) On this occasion the constants of eugenol acetate prepared by himself are also given: $d_{15^\circ} = 1{,}089$; boiling point 160° to 162° (19 to 20 mm). In our laboratory we determined the following values: $d_{15^\circ} = 1{,}087$; $n_{D_{20^\circ}} = 1{,}52069$: melting point 29°; boiling point 142° to 143° (6 mm).

which naturally should also be taken into consideration in valuing the oil of cloves.

We would still point out that in numerous examinations made by us in recent times, we have observed that the use of a 5 per cent. soda-lye in the case of rich clove oils (about 95 per cent. eugenol) is unsuitable, as the liquor dissolves such oils readily, and this leads to an incorrect estimation of the oil in question. As this evil is obviated when a 3 per cent. soda liquor is used, we have lately employed such solution exclusively, and we have thereby rendered the method more useful for practical purposes than it was hitherto.

**Cognac Oil.** The distillers on the Rhine and Moselle complain about lack of yeast from wine and endeavour to obtain higher prices for fine distillates. The latter are comparatively scarce, but oils with an empyreumatic, soapy odour are plentiful. Cognac oil can easily be produced at any price by adulteration with artificial oil, and it requires an expert knowledge to estimate it at its true value. The trade in this oil is a matter of confidence pure and simple.

**Coriander Oil.** The prices had to be raised further, as coriander from all producing countries is quoted higher. The harvest in Russia is said to have had a very modest result; Thuringia also complains about the results of the harvests. From Moravia definite reports have not yet been received. From Hungary we received a first sample consignment; in that country it is intended to increase the cultivation considerably next year. This variety may possibly have to be taken into account later on.

**Cypress Oil.** The excellent effect of this oil in whooping-cough has recently received much attention from various physicians. It is now proposed to try this oil for emphysematous patients, for whom at present oil of turpentine is frequently employed. It looks as if this remedy will at last find recognition. The indifference displayed towards it up to the present, seems inexplicable to those who have had opportunities of observing the grand results obtained with this oil.

**Erigeron Oil.** The oil of *Erechthitis hieracifolia* — a plant known in North America under the name of "*Fireweed*", — is rarely met with in commerce in the pure state, but is often substituted by the oil of *Erigeron canadensis* (Fleabane). Kebler and Pancoast[1]) have in the course of many years only twice met genuine fireweed oil; these oils had the following constants: No. 1: $d = 0{,}8412$; $\alpha_D = +1^\circ 31'$; soluble in equal parts alcohol and more. No. 2: $d = 0{,}8244$; $\alpha_D = +2^\circ 12'$; insoluble in alcohol.

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[1]) Americ. Journ. of Pharm. **75** (1903), 216.

The erigeron oils of commerce differ so much in their behaviour that it must be either assumed that the oils themselves are frequently adulterated, or that they undergo a fairly considerable change due to resinification. In six samples examined, the specific gravity fluctuated between 0,8549 and 0,8904, and the angle of rotation between + 84° 28′ and + 28° 48′.

## Essential Oils, Sicilian and Calabrian.

We have received the following original report from Messina on these important products.

As compared with that of the previous year, the trade has been much more quiet, and, as appears from the following table, did not reach the same numerical importance.

| | 1903 | 1902 | 1901 | |
|---|---|---|---|---|
| January . . . | 95975 | 132509 | 76642 | kilos |
| February . . . | 97646 | 74056 | 65735 | „ |
| March . . . | 78390 | 113977 | 61323 | „ |
| April . . . . | 67319 | 83453 | 45244 | „ |
| May . . . . | 62452 | 77291 | 53396 | „ |
| June . . . . | 36404 | 45059 | 48142 | „ |
| July . . . . | 52176 | 61247 | 35695 | „ |
| August . . . | 46340 | 52567 | 34386 | „ |
| | 536702 | 640159 | 420563 | kilos. |

At the same time, attention should be drawn to the fact that, in spite of the enormous export figure of 640159 kilos of the previous year, — a total never reached before — the important quantity of 536702 kilos could be exported during the first eight months of this year, whilst in the same period of 1901 only 420563 kilos were sent abroad. This is a clear proof of the increase of the world's requirements during the last few years, a proof which will no doubt receive further confirmation from the figures of the total export of the current year.

**Bergamot Oil.** Until about the end of July the prices remained at a level of 18 to 19 marks per kilo. In consequence of this, the trade in this oil was of no importance, as consumers abroad first used up the cheaper stocks left over from previous purchases, before deciding to buy at these high prices. In the meantime, the flowering-season and the germination of the new bergamot-crop had passed off very satisfactorily. The atmospheric conditions during the summer-months were also favourable in every respect for the development of the young fruit, so that at last even the most obstinate holder of bergamot oil became convinced that a good new crop was to be expected, and gradually became more yielding in his demands.

For a few weeks the prices fell slowly, until finally the pressure of many sellers caused an almost panic-like drop on the market of nearly 2 marks. It seems as if for the present the downward movement has come to a stop, but it is not impossible that in the course of the next few months, until the commencement of the new harvest, a further — if, perhaps, only very slow — drop in the prices may occur, as the stocks of old oil may possibly amount to about 9,000 kilos.

Up to now the prospects for the harvest are good; but it will of course depend on the oil-content of the fruit, whether the hope now entertained will be realised in a greater or smaller degree.

**Lemon Oil.** Although in the spring everyone connected with the trade in this oil expected a rise in the prices, the reverse has happened, and the quotations have slowly fallen by about 1 mark per kilo.

The fact, that at this moment perhaps not more than 40000 kilos old oil are at disposal on the island, as against about 80000 kilos in the previous year, whilst the export in the course of the summer-months has been smaller than that of the last year, shows that the drop in the prices was not justified by the statistical position of the article. If, in spite of this, the expectations were not fulfilled, this must be attributed exclusively to the large unused stocks which are still held abroad, where, in view of the low prices of the 1902 season, the requirements had been more than abundantly covered.

One thing is certain, that the production of the article has reached a stage at which a further fall of the prices is scarcely conceivable; at the same time, large movements upwards are probably also out of the question.

Thanks to the great increase in the number of lemon-gardens in Sicily in the course of the last decade, it is possible that lemon oil, which at one time was during almost every season subject to price-fluctuations of several marks, has now, leaving out of the question some minor movements, reached a comparatively firm basis of value, which should prove advantageous to the consumption of oil and to the whole trade.

The new harvest will, it is believed, turn out somewhat smaller than that of last year, but it is difficult at this time to make definite statements on the subject, as the lemons of the July blossoms are still too small to allow of a correct estimate.

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In our Report of October 1902 we mentioned that, when fractionating further the low-boiling laevorotatory first runnings of lemon oil, we also obtained a fraction whose boiling point and optical behaviour render the presence of l-camphene in lemon oil probable. This surmise has since been confirmed by the chemists of the London Essence Co.[1]). In a fraction boiling at 164° (759 mm), ($d = 0{,}869$; $\alpha_D = -22°$; $n_{D18°} = 1{,}4470$), they were able to detect camphene by converting it into isoborneol; the melting point of the isoborneol obtained by them lay at 205°.

The experiments made in our laboratory with the same substance gave identical results.

With regard to pinene, the above-mentioned chemists believe that lemon oil contains not only l-pinene, but also an almost inactive mixture of both modifications; they, however, produce no proofs in support of this.

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Parry[2]) protests against the practice recently introduced by several firms of guaranteeing a citral-content of 7 per cent. in the lemon oil sold, whereas in reality the content of citral is much lower. These views of Parry, which are also supported from various other quarters[3]), are opposed by Gulli and Stavenhagen[4]), who by means of numerous analyses endeavour to prove that in good lemon oils the citral-content fluctuates between 7 and 7,3 per cent. In estimating the citral by means of the bisulphite method, Gulli and Stavenhagen have but rarely found oils of lemon containing less than 6,5 per cent. aldehyde.

In this connection we wish to say that it is as a matter of fact impossible to make absolutely reliable statements on this subject, because, as we have shown in all cases[5]), not one of the methods for estimating the citral-content in lemon oil, which have up to now been recommended, gives sufficiently accurate results. And in view of the fact that citral is only present in lemon oil in very small quantities, the accuracy of these results is a matter of the highest importance.

For this reason we ourselves must decline to give any guarantee whatever with regard to the quantity of citral present in the oil of lemon.

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In giving an opinion on terpeneless oil of lemon, Parry[6]), as evidence of the good quality of the oil, states that the citral isolated from it did not contain any trace of methyl heptenone, and that for this reason an admixture of lemongrass citral was out of the question, as the latter always contains methyl heptenone. This conclusion is

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[1]) The Chemist and Druggist **62** (1903), 476.
[2]) The Chemist and Druggist **63** (1903), 277.
[3]) The Chemist and Druggist **63** (1903), 341.
[4]) The Chemist and Druggist **63** (1903), 401.
[5]) Report April **1900**, 24; October **1900**, 26.
[6]) Pharm. Journ. **70** (1903), 42.

erroneous; in fact, exactly the contrary is the case. Normal lemon oil namely, as we have recently shown[1]), contains methyl heptenone, even if only in very small quantity, and the latter's presence in terpeneless oil would therefore not be remarkable. Moreover, the addition of pure lemongrass citral could not bring about the presence of methyl heptenone.

**Oil of Orange, sweet,** has in the course of the last six months passed through many fluctuations in value. Whilst up to the early part of April the price was maintained at about 14 marks per kilo, it gradually dropped in the course of May and June to 12,25 marks. When at these low quotations the demand from abroad became brisk, the article advanced again in the course of July to 14 marks, and for a short time was even quoted at 14,50 marks. In August no large sales took place, chiefly because the stocks of spot-oil were almost completely exhausted.

With regard to the new orange-harvest, the reports from the individual producing districts differ. Whilst in some districts a good crop is expected, less favourable reports come to hand from others. On the whole, the coming harvest may probably give a yield approximately equal to that of the winter of 1902—3.

From this fact, taken in conjunction with the completely exhausted stocks of old oil, it may be concluded that cheap prices of the new oil appear hardly possible; but it should not be lost sight of that the oranges of the last harvest have given a low yield of oil, and that consequently, if the new fruit should give a better result, the possibility of the production of larger quantities of oil than in the previous year is not excluded.

On the other hand, the supply of not quite perfect oranges to the Upper Italian markets has been greatly facilitated by the reduction of the rates of freight which has recently been allowed by the interested railways. The rate of carriage of oranges in bulk, in truck-loads, to Milan, Turin, Bologna, and other places, has been reduced by more than half. If all these circumstances are taken into consideration, the conclusion may be drawn that the prices of new orange oil will hardly be less than those of last year.

**Eucalyptus Oil.** In our Reports of April and October 1901[2]), we mentioned that the aldehyde which occurs in a few oils of eucalyptus, and which up to that time had been looked upon as cuminic aldehyde, is, according to an examination by H. G. Smith, not identic with the above-mentioned aldehyde.

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[1]) Report October **1902**, 36.

[2]) Report April **1901**, 34; Report October **1901**, 29. Compare also Gildemeister and Hoffmann, The Volatile Oils, p. 533.

According to Smith the oil of *Eucalyptus hemiphloia* contains an aldehyde $C_{10}H_{14}O$, aromadendral, which boils at 210° with decomposition, and which has an odour reminding of cuminic aldehyde. The aldehyde forms an oxime melting at 84°, and a phenyl hydrazone of the melting point 105°. When oxidised with alkaline permanganate solution it yields as oxidation products an acid of the melting point 259°—260°, and cineol(?). Chromic acid mixture oxidises it to the acid $C_{10}H_{14}O_2$ melting at 110°.

This result differs from that obtained by us on a previous occasion[1]) with an oil of *Eucalyptus odorata*, according to which the aldehyde having an odour like cuminic aldehyde, when oxidised with permanganate, yields cuminic acid. Smith's work now has induced us to study this body once more in an Australian oil whose source could not be discovered but whose odour was exactly like that of *Eucalyptus odorata*. When extracting about 1,000 kilos oil with solution of sodium bisulphite, we obtained about 2,5 kilos aldehyde which possessed a strong odour reminding of cuminic aldehyde. In order to remove from this product the slight non-aldehydic admixture, 600 grams of the aldehyde fraction were again converted into the bisulphite compound. As the latter, on account of its slimy constituency, could only be purified with difficulty by means of alcohol and ether, we dissolved it in water and thus obtained by repeated extraction with ether a complete purification. The aldehyde liberated from this solution and driven over with steam distilled between 50° (17 mm pressure) and 85° (5 mm pressure), and of this about 470 grams at 80,5° to 85° (5 mm pressure). This portion was almost colourless, and had the exact odour of cuminic aldehyde. A fraction passing over at 82,5° to 84° (5 mm pressure), had the following physical constants: $d_{15^\circ} = 0{,}9828$; $\alpha_D = \pm 0^\circ$; boiling point 228°—238°. It had the quite remarkable property of oxidising in a short time when exposed to the air. In a solution of acetic acid the aldehyde formed a semicarbazone whose melting point, precisely as with cuminic aldehyde, lay between 202° and 207°, according to the manner of heating. The phenyl hydrazone recrystallised from ligroin showed the melting point 126°—127°. The oxime melted at 58°. On oxidation with permanganate there was formed from the aldehyde an acid of the melting point 116°—117°. A mixture of cuminic acid with this acid had the same melting point. According to these results there appears to be no doubt whatever that the aldehyde was cuminic aldehyde.

We then submitted the portions of the oil, boiling below 80° (about 120 to 125 grams) to a further examination. They consisted

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[1]) Report April **1889**, 19.

for the greater part still of cuminic aldehyde. By once more distilling the portions passing over at 39° to 76° and 76° to 80° (5 mm pressure), we obtained the following fractions:

I. 35° to 65° (5 mm pressure)
II. 65° „ 70° (5 „ „ )
III. 70° „ 80° (5 „ „ ).

Fraction I had a pronounced yellow colour and possessed a peculiar odour, which, however, did not in the least remind of cuminic aldehyde. The constants were as follows: $d = 0{,}9057$; $\alpha_D = \pm 0°$ (20 mm); boiling point 175° to 205°; quantity 5 to 6 grams. No solid derivative was obtained from the oil.

Fraction II boiled chiefly at 200° to 212°, but yielded no well-characterised oxime or semicarbazone. The quantity amounted to about 8 grams. The optical rotation was the reverse of that of aromadendral, viz: $\alpha_D = + 0° 56'$; $d = 0{,}9341$. The odour was like that of the first fraction.

Fraction III distilled between 210° and 232°, and (as was shewn by the semicarbazone produced from it) consisted chiefly of cuminic aldehyde: $d = 0{,}9533$; $\alpha_D = + 1° 36'$. The aldehyde which occurs in addition to cuminic aldehyde, cannot, according to the above-mentioned properties, be identic with Smith's aromadendral. We believe that it represents possibly a higher fatty aldehyde, or a mixture of two such aldehydes.

From J. H. Maiden, the well-known and distinguished investigator of the Australian Flora, there have again appeared several treatises, and also the first part of the larger work on the Eucalypts. In the first paper[1]), in which the question is raised whether the species of the Eucalyptus family are variable, he mentions in the first place the different characteristics and organs which have served the individual botanists for the subdivision of Eucalypts. Contrary to Baker and Smith, who are of opinion that the species have now been irrevocably determined, Maiden comes to the conclusion that this is by no means the case, but that the variation still continues. As an example he mentions the Eucalyptus designated as "gum-topped stringy bark of Tasmania", which has been described under eleven different names. Manna, kino, and also the essential oil, are, according to Maiden no fundamental, but accessory and adapted characteristics, and should not be used by themselves, but only as aids in the diagnosis. The botanical classification for the purpose of the nomenclature of the genera, species, and varieties, should rather be

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[1]) Is Eucalyptus variable? Journn. and Proceed. of the Royal Society of N. S. Wales **36** (1902), 315.

based on morphologic characteristics. Maiden then turns against Baker and Smith¹) who differentiate the various species in the first place according to the chemical composition of the essential oils produced from them.

In two further publications by the same author²), *Eucalyptus bicolor* A. Cunn. and *E. polyamthemos* Schauer are dealt with.

Finally, the first three parts have been published of a larger work on the eucalypts: "A critical revision of the genus Eucalyptus"³). In the preface Maiden points out that twenty years have now elapsed since the publication of the famous "Eucalyptographia" of Müller, and that in that period much material has been collected by means of a large number of observations, which has led to the individual species being looked upon from a partly different point of view. The introduction consists mainly of the contents of the above-mentioned first paper. The first species described is *Eucalyptus pilularis* Smith, and under this designation everything is embraced which up to now has been described under the following names: *E. discolor* Desf.; *E. persicifolia* Lodd.; *E. persicifolia* D. C.; *E. incrassata* Sieb.; *E. semicorticata* F. v. M.; *E. fibrosa* F. v. M.; Var. *Muelleriana* var. nov.; *E. Muelleriana* Howitt; *E. dextropinea* R. T. Baker; *E. laevopinea* R. T. Baker. The second part deals with *E. obliqua* L'Héritier; as synonymous the following are mentioned: *E. pallens* D. C.; *E. porcera* Dehnh.; *E. gigantea* Hook. f.; *E. elatus* Hook. f.; *E. fabrorum* Schlecht; *E. fissilis* F. v. M.; *E. falcifolia* Miq.; *E. nervosa* F. v. M.; *E. heterophylla* Miq. The third part describes *Eucalyptus calycogona* Turcz. with two varieties, namely, var. *celastroides* Maiden (syn. *E. celastroides* F. v. M. and *E. fructicetorum* F. v. M.), and var. *gracilis* Maiden (syn. *E. gracilis* F. v. M., *E. gracilis* F. v. M. var. *breviflora* Benth. and *E. yilgarnensis* Diels). As doubtful varieties are mentioned: *E. gracilis* F. v. M. var. *Thozetiana* F. v. M. and *E. ochrophloia* F. v. M. Each part contains a number of beautifully executed plates.

R. T. Baker⁴) also gives a contribution to the knowledge of the Eucalypts, under the title "On *Eucalyptus melanophloia* F. v. M. and its cognate species".

**Fennel Oil.** The fennel plants in this neighbourhood have thriven well and, in consequence of the great heat, they have also ripened well and in good time, so that at this moment new goods are already offered for sale. As usual, the large-sized first fruit again fetches this year a specially high price, and does not come under consideration for manufacturing purposes. As a matter of fact, the Lützen fruit would

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¹) A research on the Eucalypts, especially in regard to their essential oils. Sydney 1903. Report April 1903, 40.

²) Proceed. of the Linn. Soc. of N. S. Wales 1902, Part IV, 516, 527.

³) Sydney 1903.

⁴) Proceed. of the Linn. Soc. of N. S. Wales 1902. Part. II, 225.

hardly pay for distillation, as Galicia is on the market with very low offers. Several truck-loads from there have already been worked up at our factory.

Fennel is also offered in abundance from Macedonia. But the essential oil obtained from this variety does not possess the typical character of fennel, and is therefore useless as a substitute.

**Geranium Oil.** The distillation in Algeria has had a normal course. The prices have declined somewhat, but appear to be likely to remain at their present level. We have covered our requirements advantageously by firm contracts, and supply the oil in a quality which answers the very highest scientific and practical requirements.

The production of Algeria is estimated this year at about 15 000 kilos. According to official data, the export in 1900 amounted to

8300 kilos to France
1140 „ „ Germany
105 „ „ Italy.

The export to other countries cannot be ascertained, as the figures are included among those of other Algerian essential oils.

The centres of the geranium-cultivation are still Staoueli, the plain of Mitidja and Boufarik. The area covered is said to be about 1250 acres.

The geranium cultivation in Réunion has made an at least equally rapid and important advance. Thus, the export of geranium essence was:

| | | | | | |
|---|---|---|---|---|---|
| in 1898, | 16337 | kilos, | value | 615444 | francs |
| „ 1899, | 12936 | „ | „ | 613390 | „ |
| „ 1900, | 7137 | „ | „ | 302570 | „ |
| „ 1901, | 19441 | „ | „ | 902460 | „ |

This year it may possibly reach 20000 kilos, as the harvest has given an extremely rich yield. Our purchases alone come to about 5000 kilos. The exceptionally low price has frequently been taken advantage of for speculative enterprises. We shall be pleased to make contracts, and believe that there would be no risk incurred in accepting them.

The geranium is cultivated in Réunion at altitudes where neither sugar-cane grows, nor mandioc or vanilla. The number of distilling-apparatus employed in the preparation of the oil is 239.

An excellent selection of qualities of so-called East Indian geranium or palmarosa oil of the last harvest is available, and is quoted lower than at almost any previous time. According to the most recent reports from India a good yield of fine oils is anticipated also this year, and a continuation of the cheap prices is not doubted. The same applies to gingergrass oil, which for many years has not been obtainable in such good quality as at present.

The value of the essential oils exported from Bombay was as follows: —

1899—1900, 278005 rupees.
1900—1901, 341670 „
1901—1902, 610783 „

The enormous increase is probably only due to the above-named oils, as for the rest only a small quantity of lemongrass oil comes under consideration, of which the bulk, as is well known, is shipped direct from Cochin. The shipments of geranium oil from Bombay were:

from July 1st 1901 to June 30th 1902, 23460 lbs.
„ „ 1st 1902 „ „ 30th 1903, 107605 „

The turnover has therefore increased nearly five-fold.

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E. Charabot and G. Laloue[1]) have made experiments to ascertain the distribution of some organic substances in the geranium plant (*Pelargonium odoratissimum*). These have given the following results: the content of volatile acids diminishes from the leaf towards the stem. The stem and leaf stalks do not contain a trace of essential oil. The seat of the terpene compounds is exclusively in the leaves. This explains why the geranium flowers are odourless. It confirms at the same time the hypothesis that the essential oil, or at least the compounds from which it originates, produced in the chlorophyl-containing organs of the plant, and from there spread into the other parts of the plant, in which they then undergo more or less far-reaching changes. A distillation of 78,9 kilos geranium leaves by means of steam, yielded 130 grams oil. From the aqueous distillate (130 litres) additional 25 grams oil were extracted with ether. The properties of the two oils were as follows:

| | Oil separated from the distillate: | Water oil: |
|---|---|---|
| d = | 0,8979 | 0,8930 |
| $\alpha_D$ = | — 11°02′ | — 5° 13′ |
| acid number = | 47 | 16,5 |
| ester number = | 16,6 | 6,7 |
| ester-content = | 7,0 % | 2,8 % (calculated as geranyl tiglinate) |
| alcohol-content = | 70,7 „ | 77,5 „ (calculated as $C_{10}H_{20}O$) |
| citronellol = | 37,5 „ | 30,6 „ |
| geraniol = | 33,2 „ | 46,9 „ (difference) |
| composition of the alcoh. portion | 53,0 „ | 39,4 „ citronellol |
| | 47,0 „ | 60,6 „ geraniol |

A small quantity of aldehyde isolated from the water oil with sodium bisulphite was recognised as citral.

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[1]) Compt. rend. **136** (1903), 1467.

**Oil of Guaiac-wood.** The importation of raw material has ceased completely, and as a consequence the prices have advanced by more than double. We were in the fortunate position of being able to provide our clients with abundant supplies, but at present stocks are entirely exhausted and no supplies of wood in sight.

From a voluminous essay which was awarded a prize by the Medical Faculty of Rostock University, and which is entitled: "Contributions to the knowledge of guaiac preparations" [1]), we abstract the following details of the physiological action of oil of guaiac wood and of guaiol.

Both preparations have the same action on the animal organism. Oil of guaiac-wood passes without injurious effect through the organism of mammals. The central paralysis observed on frogs is produced by many essential oils already in doses of a centigram. Guaiol also is free from toxic effect on warm-blooded animals, and it has no share (or only a very unimportant one) in the paralysing effect of the oil. It passes almost completely unchanged through the organism, and only traces of glycuronic acid can be detected in the urine.

**Hop Oil.** The following estimate of this year's hop-harvest is made from a competent quarter: —

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| in the German Empire | about | 485 000 | cwt. | against | 480 000 | cwts. | last | year |
| of these in Bavaria | „ | 300 000 | „ | „ | 280 000 | „ | „ | „ |
| in Austria-Hungary | „ | 130 000 | „ | „ | 217 000 | „ | „ | „ |
| of these in the Saaz district | „ | 40 000 | „ | „ | 100 000 | „ | „ | „ |
| in Belgium | „ | 35 000 | „ | „ | 70 000 | „ | „ | „ |
| „ the United Kingdom | „ | 450 000 | „ | „ | 290 000 | „ | „ | „ |
| „ Russia | „ | 75 000 | „ | „ | 55 000 | „ | „ | „ |
| „ France | „ | 50 000 | „ | „ | 40 000 | „ | „ | „ |
| „ the United States | „ | 400 000 | „ | „ | 320 000 | „ | „ | „ |

The result in the individual countries may either be somewhat better, or worse, according to the weather-conditions prevailing during the next five weeks.

Whilst last year important stocks were carried over into the new season, both by brewers and by merchants, this will not now be the case, and for this reason it will be necessary to reckon from the first on a larger demand. On the same grounds higher prices must be expected.

The present quotations of our genuine hop-distillate are based on low purchase prices, and they may have to be raised.

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[1]) Contributions to the knowledge of guaiac-preparations, by W. Frieboes. Stuttgart, 1903.

In continuation of his earlier work, Chapman[1]) reports on recent examinations of hop oils from flowers of different origin The physical constants agreed sufficiently well: the specific gravity of the oil from Bavarian hops of the year 1894 was 0,8676 $\left(\frac{15^\circ}{15^\circ}\right)$ or 0,8645 $\left(\frac{20^\circ}{20^\circ}\right)$; the oil from flowers of 1901 showed 0,8403 and 0,8357 respectively, and Californian oil from flowers of 1899, 0,8639 and 0,8610 respectively. The molecular rotatory power of the Bavarian oil was $+$ 0,30° and — 0,08°; that of Californian oil — 0,20°. On fractional distillation *in vacuo* there was collected in the lowest boiling fraction, in addition to small quantities of dipentene, a very light myrcene-like hydrocarbon $C_{10}H_{16}$, which on hydration according to Bertram and Walbaum yielded an ester with a lavender-like odour. In the middle fractions linalool could be detected, and also a volatile acid $C_9H_{18}O_2$, in the form of ester, probably isononylic acid. The presence of a geranyl ester was moreover suspected. The highest boiling portions consisted almost exclusively of the sesquiterpene humulene. The oxidation of hop oil with chromic acid mixture yielded in addition to volatile acids (acetic acid and homologues), also succinic acid and asymmetric dimethyl succinic acid. The hydrocarbons myrcene and humulene represented more than 80 per cent. of the oil.

**Jasmine Oil "Schimmel & Co.".** The use of this product, which was introduced by us into commerce as the first artificial flower-oil, is constantly increasing. There can be no doubt that on the one hand the natural products of the jasmine-flowers can be improved in a marked degree by the addition of artificial oil of jasmine, and the artificial oil on the other hand by adding natural jasmine oil; our own oil of jasmine has from the first contained large quantities of the latter. It requires no further proof to demonstrate the enormous advantage which the perfumery-industry derives from this product.

**Oil of Juniper-berries.** The harvest of juniper-berries in Upper Italy has given such an uncommonly rich yield, that the smaller crop, which is said to be the result of the Hungarian harvest, is more than counterbalanced. Our supplies come decidedly cheaper, and allow of a reduction in the quotations of our own two distillates from berries whose excellent qualities we specially desire to emphasise.

**Lavender Oil.** The reports on this year's lavender-distillation are not quite so unfavourable as was at first expected. In the lower-lying districts of the departments Alpes-Maritimes, Hautes-Alpes, and Drôme, the yield is even characterised as favourable, and the producers themselves estimate it at a third higher than last year. Only in the high altitudes the distillers complain about the small yield from

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[1]) Journ. Chem. Soc. **86** (1903), 505. Pharm. Rev. **21** (1903), 155.

the plants which have been injured by frost, but these are exceptions: the average result is good. The plants in the Gard, however, appear to have suffered more from frosts in the spring, but there also the total yield is said to exceed that of last year.

At the same time, the price paid for the plants for distillation-purposes was 7 to 8 francs per 100 kilos, against 5 francs formerly. The yield of oil this year was good.

In view of these facts the prices of fine lavender oils would no doubt have fallen considerably, if at the beginning of the season the stocks of oil from the previous harvest had not been totally exhausted. In consequence of the general and partly very urgent demand caused thereby, the new oil was immediately bought up at high prices, and all our attempts to induce the producers to become more accommodating only proved futile.

In face of this peculiar state of affairs, and of the constantly growing consumption of lavender oil, it will be necessary also this season to reckon upon high quotations.

We purchase this article first-hand at the principal markets; our buyer is trained in the proper examination of the samples which are submitted to him.

The parcels bought by us up to the present are throughout of exceptionally fine quality, containing ester up to 45,3 per cent., and that without any artificial increase of the ester-content, an occurrence for which we were constantly watching, in view of previous experience.

In our Report of April 1902, p. 46, we mentioned a case of adulterated lavender oil with benzoic acid for the purpose of artificially raising the ester-content; this case has led to an action for damages, which after several trials has had this result, that the person who committed this adulteration has offered, of his own accord, to bear the heavy expense and loss of material resulting from the working up of the oil. This person has now probably lost the taste for a second attempt to palm off his goods on us.

In our last April Report[1]) we published the result of our work on French oil of lavender. We can now amplify this somewhat. The amyl alcohol isolated from the first runnings of the oil by means of phthalic acid anhydride, formed with carbanil a phenyl urethane of the melting point 39° to 41°. Elementary analysis of the latter gave the following figures:

0,1356 g of the substance yielded 0,0974 g $H_2O$ and 0,3444 g $CO_2$.

| | Found: | Calculated for $C_{12}H_{17}O_2N$: |
|---|---|---|
| C = | 69,27 per cent. | 69.56 per cent. |
| H = | 7,98 „ „ | 8,21 „ „ |

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[1]) Report April **1903**, 45.

We were unable to decide with certainty the question which amyl alcohol this was, as an attempt to identify this body further by means of $\alpha$-nitrophthalic acid, according to Marckwald's method[1]), failed on account of scarceness of material. In view of the properties of the alcohol, which have already been mentioned, the fact that we found the melting point of the phenyl urethane of an amyl alcohol melting at 130° to 130,5°, fractionated from a commercial preparation, at 53° to 54°, justifies the conclusion that the alcohol in question represented a mixture of isoamyl alcohol and an isomer.

We are now also able to publish the constants of the previously mentioned ethyl amyl ketone. It was produced in the pure state from the semicarbazone whose melting point we found at 117° to 117,5°, which differs from our first statements. The figures of the second combustion of the semicarbazone, which confirm the formula $C_8H_{16}O$ for the ketone, are as follows:

0,1801 g of the substance yielded 0,1630 g $H_2O$ and 0,3860 g and $CO_2$.

| Found: | Calculated for $C_9H_{19}N_3O$: |
|---|---|
| C = 58,45 per cent. | 58,38 per cent. |
| H = 10,05 „ „ | 10,27 „ „ |

The decomposition was effected by means of 10 per cent. sulphuric acid at the temperature of the water bath, with frequent agitation. The ketone which readily volatilised with steam, had, after rectification, the following physical constants: $d_{15^\circ} = 0{,}8254$; $d_{0^\circ} = 0{,}8371$; $\alpha_D = \pm 0^\circ$ (20 mm); $n_{D20^\circ} = 1{,}41536$; boiling point 169,5° to 170° (754 mm pressure).

The pure ketone forms no solid compound with sodium bisulphite, which agrees with previous observations. A preliminary analysis proved that the ketone has the formula $C_8H_{16}O$:

0,1757 g of the substance yielded 0,1973 g $H_2O$ and 0,4810 g $CO_2$.

| Found: | Calculated for $C_8H_{16}O$: |
|---|---|
| C = 74,67 per cent. | 75,00 per cent. |
| H = 12,48 „ „ | 12,50 „ „ |

With hydroxylamine the ketone reacts with formation of a liquid oxime of the boiling point 91° (5 mm pressure), and a strong, peculiar odour. At —18° it represents a viscid oil, which does not congeal even after prolonged cooling. The analytical figures agree with those required theoretically:

0,2903 g of the substance yielded 0,3103 g $H_2O$ and 0,7158 g $CO_2$.

| Found: | Calculated for $C_8H_{17}NO$: |
|---|---|
| C = 67,24 per cent. | 67,13 per cent. |
| H = 11,88 „ „ | 11,89 „ „ |

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[1] Berichte **34** (1901), 485.

Oxidation of the ketone with chromic acid was once more carried out, and yielded again caproic acid of the boiling point 203° to 206°, from which it might be concluded that the amyl group is normally constituted. As synthetic ethyl-n-amyl ketone1) is a body difficult of access, we have for the present desisted from a comparison between it and the ketone isolated from lavender oil.

We will, however, return to this subject at a favourable opportunity, and hope to be able by some shorter process to clear up the constitution of the ketone completely.

Analysis of the silver salt:

0,2523 g of the substance yielded 0,1109 g $H_2O$ and 0,2962 g $CO_2$
0,2463 „ „ „ „ left behind 0,1193 g Ag.

| | Found: | Calculated for $C_6H_{11}AgO_2$: |
|---|---|---|
| C = | 32,02 per cent. | 32,29 per cent. |
| H = | 4,88 „ „ | 4,93 „ „ |
| Ag = | 48,44 „ „ | 48,43 „ „ |

The fractions from which after oxidation with potassium permanganate the above-mentioned ketone was isolated, appeared also to contain also esters. For example, a fraction of the boiling point 155° to 162° showed the saponification number 134,8; another boiling at 162° to 172°, the number 84,2. The quantity of the silver salt of the acid isolated from the alkaline liquors was not sufficient for an analysis. The neutral products of saponification appeared to contain (judged by the odour) isoamyl alcohol. We will return later on to these examinations.

We may mention incidentally, that in the fraction amounting to several kilos of the first runnings of lavender oil, which corresponded to the boiling point of furfurol, we succeeded in detecting this aldehyde by the reaction with the solution of aniline hydrochloride in aniline.

**Lemongrass Oil.** The value of this article unfortunately appears to remain at its present exceedingly high level; it should prove highly remunerative to the manufacturers on the Malabar coast, if it is taken into consideration that the former normal price was less by half than what it is now.

The export again shows a large increase. It was: —

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| from | July | 1st 1902 | to | June | 30th 1903 | 2807 | dozen bottles |
| against | „ | 1st 1901 | „ | „ | 30th 1902 | 2322 | „ „ |
| „ | „ | 1st 1900 | „ | „ | 30th 1901 | 1933 | „ „ |
| „ | „ | 1st 1899 | „ | „ | 30th 1900 | 2792 | „ „ |

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1) In our last Report in our notes on lavender oil we erroneously gave the boiling point of the synthetic ethyl amyl ketone as 164° to 166°. According to Ponzio de Caspari (Gazz. chim. ital. **28** II. (1898), 273, ethyl amyl ketone boils at 169° to 170° (737,8 mm pressure). Our observation of the boiling point therefore agrees with this statement.

Stocks of any importance exist nowhere. There can therefore be no doubt that the high prices will remain in force.

We have repeatedly mentioned in our reports that the cultivation of andropogon grasses in the West Indian Islands appears to be extending more and more, as during the last few years we have frequently received from those countries samples of oils which were derived from this species of grass, and which were partly citronella oils, and partly oils of lemongrass.

It is clear that this cultivation now also extends to the Continent; this appears to be confirmed by a larger sample from a species of grass called "Te limón", sent to us from Mexico. The oil obtained by us from this grass in a yield of 0,916 per cent. proved to be oil of lemongrass; in its properties it fairly closely resembles the West Indian lemongrass oils, it is only a little lighter and shows a somewhat greater solubility. It makes a fine clear solution in 1 volume 80 per cent. alcohol, although when more solvent is added, opalescence occurs very rapidly. Its behaviour is the same when 90 per cent. alcohol is used, whilst 98 per cent. alcohol gives in every case a clear solution.

The remaining properties of the Mexican oil of lemongrass were: $d_{15^\circ} = 0{,}8852$; $\alpha_D = \pm 0^\circ$; aldehyde-content, about 70 per cent.

We mentioned on page 23 of our Report of April 1903, that Dr. Strunk, the chemist of the Botanical Garden of Victoria, Cameroons, had obtained from a species of grass which is cultivated there under the name *Andropogon citratus*, an essential oil which, according to the results of his examinations made with the insufficient means at the disposal of the local laboratory, appeared to be citronella oil. Strunk was therefore of opinion that the plant from which he had distilled the oil was not *Andropogon citratus*, but *A. nardus*. The same oil has now also been examined in the Pharmaceutical Institute of Berlin by C. Mannich[1]), when it was found to contain not citronellal, but on the contrary large quantities of citral, namely 70 per cent. The oil is therefore lemongrass oil, and the mother-plant *Andropogon citratus.* The specific gravity of the oil was 0,885. With alcohol it makes a somewhat cloudy solution. By means of sodium sulphite, according to Tiemann's method, 68,2 per cent. pure citral of the boiling point 101° to 103° at 9 mm was isolated, and further identified by conversion into the semicarbazone melting at 164°. Citronellal and geraniol could not be detected in the oil with certainty.

Parry[2]) found that acetone is used as an adulterant of lemongrass oil. Apart from its exceptionally low specific gravity (0,893)

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[1]) Berichte der d. pharm. Ges. **13** (1903), 86.

[2]) The Chemist and Druggist **62** (1903), 768.

and its peculiar odour, the oil behaves in an absolutely normal manner, and apparently also had a fairly high citral-content (76 per cent.). The above-mentioned abnormal properties induced Parry to submit the oil to a fractional distillation, when the adulteration was readily detected.

**Linaloe Oil.** By holding back the stocks, the Mexican exporters have succeeded in forcing up the prices, and maintaining them for a time at a high level. At the present time attempts are made to dispose here and there of small parcels at a somewhat lower price. For the rest, abundant quantities of inferior oil are on the market.

In order to meet a repeatedly expressed request, we now also keep in stock the fine linaloe oil from Cayenne (*Essence de bois de rose femelle*) which is said to be specially adapted for muguet. In our opinion nothing excels in point of quality the pure linalol, the use of which is all the more to be recommended, as it is not more expensive than the Cayenne distillate.

In the "Annuaire Colonial" of 1903—4, we find some notes on the manufacture of *Essence de bois de rose femelle,* according to which this material is produced in three small factories, of which two are situated in Cayenne, and one in Sinnamary. This industry is said to be capable of great development, and to deserve the attention of capitalists in the metropolis. The wood is found everywhere in the interior of the colony, and can readily be transported to the factories situated at the mouths of the rivers. 1000 kilos wood yield about 10 kilos essence. The price of the wood is 80 francs per 1,000 kilos, so that 1,000 kilos raw material supply a product worth about 280 francs.

For the purpose of erecting factories, sites in the vicinity of the rivers can be obtained free of cost. Sinnamary, Montsinéry, Tonnégrande, situated on the deep river-courses, and in the regions where the wood grows in abundance, are places specially suited for this industry.

**Mignonette (Reseda) Geraniol.** In order to supplement our stock, we have this year carried on the distillation of pure geraniol over fresh mignonette-flowers. Only the pure flowers without stalks are worked up, and that in the proportion of 500 kilos flowers to 1 kilo geraniol

The flowers grown here have the finest aroma, which is not excelled even by the French flowers.

**Monarda Oils**[1]. I. Oil of *Monarda didyma* L. According to previous statements, the presence of thymol in this oil would have

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[1] Notes on rare monarda oils. Reported by Edward Kremers. Pharm. Review **21** (1903), 109.

to be taken as settled. But a more recent examination made by J. W. Brandel[1]) shows that this is by no means the case, and it must therefore be assumed that the earlier investigators have had to do with the oil of another species of monarda. When distilling 100 lbs. of the dried herb, Brandel obtained only 14 cc. oil, equal to a yield of 0,03 per cent. It represents a bright red-brown liquid with a sweet balsamic odour, whose specific gravity was 0,902, and angle of rotation — 10°. Tests for carvacrol and thymol by Flückiger's method gave negative results. Further experiments could not be made on account of the small quantity of oil at disposal.

*Monarda didyma* which is occasionally found in flower gardens in Germany, has a very pleasant odour, reminding of linalool and its esters, which becomes specially pronounced on rubbing the leaves.

II. Oil of *Monarda fistulosa* L. An earlier examination of this oil by Brandel and Kremers had led to the detection of two bodies which had up to then not been found in essential oils, viz. thymoquinone and thymohydroquinone, as well as carvacrol. It was then assumed that the dark colour of the oil was caused by a combination of the two above-mentioned bodies into a dark-coloured quinhydrone.

J. J. Beck and J. W. Brandel[2]) now have tried to discover the distribution of these substances in the individual parts of the plant.

The red corolla is covered with viscous hairs which under the microscope show a reddish-brown colour; these hairs are filled with an essential oil which presumably consists of a solution of thymoquinhydrone in carvacrol. This is supported by the results of the examination of the oil distilled from the petals. 340 grams dried petals yielded 9,24 grams = 2,71 per cent. of a dark red-brown oil having the specific gravity 0,9586, which showed Flückiger's carvacrol reaction. Larger quantities of oil will be produced for a more detailed examination.

When distilling the leaves without the stalks, a straw-coloured oil of the specific gravity 0,9241 (at 20°) and the angle of rotation — 0° 9′ was obtained, which contained carvacrol, and which according to its colour, cannot contain thymoquinhydrone.

As the chemical process which takes place in the leaves chiefly consists of the conversion of carbonic acid and water into hydrocarbons, that is to say, represent a reduction and condensation process, it can cause not surprise that the oxidation products of carvacrol found in the stalks and petals, are not present in the leaves. Whether later on, in the period of growth when the formation of starch in all probability takes place much more slowly, thymohydroquinone is also produced in the leaves, is a matter which has still to be determined.

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[1]) Pharm. Review **21** (1903), 109.

[2]) Ibid. 111 and 113.

**Mustard Oil, artificial.** The manufacture of this oil has now for some time been carried on regularly at our Works. Our plant is fully employed for important orders from Europe and America. The entirely new process used by us enables us to meet all competition, and every consumer who has asked us for special quotations has had an opportunity of satisfying himself on this point.

**Neroli Oil (oil of bitter Orange-blossoms).** As in previous years, Mr. Jean Gras of Cannes has again supplied us a table showing the results of his distillation this year, and the properties of the oils thereby obtained. We reproduce here this table:

| Date of Manufacture | Yield per cent | Specific Gravity at 15° C. | Optical Rotation l = 100 mm t = 20° | Saponification number | Solubility in alcohol of 80% at 22° |
|---|---|---|---|---|---|
| May 11. | 0,65 | 0,874 | + 1° 31′ | 43 | 1 vol. in 1 vol. alcohol, insoluble when more alcohol was added |
| „ 12. | 0,80 | 0,874 | | | |
| „ 13. | 0,89 | 0,874 | + 1° 45′ | 45 | 1 vol. in 1,5 vol. alcohol, insoluble when more alcohol was added |
| „ 14. | 0,81 | 0,875 | + 2° 8′ | 46 | insoluble |
| „ 15. | 0,83 | 0,874 | + 1° 32′ | 45 | do. |
| „ 16. | 0,78 | 0,874 | + 1° 33′ | 47 | do. |
| „ 17. | 0,87 | 0,874 | | | |
| „ 18. | 0,77 | 0,875 | + 2° 8′ | 53 | do. |
| „ 19. | 0,77 | 0,875 | + 1° 45′ | 56 | do. |
| „ 20. | 0,77 | 0,875 | + 2° 20′ | 45 | do. |
| „ 21. | 0,87 | 0,875 | + 2° 21′ | 47 | 1 vol. in 1 vol. alcohol, insoluble when more alcohol was added |
| „ 22. | 0,90 | 0,876 | + 2° 21′ | 46 | 1 vol. in 1,2 vol. alcohol, insoluble when more alcohol was added |
| „ 23. | 1,00 | 0,875 | + 2° 30′ | 43 | do. |
| „ 24. | 1,03 | 0,874 | + 2° 44′ | 45 | 1 vol. in 1 vol. alcohol, insoluble when more alcohol was added |
| „ 25. | 1,06 | 0,874 | + 3° 5′ | 46 | do. |
| „ 26. | 1,07 | 0,874 | + 3° 8′ | 44 | do. |
| „ 27. | 1,07 | 0,874 | + 3° 30′ | 45 | do. |
| „ 28. | 1,02 | 0,874 | + 3° 12′ | 47 | do. |
| „ 29. | 1,11 | 0,874 | + 3° 31′ | 48 | do. |
| „ 30. | 1,15 | 0,874 | + 3° 48′ | 50 | 1 vol. in 1 vol. and in every proportion |
| „ 31. | 0,91 | 0,874 | + 2° 51′ | 48 | do. |
| June 2. | 0,80 | 0,875 | + 4° 20′ | 49 | do. |
| Total Quantity | 0,97 | 0,875 | + 2° 50′ | 47 | 1 vol. in 1 vol. alcohol, insoluble when more alcohol was added |

We have still to communicate briefly the results which we obtained in an examination of volatile extract oil of orange-blossoms. This examination was made in continuation of our work on neroli oil, which has already been reported in these pages[1]. About 3 kilos of an extract supplied by Mr. Jean Gras of Cannes were worked up. After dividing in two portions, we treated it in the usual manner with alcohol, and after removing the alcohol, distilled the essential oil *in vacuo* with steam. 2300 grams extract yielded about 280 grams oil of the following physical constants: $d_{15^\circ} = 0{,}9293$; saponification number 91,3, corresponding to 32 per cent. linalyl acetate; the content of methyl ester of anthranilic acid was found after Erdmann's method at 9,6 per cent., after that of Hesse and Zeitschel at 9,5 per cent. In consequence of the deep dark-brown colour of the oil, the optical rotation could not be ascertained. The remaining portion of the extract yielded still 120 grams essential oil. What was specially remarkable in this oil was the unusually high content of anthranilic acid ester, which we determined at 15,0 per cent. We were, namely, able to isolate from the oil about 18 grams solid ester of the boiling point 104° (4 to 5 mm pressure), of the melting point 24,2°, and having the congealing point 23°. Hesse and Zeitschel[2]) mention the content of anthranilic acid ester in an essential extract oil as 6,5 per cent. Their statements as regards the other constants also differ considerably from our figures, from which it may be concluded that the composition of essential extract oils of orange blossoms is subject to quite important fluctuations.

The first-named oil passed over between 80° (30 mm pressure) and 150° (5 mm pressure). In the lowest boiling portion of the oil, which amounted to only a few grams, we were able to detect traces of benzaldehyde by means of its semicarbazone. The crystals which dissolved with difficulty in alcohol melted at 214°; when heated with dilute sulphuric acid, they developed the characteristic odour of benzaldehyde. The specific gravity of this fraction was 0,8591, the optical rotation, $\alpha_D - 4^\circ 42'$, the boiling point 162° to 185°.

In the oil partly freed from benzaldehyde, which probably consisted chiefly of terpenes, we endeavoured to detect pinene and dipentene or limonene. We did not, however, succeed in obtaining from it either the nitroso chloride of the first-named, or a bromide of one of the two last-named terpenes.

l-linalool forms one of the principal constituents of the oil. It was identified by means of a fraction of the boiling point 70° to 72° (5 mm pressure), from which we obtained by repeated fractionating an oil of the following properties: boiling point 197° to 198°;

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[1]) Report October **1902**, 52. April **1903**, 55.

[2]) Journ. f. prakt. Chemie II. **66** (1902), 513.

$d_{15°} = 0{,}8735$; $\alpha_D = -9° 8'$. It was recognised as linalool already by its odour. With phenyl isocyanate it formed a phenyl urethane of the melting point 65°. Chromic acid mixture converted it into citral; when heated slowly with formic acid of high percentage, it split off water, an occurrence characteristic of some terpene alcohols.

Linalyl acetate we discovered in a fraction which boiled between 70° and 90° (5 mm pressure). The saponification number of the oil was 116,3, corresponding to an ester-content of 40,6 per cent. From the liquid obtained on saponification, an oil of the boiling point of linalool could be fractionated, which formed a phenyl urethane of the melting point 65° and which for the rest had all the properties of this alcohol. In the saponification liquor there was detected, in addition to phenyl acetic acid of the melting point 76°, also acetic acid. The silver salt formed from it had the silver-content required for silver acetate:

0,1782 grams of the substance left 0,1148 grams Ag.

| Found: | Calculated for $C_2H_3AgO_2$: |
|---|---|
| Ag = 64,42 per cent. | 64,67 per cent. |

In order to remove the anthranilic acid ester from the portions boiling above 80° (at reduced pressure), the latter were shaken three to four times with dilute sulphuric acid. The ester separated from the acid solution contained an admixture of a small quantity of a basic body with a strong nicotine-like odour, which distilled above 110° (6 mm pressure).

According tho the observations made by us up to the present, phenyl ethyl alcohol appears to form a highly important constituent of the extract oil. We abstracted this alcohol in a fairly considerable quantity, by means of phthalic acid anhydride, from the fractions passing over between 80° and 100°. The body was heavier than water, and boiled at 215° to 218°. Its phenyl urethane melted at 79°. An analysis of this compound gave the following values:

0,1616 g of the substance yielded 0,0895 g $H_2O$ and 0,4426 g $CO_2$.

| Found: | Calculated for $C_{15}H_{15}O_2N$: |
|---|---|
| C = 74,66 per cent. | 74,69 per cent. |
| H = 6,15 „ „ | 6,22 „ „ |

The diphenyl urethane, which had not hitherto been produced, melted at 99° to 100°. This body may perhaps be found suitable for the detection of the alcohol in cases where it is a question of identifying the phenyl ethyl alcohol in mixtures of bodies (benzyl alcohol, nonyl alcohol), whose phenyl urethanes melt close to 79°. The compound is characterised by great capability of crystallising.

Geraniol was detected in a fraction of the oil boiling slightly above phenyl ethyl alcohol, and which had been esterified by means of phthalic acid anhydride. The geranyl diphenyl urethane produced from it showed the melting point of 81°.

As had already been the case with neroli oil, we also observed here, on saponifying a portion of the oil which did not react with phthalic acid anhydride, that ammonia was split off. Our assumption that a nitrile might be present here was confirmed by the fact that we succeeded in obtaining, during the fractional distillation of the non-saponified portion, an oil of the boiling point 225° to 232°, which had a characteristic odour, and showed the saponification number 84,2.

During this saponification the occurrence of ammonia became particularly noticeable. We could at the same time detect in the saponification liquor phenyl acetic acid, identified by its melting point 76°. From this it may be concluded with some degree of certainty that the fraction under consideration contained phenyl acetic acid nitrile. This body boils in the pure state at 231,7°. Hesse and Zeitschel[1]) already referred to this product in their work on neroli oil.

Indol, which had already been found by the above-named chemists in the extract oil, could also be detected in the fractions boiling above 90° (5 mm pressure) by means of the picric acid compound. The indol, separated from this with the help of sodium carbonate, and readily volatilised with steam, melted at 51°. The extract oil contains a higher percentage of this body, which possesses such an intensive odour, than neroli oil.

We were also able to prove the presence in the extract oil of the nitrogenous substance of the melting point 159°, which had been detected by Hesse and Zeitschel[2]) in orange blossom water-oil. We obtained it after saponification of a fraction passing over between 90° and 100°, by repeated extraction with ether of the acidified saponification liquors. The difficult solubility of the compound in ether may possibly be the cause that we only detected it in the saponification liquor, contrary to the above-named chemists. The colourless laminæ melted at 158°.

The portions of the oil boiling between 120° and 124° (5 mm pressure), from which the anthranilic acid ester and the bulk of indol had been removed, contained a ketone with a jasmine-like odour, to which we have already referred in our last Report[3]). Unfortunately the quantity of this fragrant body contained in the oil was so small, that a more detailed identification was not possible. As we found

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[1]) Journ. f. prakt. Chemie II. **66** (1902), 515.

[2]) Journ. f. prakt. Chemie II. **66** (1902), 515.

[3]) Report April **1903**, 55.

the ketone chiefly in a fraction whose boiling point agrees with that of jasmone, we consider it probable that it is jasmone. This supposition is supported by the fact that a fraction boiling at 250° to 260° formed with semicarbazide a semicarbazone of the melting point 204° to 205°, the same melting point as the jasmone semicarbazone. Like the latter, the semicarbazone obtained by us was also difficultly soluble in alcohol. The material only sufficed for one combustion analysis, whose values, however, did not agree well with those calculated for the ketone. The quantity of the analysed substance amounted only to 0,098 gram. It should be mentioned that this ketone is very important for the odour of the extract oil.

The highest boiling portions of the oil appear to be formed by a sesquiterpenic alcohol, which up to the present has not yet been examined by us.

**Neroli "Schimmel & Co."** The low prices of the natural product induced us already in July to lower our quotations somewhat. For orders of 20 kilos and more we would be prepared to meet our clients still further, and we invite correspondence on the subject. The quality of our original product is unparalleled.

**Orris Oil.** With regard to the unheard-of depreciation in the value of Florentine orris-roots, the German Consul at Florence says in his official report (D. H.-Archiv **1903**, April number): —

> The trade in the aromatic roots of the white flag, called orris-root, has now for some years suffered very considerably.
>
> The production has no doubt increased from year to year as the demand has not grown less, but the price has fallen so low that the cultivation pays no longer.
>
> In 1890, the price paid for 100 kilos was 130 lire; in 1891, 176 lire. In 1892 it advanced to 310 lire. In 1893 and 1894 the price was still as high as 200 lire, but it then fell rapidly, in 1897 to 135 and in 1898 even to 65 lire. In 1899 the price was 70 to 100 lire, in 1900, 80 to 100 lire. But in 1901 it had declined to 50—65 lire, and for 1902 not more than 40 to 50 lire may be expected.
>
> Contrary to the movement in the value, the production has increased, from 400 tons in 1892 to 500 tons in 1893, 600 tons in 1894, 700 tons each in 1895 and 1896, 800 tons in 1897, 850 tons in 1899, 950 tons in 1900, 1000 tons in 1901. For 1902, a further increase is anticipated.
>
> According to the enquiries made by the Tuscan Agricultural Society, the present wretched situation is due to the exaggerated prices of the year 1892. At that time the stocks of the whole province had, through special circumstances, dwindled to 250 tons, and the exaggerated price caused by this tempted the producers to apply themselves more to the cultivation of orris-root, in consequence of which that what had hitherto been a subordinate industry now often became one of the principal means of livelihood.
>
> This, however, was not the only result of the above-mentioned rise in the prices. It also attracted attention outside the Province of Tuscany, and in the district of Verona the merchants endeavoured to palm off their inferior product as the better Tuscan article. In this they succeeded, and the Veronese root,

which is much inferior in aroma and density to the Tuscan variety, and which is not suitable for distillation, yet found a ready sale for the more common industrial purposes, and on account of its lower price, especially in America.

Our chief pourveyor in Florence reports as follows: —

Stocks of Florentine root end of February 1903 about . . . 930 tons
Shipments since then up to end of August about . . . . . . . 370 „
Present available stock from previous harvests about . . . . . . 560 tons.

The total shipments during the twelve months from September 1902 to August 1903 amounted to about 840 tons, against a maximum of about 1000 tons in previous years. The average annual shipments, and consequently also the world's average annual consumption of *Iris Florentina* amounts, according to our observations, to about 900 tons. The yield of the new harvest, which commenced a short time ago, cannot as yet be determined; the estimates range from 700 to 1000 tons, of which the former allows for a (hitherto still problematical) diminished gathering of roots which become mature, whilst the latter represents the actual available total quantity of ripe roots. The producers say that they will only gather the three-year old roots, by means of which they hope to influence the course of the prices in their favour; but experience has repeatedly shown, especially in November 1902, that an improvement in the prices undoubtedly leads to an increase in the result of the harvest, and to a correspondingly larger planting out of new roots. The harvest commences in the second half of August and lasts until the end of October, — in favourable weather even into November; — after that further harvesting and especially trimming becomes impossible.

It is clear from the foregoing that a reliable estimate of the result of the harvest cannot as yet be made, but if we take the low quantity of 700 tons
and add the old stocks, as above . . . . . . . . . . . . . 560 „
we arrive at a total quantity of . . . . . . . . . . . . . . 1260 tons,
which would therefore be 360 tons more than the world's annual consumption.

The prices of good assorted roots moved as follows: —

| | | assorted roots | pickings | |
|---|---|---|---|---|
| 1902 | Sept./October | 38 to 44 marks | 35 to 40 marks | all per 100 kilos cif. Hamburg. |
| „ | Nov./December | 44 „ 42 „ | 40 „ 38 „ | |
| 1903 | Jan./August | 42 „ 36 „ | 38 „ 34 „ | |

In roots of the new crop of which, as it is somewhat late, no large quantities have as yet come on the market, a few small transactions have taken place at the parity of

35 marks cif. Hamburg for assorted roots
30 „ „ „ „ pickings.

No large transactions have so far been made, as the majority of the producers are not yet prepared to fall in with the wishes of the purchasers who, in the absence of export-orders, do not seem willing to go beyond the last-named prices. The bulk of the harvest, as is well known, is placed on the market in September and October, and in comparing an available total
quantity of . . . . . . . . . . . . . . . . . . 1260 to 1560 tons
with the world's annual consumption of . . . . . . . 900 tons,
it is probable that the owners and producers will have to give way, unless larger orders from abroad should bring about a temporary improvement in the quotations.

As long as the producers, as hitherto, only work for their own benefit with fine words, instead of agreeing upon a general reduction in the planting out of the roots, so long will it be difficult to improve the position of this article, which, in view of its importance, deserves a better fate. Not until November will it become clear whether and in how far the evil experience of the last few years has taught a useful lesson to the producers with regard to the new planting out of the roots.

In view of what has been said above it may be taken for granted that the low prices of orris oil will for the present still remain in force. The manufacturers have probably laid in good stocks of cheap roots.

**Oil of Para Cress.** From the essential extract of the Para cress (*Spilanthes oleracea* Jaquin) E. Gerber[1]) obtained by steam distillation, in the yield of 0,27 per cent., an oil which had the following physical constants: $d = 0{,}847$; $\alpha_D = + 1{,}85^\circ$; molecular weight 215. It has an acrid taste, and the bulk distils over between 135° an 190° (35 mm pressure). The principal fraction boiling at reduced pressure at 145° to 155°, consists chiefly of a hydrocarbon $C_{15}H_{30}$, spilanthene, which can be purified from foreign admixtures by oxidation with permanganate at the temperature of the water bath, and in that condition shows the boiling point 135° to 138° (25 mm) or 220° to 225° (at ordinary pressure). $d = 0{,}845$. Bromine, dissolved in chloroform, absorbs the hydrocarbon with blue discolouration which later on turns into a brown colour. The product of the reaction is a yellow, viscid oil of the composition $C_{15}H_{30}Br_2$. An acid isolated from the oxidation liquid has the melting point of 180°. It crystallises from water, and when treated with silver nitrate and sulphate of copper it forms crystalline deposits. The barium salt is amorphous.

**Patchouli Oil.** We are in the pleasant position of being able to deliver this oil (which has become rare) in the most abundant manner, and that exclusively from our own distillate from choice leaves, for which we have a source of supply which has not failed us even in times when there was a general lack of material.

**Peppermint Oil, American.** The position taken up by us from the first with regard to the peculiar state of the peppermint-oil market has not been fruitless; the prices, after reaching in March of this year the culminating point at about $ 5,— per lb., have since then declined without interruption down to about $ 2,30, and only during the last weeks they have again hardened considerably owing to unfavourable reports on the new peppermint-harvest. The American "bulls" appear to be preparing for a new attack, but, it is hoped, will not succeed with it, as at the last-mentioned figure much oil has been taken up by the consumers, and the principal channels of demand are now blocked for a long time to come. We can only advise the hotspurs to abandon

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[1]) Archiv der Pharm. **241** (1903), 270.

their schemes, and to be content with prices of about $ 2,50 to 3,— at which the producers can comfortably exist.

We have before us the original reports on the harvest in more than 50 localities in Michigan and Wayne County, and although some of them are very unfavourable, a large proportion expresses great satisfaction with the results. In some, a rich yield and increased cultivation are even reported. In a few Michigan counties the crop has produced up to a third more than that of the previous year. It is to be hoped that the speculators will not enter upon the scene; the producer is undoubtedly content with a price of about $ 2,50, for the exaggerated values have done more harm to this article than good.

For a correct view of the situation it is necessary to consider that large parcels of old oil are probably still in the hands of the speculators, and among these much adulterated stuff, which for a long time will float about the market. Moreover, the new harvest in Japan has meanwhile also become due, and of this large parcels of liquid oil can now be bought at about 7/- per lb.

Under such conditions we would consider it inexcusable to support a bull-movement above $ 3,—; there is no ground for such proceedings. On the other hand, we do not consider it probable that the prices will fall to any extent, or perhaps come down to the level at which they stood some two years ago. If such a depreciation in the values should ever occur again, it would be a matter greatly to be regretted, for everyone connected with the peppermint-oil trade has an interest in seeing the industry prosper, and not pining away owing to starvation-prices.

We have regulated the selling-prices of our two qualities in accordance with the present state of the market.

**Peppermint Oil, Japanese.** In July we were informed from Japan that the peasants in the peppermint-district had greatly extended the cultivation of peppermint owing to the splendid prices obtained during the last season, and that the result of this year's distillation might be estimated at a total of about 250000 catties, or about 150000 kilos. The stocks of old oil are estimated at 50000 catties.

In consequence of these favourable prospects the prices fell considerably as early as August, and in the beginning of September they again came down to the healthy, normal level of 5/- per lb., as against 13/- in January of this year.

It is well known that last year the value of this article was artificially inflated by the situation in America, and a few weeks ago, when an effort was made to drive up the prices on the other side, a reaction immediately took place again in Japan. But as there is no prospect of a possible repetition of last year's comedy, the artificially promoted upward movement soon collapsed, and the market of Japanese oil is now rather weak.

The admixture of Japanese oil has frequently brought the Americans into trouble, and this dishonest practice has now probably been abandoned.

**Peppermint Oil, Mitcham.** Reports from the English peppermint-districts are one and all unfavourable. The development of the plants has been retarded by the cold and damp weather in July and August, and when subsequently the weather changed, the plants had already been cut, so that a favourable influence was no longer possible. Not only has the cultivation been on a reduced scale, but the yield was also lower, whilst the plants themselves suffered from mildew. The yield does not amount to more than one-half of that of an average crop.

In consequence of these unfavourable conditions, and in the absence of all stocks of old oil, the prices asked for this year's oil are very high. As soon as our own stocks are exhausted we shall be compelled to raise our quotations to a corresponding extent. For reliable distillates the price asked is 32/- per lb., which would be equal to a price of 76 marks per kilo for the rectified oil.

**Peppermint Oil, Saxon.** The yield from our own cultivation has, like that in England, suffered considerably from cold, damp weather, and is about equal to that of half a usual crop. The second cut has not taken place at all. The result of the distillation comes to about 320 kilos, against 580 kilos in 1902.

The stocks of our own distillate may possibly be exhausted in the course of a few months, as orders for forward delivery have already been booked.

As a continuation of their work on the influence of the character of the external surroundings on the peppermint plant, E. Charabot and A. Hébert¹) have made observations on the effect of mineral salts on the content of volatile acids in the plant. The tests were made by ascertaining the proportion of the esterified volatile acids to the total quantity of volatile acids. This value is of particular interest for the study of the conditions under which the esterification of the alcohols takes place. It has now been proved that the mineral salts supplied to the soil²) increase the content of volatile acids in the plant; the chlorides and sulphates effect a slight increase of acidity, di-sodium phosphate a considerable one, whilst the nitrates appear to bring about a decrease of acidity. The content of esterified and free acids is approximately the same. The volatile acids are found above all in the leaves. In comparing the results of the above work with those mentioned before³), it is seen, that with the salts which effect

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¹) Compt. rend. **136** (1903), 1009. Bull. soc. chim. III. **29** (1903), 612, 698.
²) Report April **1903**, 61.
³) Report April **1903**, 61.

a diminishing of the water-content of the plant, the content of esterified, volatile acids in proportion to the total quantity of volatile acids, is largest.

In connection with these experiments, Charabot and Hébert[1]) have also studied the influence of mineral salts on the development of the odorous substance in the peppermint plant, and they have found that the content of essential oil in the plant is increased in a marked degree by ammonium chloride. The sulphates of manganese and potassium and of ammonium appear to have a favourable effect in this respect. Sodium chloride and potassium chloride, on the other hand, exert no appreciable influence. Potassium nitrate and di-sodium phosphate act like the sulphates mentioned above.

In view of the manifold adulterations of peppermint oil, A. M. Todd[2]) lays special stress on the value which above all the determination of the optical rotation has, in addition to the specific gravity, for judging peppermint oil.

These two constants taken together give very valuable information on the purity of the oils, as it would be difficult to find adulterants which, when added to the oil, would not alter at least one of these properties to a considerable extent. As the adulterators pay special attention to the "balancing" of the specific gravity, the alteration of the rotatory power frequently reveals the adulteration.

Bennett and Parry report on some adulterations recently observed. The former[3]) proved an adulteration with acetine, the acetic ester of glycerin. As the constants given by Bennett for the oil examined show, the oils which have been adulterated in this manner differ very considerably from pure peppermint oil, and are distinguished above all by their very high specific gravity ($d_{15^\circ} = 0{,}964$), and the exceptionally high ester-content (71,2 per cent., calculated as menthyl acetate).

In the other case which Parry and Bennett[4]) mention, it was a question of adulteration with African copaiba oil. This adulterant affected chiefly the rotatory power and the solubility. The oils examined showed a rotation of $-3^\circ$ to $+3^\circ 30'$, and were insoluble in 70 per cent. alcohol. When the alcoholic mixture was left standing, oily drops separated out at the bottom of the vessel. The menthol-content is naturally much reduced by this adulterant; Parry and Bennett found on the average 34 per cent. total menthol.

In our laboratory such adulteration has not been observed in a single case.

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[1]) Compt. rend. **136** (1903), 1678.

[2]) The Chemist and Drugg. **63** (1903), 369.

[3]) The Chemist and Drugg. **62** (1903), 591.

[4]) The Chemist and Drugg. **63** (1903), 154.

**Petitgrain Oil, Paraguay.** The over-production continues. We do not know where the extreme limit lies, but one thing is certain, that the consumption of this oil cannot be forced by a further depression of the prices. The manufacturers may yet experience bitter results if they continue to carry on the production on the present scale. The "ring" which existed at one time, has not been formed again, in consequence of the disinclination of one of the oldest producers.

The quality of the oil varies very considerably. Its fineness is judged by the content of esters, linalyl acetate, and geranyl acetate, fluctuating between 40 and 85 per cent.

**Pine-needle Oils.** In all the different kinds of these oils which we keep in stock there has been, and partly still is, a great scarcity. The extrafine quality from the shoots of *Abies pectinata* can at present only be obtained in small parcels, and may possibly not be obtainable in greater abundance before November. There has lately arisen an enormous demand for the excellent Siberian distillate — a demand which could only be satisfied with the greatest difficulty.

The transport from some places in the Ural mountains was periodically impossible, owing to the destruction of the roads through bad weather. We hope soon to be able to keep some stock.

The demand for the oil from *Pinus pumilio* has increased to such an extent, that new sources of supply would be welcome. There are only very few manufacturers who supply this oil in the original quality. The oil mixed with chloroform offers an active remedy for rubbing on in articular rheumatism. The fine fragrant oil from *Abies alba*, which is used by preference for pine-odour or "Tannenduft" perfumes for the room, also becomes more and more scarce. Such perfumes have lately again come more into fashion.

**Rose Oil, artificial, "Schimmel & Co."** (German Patent No. 126736). In consequence of the cheap prices of Turkish oil, we have some months ago also slightly reduced our selling-prices of the artificial oil. If it is taken into consideration that this beautiful product can be obtained at half the price of Turkish oil, and moreover free from stearoptene, the advantages connected with the use of our oil need no further illustration. Its consumption is growing constantly.

**Rose Oil, German.** Our total production this year amounts to only about 14 kilos, as we had to work up the bulk of our rose-harvest for rose-water. We had urgent orders for some 10000 kilos of the last-named article, which we were able to execute still in July.

Owing to the cool weather, the roses were gathered under very favourable circumstances, and the result was a flower-material of faultless quality. Our rose-products this year are of a very high order.

**Rose Oil, Turkish.** It is of course well known that fate has been exceptionally kind this year to the Bulgarian rose-harvest, and that in consequence the rose-oil distillation has given a result as never before within living memory. The total yield is estimated at

about 6260 kilos
against 3900 „ in 1902
and 3200 „ „ 1901.

This enormous increase has naturally led to a further depression in the prices, and has caused such fluctuations especially in ordinary commercial qualities, that a fixed price for the latter is practically out of the question.

The fall would probably have acquired still greater dimensions, if a brisk demand had not suddenly sprung up towards the end of August, which arrested the downward tendency. The absurdly low prices have attracted the interest of financially powerful speculators, and the latter, in conjunction with the usual regular purchasers, have bought up in the course of a few weeks more than 4000 kilos, that is to say two thirds of the whole harvest. The remainder is in the hands of producers who speculate with it, or sell it only at high prices. The sudden speculative enterprises of such remarkable extent are explained thus, that many rose-cultivations have been given up on account of their unremunerative character, and that in their place the cultivation of Turkish tobacco is taken up, which is highly remunerative and offers excellent prospects, in view of the great demand for the manufacture of cigarettes. This statement has reached us from a reliable source, and it appears to us in so far plausible, as the cultivation of roses, as a matter of fact, is at present wholly unable to show a profit.

On the other hand, the trade in rose oil still seems to pay well, if the quantity produced is compared with that exported. For example

in 1900 there were exported 5846 kilos
produced 3789 „
and therefore exported 2057 kilos more;

in 1901 exported 5167 kilos
produced 3260 „
therefore a surplus of export of 1907 kilos.

The export-figures are those given by the Direction of the Statistical Department of Bulgaria[1]), whilst the figures of the production represent the average of the figures given by the principal rose-oil merchants and producers. It will be seen from these data with a fair

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[1]) Compare statistics, Report October **1900**, 51.

amount of certainty, that the yield of rose oil is on the average "enlarged" every year by some 2000 kilos, and that about £ 50000 extra profit is made annually by the merchants by means of adulteration of the rose oil. The largest consumption of rose oil is in France. The United Kingdom takes the second place, Germany the third. In our opinion speculation should be confined to one single good quality of rose oil, which has a real, honest value, and advantage may be taken without hesitation of the present prices to conclude larger transactions.

In a short note on the value of the refractive index, Parry[1]) inter alia expresses the opinion, that the determination thereof may in certain cases afford very valuable information regarding the purity of the oil. Parry has, for example, recently examined several rose oils, which by their high refractive indices seemed open to suspicion. Whilst in pure rose oils of this year's crop he observed exponents of refraction of 1,46095 to 1,46208, the samples referred to had refractive indices of 1,46700 to 1,47100. From these observations Parry draws the conclusion that an admixture of geraniol or of palmarosa oil had taken place.

**Rosemary Oil.** In the leading French departments the distillation has given a normal result, and has now come to an end, but in some districts it is taken up again after completion of the vintage — provided the weather-conditions are favourable. Fine distillates can be had in excellent selection and in abundance, but a further downward movement of the value seems improbable, as practically nothing is left from last year's distillation.

In Dalmatia the yield has been normal, but the demand is so brisk, that a fall in prices must not be reckoned upon. From this source more adulterated than pure oil is on the market. This fact sufficiently explains the differences met with in the quotations.

**Sandalwood Oil, East Indian.** Since the time of the last Indian wood-auctions in December 1902, the prices of sandalwood have not changed; but the quotations of sandalwood oil (the production of which has been carried on with quite exceptional energy) have been depressed gradually to such an extent, owing to overproduction, that the present selling-price, if calculated in a rational manner, no longer pays. Possibly the dispositon of the manufacturers is now quite as depressed as the prices.

On the other hand, for pure santalol, which we were the first to introduce into commerce, there is now a fairly strong demand. The

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[1]) The Chemist and Druggist **63** (1903), 246.

number of manufacturers producing santalol-capsules seems to increase continually.

With regard to this year's auctions of wood, we have received the following official programme:

| District | Koti | Date of auctions | Quantities |
|---|---|---|---|
| Shimoga | Tirthahalli | 16th Nov. 1903 | 125 tons |
| „ | Sagar | 20th „ „ | 100 „ |
| „ | Shimoga | 24th „ „ | 525 „ |
| Kadur | Tarikere | 26th „ „ | 150 „ |
| „ | Chikmagalur | 28th „ „ | 200 „ |
| Hassan | Hassan | 3rd Dec. „ | 200 „ |
| Bangalore | Bangalore | 7th „ „ | 84 „ |
| Mysore | Seringapatam | 10th „ „ | 200 „ |
| „ | Hunsur | 14th „ „ | 500 „ |
|  |  |  | Total 2084 tons |

The "spike"-disease which has broken out among the sandalwood trees in some districts of East India, and to which we referred in our two last Reports 1), has spread further, and continues to draw the serious attention of all interested parties, — in the first place the Indian Government. The latter has recently published a third report 2) from the pen of the Government botanist Dr. Butler, which in the main agrees with the earlier work by McCarthy and Barber. The detailed microscopical examination of all tissues, from the leaves to the root, showed an extraordinary overloading of the parenchymal tissues with starch. The leaves, which during the attack become stiff and sharp (the first symptom of infection), become decidedly thicker in consequence of the overloading of the mesophyl-cells with starch. The stomata increase considerably in number in comparison to healthy leaves of equal surface. In the trunk an irregular formation of the vascular tissues was only observed in trees which had reached an advanced state of the disease. The roots, with the exception of their extremities, are healthy, — a fact also observed by Barber. In consequence of the excessive assimilating action of the tree, no blossoms are produced, and instead of these the typical stiff-bristled leaves develop. A satisfactory explanation of this strange hypertrophy could not be given; in Butler's opinion it is probably due to the presence of a poison in the sap. The disease does not appear to be of a parasitic or bacterial origin. Butler recommends as preventive measures, the immediate cutting down of all infected trees, if healthy trees are near; and further, in working up the wood, the immediate and complete

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1) Report October **1902**, 77; April **1903**, 70.

2) Indian Forester **29** (1903), Appendix to No. 4.

destruction of all chips and other waste. The object of the scientific investigation of the "spike"-disease, which is now progressing, is that of ascertaining the manner of propagation, and the period of incubation of the poison, and further the study of the vegetal companions of the sandalwood-tree.

According to recent publications[1]) no active remedy has as yet been discovered. With regard to the evil itself, the view is now taken that the "spike" is probably not an actual disease, for it has been discovered that the peculiar bristle-like deformation of the leaves of the so-called spike-trees is not a symptom of disease, but on the contrary is usually found on all trees which perish either from age, or from injury to the roots by fire, strangulation by creepers, or fungoid, parasitic, or epiphytic growths. It is also believed that a poor, low-lying soil, especially if it contains much "kankur" or lies on a stratum of kankur, causes the permanent decay of the root-system and consequently of the tree. It has been observed that unhealthy sandalwood-trees were always found only in places where the remaining vegetation also showed an unhealthy appearance, whilst diseased sandalwood-trees are never met with on good soil with luxuriant vegetation.

A report by Peter[2]) shows once more how necessary it is to exercise care in purchasing gelatine capsules filled with sandalwood oil. Peter has examined the oil of a few commercial caps. gel. c. ol. santal. repl. The oils were partly found considerably adulterated, a matter which is of great importance in view of the exclusively therapeutic use of these capsules. Three of the samples examined had a santalol-content of 57,4, 71,4 and 77,3 per cent. respectively, whilst a good quality sandalwood oil should contain at least 90 per cent. santalol[3]).

Peter at the same time calls attention to the fact that if a sandalwood oil differs in its behaviour from the normal distillate, it should not forthwith be concluded that the oil is adulterated, and he endeavours to prove by an example that an inferior oil may also be obtained "by exactly following the directions". An oil distilled by Peter himself had a specific gravity of 0,972 (15°), and a santalol-content of only 82,3 per cent.

In view of the small quantity sandalwood (10 kilos) which Peter submitted to distillation, and the doubtless unsuitable method of distillation which must have been employed in this case, but which in the case of sandalwood oil plays a most material part, the example quoted

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[1]) The Planter's Opinion, 25. July 1903. Indian Forester **29** (1903), 340.

[2]) Pharm. Ztg. **48** (1903), 573.

[3]) On this occasion we would point out that the formula $C_{15}H_{26}O$ is still frequently accepted for santalol, whereas according to more recent examinations the formula $C_{15}H_{24}O$ belongs to it (comp. Report October **1900**, 58).

by him is of little importance. It is clear that Peter only wishes to show that by following an unreliable method of working, inferior sandalwood oils are obtained.

On the strength of our experience extending over many years, we are in a position to state that sandalwood oil distilled on a large scale in a proper way, always answers the requirements which are nowadays specified for East Indian Sandalwood oil.

**Spearmint Oil.** This article is at present still extremely scarce, and can only be had at higher prices. Up to now we have been able to obtain the necessary supplies of fine American distillate, but according to advices from America, the result of this year's distillation has been very small, and quotations are only made "without engagement".

**Spike Oil.** The distillation will come to an end in a few weeks' time. The result is on the whole equal to that of last year, as the frost has caused a considerable amount of damage. The yield of oil, however, is very satisfactory. In the Gard department there is a great lack of labourers for gathering the plants, as this work coincides with the vintage. For this reason a fairly large quantity of material remains unused. Up to now the prices have undergone no pronounced change, although a rise is expected, as the demand is said to be extraordinarily brisk.

Spike oil is used to a large extent for the production of the more common qualities of lavender oil.

**Star-anise Oil.** The value of this important article has hardly changed during the summer months. In May reports were current that the harvest of star-anise in Tonquin promised to be a very rich one. But these reports were soon contradicted, and a letter from Langson dated 26th of May, stated that the yield of the plants had been much reduced by caterpillars and by heavy storms. Instead of the expected fall in the prices an upward movement took place.

In China also the market is firm and prices went up from 4/- to 4/9 during the last weeks.

We have already mentioned¹) that star-anise oil occasionally shows a slight dextrorotation, whereas it is usually faintly lævorotatory. Such an oil has recently again been examined in our laboratory. The constants of the oil were as follows: $d_{15^\circ} = 0{,}9893$; $\alpha_D = + 0^\circ\, 18'$; congealing point $+ 18^\circ$; soluble in 2 vol. and more 90 per cent. alcohol. It is clear from the properties mentioned that we have here to deal with a perfectly good, unadulterated star-anise oil, — and in fact the reputation of the firm from whom the oil was obtained is a

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¹) Gildemeister and Hoffmann: "The Volatile Oils", p. 361.

sufficient guarantee hereof. We confine ourselves in this instance to once more confirming the fact of the dextrogyration, with the reservation that we may possibly return to the subject later on.

**Thyme Oil.** The principal producers of this oil were up to now France, Algeria and Spain. Recently, however, Cyprus seems also to come under consideration.

According to the Annual Report of the Director of Horticulture in Cyprus, the production of thyme oil in this island, in the financial year 1901—2, was 1086 lbs., against 615 lbs. in 1900—1, and 237 lbs. in 1899—1900. Of the quantity distilled in 1901—2, $871\frac{1}{2}$ lbs. were sold to Leipzig. Although the distillation of oil of thyme is a new branch of industry, it has, as the above figures show, already acquired fairly important dimensions, and is making rapid progress.

As the flowering herb of thyme, from which thyme oil is distilled, is gathered chiefly in the fiscal forests, the Government derives an annually increasing profit from this industry, whilst at the same time work is provided for the poorest classes of the rural population of the island.

The plant grows at present only in the wild state, and that chiefly in the forests. In view of the advantages derived from this industry, it is believed that the cultivation in various parts of the island would prove remunerative.

We would here point out that so far we ourselves have received no offers from this new source, and that we are not in a position to confirm the correctness of the above statements.

**Oil of Tuberose Blossoms.** In our last Report¹), we occupied ourselves with the essential oil of tuberose blossoms, which had been produced by us by steam distillation of 100 grams blossom-extract. The quantity of the essential oil obtained in this manner was 5 grams, and served for some preliminary examinations which we made by way of preparation of the more detailed examination of this hitherto almost completely unknown oil. These preliminary examinations proved that the essential oil of tuberose blossoms has a blue fluorescence; from this, according to the observations made by us with oil of orange blossoms and other blossom-oils, the presence of methyl ester of anthranilic acid appeared very probable. We were also able by saponification of the oil to isolate benzoic acid of the melting point 122°, which is present in the oil in the form of ester. This ester was not attacked by potassium permanganate solution, was fairly volatile with steam and reminded in the odour of methyl ester of benzoic acid. For the exact identification the quantity was too small.

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¹) Report April **1903**, 74.

In the meantime A. Hesse[1]) has now published a more detailed study on the same subject, which agrees in the main points with our statements. He also obtained from the tuberose extract an essential oil in which he detected methyl ester of anthranilic acid and ester of benzoic acid, and from 100 grams essential oil he was able to isolate not only the ester of anthranilic acid, but also, by oxidising the oil with potassium permanganate solution[2]), the stable ester of benzoic acid. The content of methyl ester of anthranilic acid was 1,13 per cent. It was separated by conversion into the difficultly soluble sulphate discovered by us[3]), according to the quantitative estimation-method worked out by Hesse and Zeitschel.

The ester mixture not attacked by potassium permanganate distilled from 199° to above 240°; benzoic acid and benzyl alcohol could be obtained from it by saponification. A portion of the esters is accordingly in any case benzyl benzoate; whether a part of the benzoic acid is moreover combined with methyl alcohol, as we suspect, is doubted by Hesse, who considers the quantity of the acid in any case very small.

It is all the same a remarkable fact that the ester mixture isolated by oxidation is, comparatively speaking, readily volatile. Hesse gives the boiling point of the first half of the mixture at from 199° to above 240°, whilst the other half boils at above 240°. The boiling point of benzyl benzoate, however, lies at 324°. According to this, lower boiling esters are also present, and the presence of methyl ester of benzoic acid (boiling point 199° to 200°) is therefore not excluded.

Hesse was further able to isolate from the oil, by treatment with phthalic anhydride, an alcohol which according to its boiling point 206° to 214° and other behaviour must consist chiefly of benzyl alcohol. The latter is consequently also present in the free state in oil of tuberose blossoms.

Oil of tuberose blossoms is not only obtained by extraction, but also by the enfleurage method. Hesse has ascertained by an experiment made on a large scale, that in the enfleurage of 1770 kilos tuberose blossoms, 1374 grams essential oil pass over into the fat. This essential oil of tuberose blossoms had the following constants: $d_{15^\circ} = 1{,}012$; saponification number 256,3; acid number 32,7. Content

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[1]) Berichte **36** (1903), 1459.

[2]) The method applied by us in this case for the first time on oil of tuberose blossoms, of separating, by shaking with potassium permanganate solution, the difficultly oxidisable substances from those which oxidise more readily, has long been known. We have used it also with success, for example, for separating the amyl methyl ketone from furfurol in oil of cloves, and also for separating cymol from terpene in Ceylon cinnamon oil. See Report April **1897**, 50; Journ. f. prakt. Chemie II, **66** (1902), 50.

[3]) Journ. f. prakt. Chemie II. **59** (1899), 350.

of anthranilic acid ester 5,1 per cent. From the waste blossoms of the enfleurage process a further small quantity of essential oil could be obtained by extraction and steam distillation, so that it can be calculated that the enfleurage method yields in all 13,32 times more essential oil than the extraction of fresh blossoms.

It follows from the foregoing that during the treatment with fat, the tuberose blossoms, like the jasmine-blossoms, still develop quite considerable quantities essential oil. This shows that in the blossom industry, since olden times, the enfleurage method in a wholly empirical manner has been discovered and employed, as the process which is undoubtedly the most rational one for the production of many blossom odours.

In the pomade oil Hesse could still prove the presence of methyl ester of salicylic acid, which could not be detected in the extract oil. An attempt made by him to obtain the essential oil of tuberose blossoms by distillation of the fresh blossoms with steam, yielded a distillation product with an offensive odour, which was not examined further.

**Wintergreen Oil, natural.** Recent shipments made by our New York branch are decidedly cheaper, and we are thereby in a position to reduce our quotations.

At present the lowest price would be 13 marks per kilo, in bond at Hamburg.

Our method of packing in cases of 6 × 6 lb. glass-bottles ensures a perfectly colourless oil, whereas packing in tins is not recommended for this article.

**Wormwood Oil.** We shall soon again be able to supply, at a cheap rate and in excellent quality the American oil, which at one time we used to keep in stock, as this year's distillation is said to have given very good results.

Cultivation trials, which we have carried on for several years in our experimental plantations here, may possibly be concluded in the course of next year, and, as far as can be judged, may lead to the introduction of the cultivation of wormwood on a large scale.

**Ylang Ylang Oil, Sartorius.** By forcing the distillation, our friends in Manila have been able to expedite the shipments to some extent, so that we are now at last, after many years, once more in a position to dispose of some original cases. At our urgent representations the manufacturers have agreed to a slight reduction in the price, although, as they assure us, there are absolutely no grounds for it, as the severe competition in the purchase of the flowers continues, and the demand for the fine essence is exceedingly brisk. As a rule it increases largely up to shortly before Christmas.

Second qualities can now as before be had in abundance, but owing to the excellent artificial oil which we supply, the demand for them is constantly decreasing.

**Ylang Ylang "Schimmel & Co."** A German patent No. 142858 has been granted to us for our discovery of various important constituents in ylang ylang oil. We intend shortly to avail ourselves of the rights which we have thereby obtained.

We think it superfluous to say anything further on the quality of our product. It is beyond all praise.

## Supplement to the Dutch Pharmacopœia.
## Belgian Pharmacopœia.

On the occasion of a discussion[1] of the essential oils included in the Swedish Pharmacopœia, it was pointed out that here, as in the last edition of the German Pharmacopœia, the directions for testing have been greatly improved and brought up to date, in accordance with the progress made during the last few years in the examination of essential oils. The same applies to the above-named pharmacopoeias, viz., the Supplement to the Dutch Pharmacopoeia published by the Dutch Association of Chemists[2], and the new Belgian Pharmacopoeia now in preparation; especially in the case of the last-named, the advance, as compared with the Pharmacopoeia at present in use, is very considerable. In spite of this, an improvement, or correction (as the case may be), of several prescribed tests is advisable; the various corrections suggested will be discussed in the following pages, taking in each case the requirements as specified by the Pharmacopoeias. With regard to the strengths of alcohol, we would mention that the Dutch Pharmacopœia gives a Spiritus fortior of 89 to 91 per cent. by volume, and a Spiritus dilutus of 69 to 71 per cent. by volume, whilst the Belgian Pharmacopœia has only one Alcohol, of 92 per cent. by volume.

## Supplement to the Dutch Pharmacopœia.

**Oil of Amber,** purified (*Ol. Succini depuratum*). Colourless or light yellow; $d_{15^\circ} = 0{,}86$ to $0{,}89$[1]; soluble in 10 to 12 parts Spiritus fortior.

[1] The specific gravity of our oil rectified by ourselves, of which we fully guarantee the purity, is decidedly higher, and fluctuates between 0,925 and 0,930. The lighter oils are usually adulterated.

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[1] Report April **1902**, 68.

[2] In Holland no new edition of the Pharmacopoeia has been published since 1889, and for this reason the Chemists' Association of that country has now issued the above-mentioned Supplement.

**Oil of Bergamot** (*Ol. Bergamottae*). Light green[1]); $d_{15°} = 0,882$ to 0,886[2]); neutral reaction[3]); miscible in every proportion with Spiritus fortior; evaporation-residue not above 6 per cent.[4]).

[1]) It is not correct to require simply a green bergamot oil, as pure bergamot oil in the fresh state has a brown-yellow or honey-like colour, and the green colour frequently originates only from a content of copper gradually absorbed by the oil through long storage in the estagnons. Compare our Report, April **1889**, 16.

[2]) We have had before us on various occasions oils whose specific gravity was but little above 0,881, and therefore recommend as a limit for $d_{15°}$ : 0,881 to 0,886.

[3]) Almost all bergamot oils show a minute content of free acid; the same applies to the other oils mentioned here.

[4]) Per contra, the residue on evaporation should not be below 5 per cent., as this would point to an adulteration with oil of turpentine, oil of sweet oranges, or a similar oil.

An ester value would also be advisable; the lowest content of linalyl acetate should be 30 per cent.

**Oil of Caraway** (*Ol. carvi*). Colourless or light yellow; $d_{15°} = 0,905$ to 0,915; neutral reaction; makes a clear solution in an equal volume of Spiritus fortior, and the solution must not be coloured violet by a drop of ferric chloride solution.

For the further test of caraway oil a determination of the rotatory power would be advisable; normal oil shows a dextrorotation of 70° to 80°.

**Oil of Cherry laurel** (*Ol. Laurocerasi*). Colourless or light yellow; $d_{15°} = 1,054$[1]) to 1,066; weak acid reaction; soluble in 300 parts water, in 2 vol. Spir. dilut., in every proportion in ether; when shaken with double the volume concentrated solution of sodium bisulphite, a solid crystalline mass should be formed; it is further tested in the usual manner for artificial chlorinated benzaldehyde and for nitrobenzene.

[1]) We recommend a lowest limit of 1,050.

**Oil of Juniper berries** (*Ol. Juniperi*). Colourless or light yellow; $d_{15°} = 0,860$ to 0,900; neutral reaction; oil of juniper berries should make a clear solution with 10 parts Spiritus fortior[1]).

[1]) Generally, only oils which are quite freshly distilled answer this test.

**Oil of Myrtle,** rectified (*Ol. Myrti rectificatum*). Colourless; $d_{15°} = 0,88$ to 0,89; boiling point 160° to 170°[1]); neutral reaction; soluble in every proportion in Spiritus fortior.

[1]) It will be seen from the specific gravity and the boiling point that it is here not a question of myrtle oil, whose specific gravity lies between 0,890 and 0,915, but of a myrtle oil fraction.

**Oil of Origanum** (*Ol. Origani*)[1]). Light yellow; $d_{15°} = 0,870$ to 0,910; neutral reaction; completely soluble in Spiritus fortior.

[1]) It is difficult to explain why this oil, which in practice is used only in extremely rare cases, has been included. Was it perhaps intended to be oil of Cretian origanum (*Ol. Origani cretici*)?

**Oil of Parsley** (*Ol. Petroselini*). Colourless or greenish-yellow, fairly viscid; $d_{15°}$ = 1,050 to 1,100; soluble in Spiritus fortior in every proportion; sulphuric acid is coloured blood-red 1) by one drop oil of parsley.

1) Such colour-reactions are of quite subordinate importance in judging an essential oil, and are moreover frequently misleading.

**Oil of Pimenta** (*Ol. Pimentae*). Colourless or pale-yellow, subsequently brown; $d_{15°}$ = 1,045 to 1,055 1); soluble in Spiritus fortior in every proportion; when shaken with the same volume caustic soda lye, an almost solid mass should be formed; the solution in an equal volume Spiritus fortior should only have a very feeble acid reaction; test for carbolic acid.

1) As normal pimenta oils often have a lower specific gravity, the lowest limit should be taken as 1,020.

**Oil of Pine needles** from *Pinus silvestris* (*Ol. Pini silvestris; Ol. foliorum pini*). Colourless or yellowish; $d_{15°}$ = 0,870 to 0,880; soluble in about 7 parts Spiritus fortior.

As the oil distilled from the needles of *Pinus silvestris* has a less pleasant odour and cannot be obtained in commerce, and as moreover the name *Ol. Pini silvestris* is an old but incorrect designation of oil from cones of *Abies alba*, it would be more correct to require *Ol. Templini*, whose specific gravity lies between 0,853 and 0,870.

**Oil of Rue** (*Ol. Rutae*). Colourless or yellow; $d_{15°}$ = 0,830 to 0,840; neutral reaction; congeals in the cold; soluble in two to three parts Spiritus dilutus; when heated with potassium bichromate and sulphuric acid with the addition of a small quantity of alcohol, the odour of geranium oil occurs 1).

1) The decomposition of the methyl nonyl ketone into acetic acid and pelargonic acid, caused by the oxidation, does not by any means occur as rapidly and easily as would appear to be the case from the above directions. For this reason such a test of the oil is valueless, as in most cases it will not have the desired result.

**Oil of Sandalwood,** East Indian (*Ol. Santali indicum*). Yellow or light yellow; $d_{15°}$ = 0,975 to 0,990 1); neutral or faint acid reaction; soluble at 20° in five vol. Spiritus dilutus; santalol-content at least 90 per cent. 2).

1) The higher limit might be reduced to 0,985.

2) The santalol-content is calculated on the formula $C_{15}H_{26}O$; recalculated on the correct formula $C_{15}H_{24}O$, the minimum content is 89,26 per cent.

For the saponification of santalyl acetate it is better to use alcoholic potash.

**Oil of Spearmint** (*Ol. Menthae crispae*). Colourless or light yellow 1); $d_{15°}$ = 0,920 to 0,940; neutral reaction; soluble in Spiritus fortior, at first clear, but cloudy when more of the solvent is added.

1) Spearmint oil has also very often a greenish-yellow colour.

**Oil of Spike** (*Ol. Spicae*). Yellowish; $d_{15°}$ about 0,910; soluble in two to three and more parts Spiritus dilutus.

**Oil of Wintergreen** (*Ol. Gaultheriae*). Colourless, subsequently reddish-yellow; $d_{15^\circ}$ = 1,175 to 1,188 ¹); feeble acid reaction; scarcely soluble in water, readily soluble in Spiritus fortior; the aqueous solution should be coloured violet by ferric chloride; when shaken with an equal vol. nitric acid no red colouration should occur ²).

¹) The following limits are more correct: 1,185 to 1,190.
²) Test for adulteration with sassafras oil.

**Oil of Wormwood** (*Ol. Absinthii*). $d_{15^\circ}$ = 0,925 to 0,955 ¹); neutral reaction; soluble in equal vol. alcohol; wormwood oil is coloured by nitric acid first green, then blue; by sulphuric acid, first blue, then violet.

¹) We recommend the lower limit as 0,900.
²) We have already referred under oil of parsley to the low value of such colour-reactions.

## Belgian Pharmacopœia.

(The following particulars are taken from the "Annales de pharmacie" **9** (1903), 193.)

**Anethol.** $d_{25^\circ}$ = 0,984 to 0,986; $\alpha_D = \pm 0^\circ$; boiling point 232° to 234°; sparingly soluble in water, soluble in alcohol; freshly prepared anethol melts at 22° to a colourless, strongly refractive liquid.

**Oil of Balm** (*Melissae essentia*). Colourless or yellowish; $d_{15^\circ}$ = 0,850 to 0,920; soluble in 5 to 6 vol. alcohol; insoluble in carbon disulphide ¹).

¹) The test for solubility in carbon disulphide is of no value, as the strong turbidity which thereby occurs is simply due to the small content of water in the oil; there is, however, no question of an actual insolubility of the oil.

**Benzaldehyde** (*Aldehydum benzoicum*). Produced from oil of bitter almonds or oil of cherry laurel, or synthetically. Colourless, $d_{15^\circ}$ = 1,050 to 1,055; $\alpha_D = \pm 0^\circ$; boiling point 179°; sparingly soluble in water; soluble in every proportion in alcohol; when freshly produced it is neutral, but soon acquires an acid reaction on exposure to the air; test for absence of hydrocyanic acid, foreign oils, and nitrobenzene.

**Oil of Bergamot** (*Bergamottae essentia*). Green colour ¹); $d_{15^\circ}$ = 0,880 to 0,890; makes clear solution with $^1/_4$ vol. by weight of alcohol or carbon disulphide, which becomes cloudy when more solvent is added ²); residue on evaporation five to six per cent.; ester-content (determined after neutralising the free acid): 30 to 45 per cent. linalyl acetate (ester number = 85,4 to 128,8).

¹) With regard to the colour, the same remarks apply which have already been made with reference to the Dutch Pharmacopoeia; compare p. 70.
²) The solution of bergamot oil in 92 per cent. alcohol remains clear even when more alcohol is added; cloudiness of the carbon disulphide solution points to a slight content of water always present in the oil; the last-named test is moreover useless.

**Oil of Chamomile,** Roman (*Chamomillae essentia*). Blue[1]); $d_{15^\circ} = 0,905$ to 0,915; soluble in 8 to 10 parts alcohol[2]).

[1]) In the course of time, under the influence of the air and light, the blue colour changes into green to brownish yellow.

[2]) The oil already dissolves in 1 to 2 vol. 80 per cent. alcohol.

It is further recommended to determine the saponification number; 250 to 300.

**Oil of Cinnamon** (*Cinnamomi essentia*)[1]). The distillate from the bark of *Cassia lignea*, or *Cinnamomum Ceylanicum*; $d_{15^\circ} = 1,050$ to 1,070; soluble in three parts 70 per cent. alcohol; soluble in every proportion in strong alcohol; the mixture of equal parts cinnamon oil and fuming nitric acid, when cooled to a temperature below 5°, condenses into a crystalline white mass[2]); when evaporated on the water bath, the oil should leave not more than 8 per cent. residue; the alcoholic solution of the oil (0,2 : 10,0) should become brown (not blue or green) on addition of a drop of ferric chloride solution; aldehyde-content: at least 70 per cent.

[1]) It does not appear from the above which cinnamon oil is really meant. The oil from the bark of *Cassia lignea* is not, as a matter of fact, a commercial article, as it is not produced on a large scale. The oil produced from the bark of *Cinnamomum Ceylanicum*, on the other hand, has a quite different specific gravity (1,023 to 1,040), than the one required, which belongs simply to cassia oil, obtained from the leaves and branches of *Cinnamomum Cassia*. The specified solubility and residue on evaporation again refer to Ceylon cinnamon oil. It would be desirable to correct the requirements which are in direct contradiction to each other.

[2]) This test gives no information on the purity of the oil. See Gildemeister and Hoffmann, "The Volatile Oils".

**Eucalyptol.** $d_{15^\circ} = 0,93$[1]); $\alpha_D = \pm 0^\circ$; boiling point 176° to 177°; almost insoluble in water, readily soluble in alcohol, ether and chloroform; makes a clear solution with an equal vol. *Paraffinum liquidum;* if some bromine vapour is introduced in a test tube of which the inside has been moistened with a few drops eucalyptol, fine red crystals should be formed; in a freezing mixture, at 1°, eucalyptol should solidify into long colourless needles[2]); on the water bath it should evaporate without weighable residue.

[1]) The specific gravity of pure eucalyptol lies between 0,928 and 0,930.

[2]) The solidifying or melting point of eucalyptol does not lie at $+ 1^\circ$, but at $- 1^\circ$; the solidification has sometimes to be brought about by the introduction of a small crystal of solid eucalyptol.

**Eugenol.** Colourless or yellowish, becomes brown on exposure to the air. $d_{15^\circ} = 1,072$ to 1,074; boiling point 251° to 252°[1]); sparingly soluble in water, readily in alcohol, ether, and glacial acetic acid. 1 gram eugenol makes a clear solution with 2 cc. caustic soda lye ($d_{15^\circ} = 1,33$) and 28 cc. water, which gradually becomes cloudy when air is admitted. When shaking 5 drops eugenol with 10 cc. lime-water a flocculent precipitate should be formed; identity-reaction with ferric chloride, and test for carbolic acid.

[1] For the boiling point the example of the German and Swedish Pharmacopoeias should be followed: 251° to 253°.

**Oil of Fennel** (*Foeniculi essentia*). Colourless or yellowish; $d_{15^\circ} = 0{,}965$ to $0{,}975$; at about 0° anethol crystals separate out, which dissolve again at $+ 5^\circ$[1]; completely soluble in an equal vol. alcohol.

[1] The separation of anethol may have to be brought about by inoculation with a small crystal of pure anethol.

**Oil of Lavender** (*Lavandulae essentia*). Colourless[1], yellowish, or yellowish-green; $d_{15^\circ} = 0{,}885$ to $0{,}895$; soluble in three parts 70 per cent. alcohol; ester-content (determined after neutralisation of the acid): at least 29,4 per cent. linalyl acetate[2].

[1] Only the rectified oils are colourless, but these are inferior. Compare our Report October **1894**, 30.

[2] For 2 grams oil a minimum of 13 cc. semi-normal potash solution is required, which would correspond to an ester number of 182 = 63,7 per cent. linalyl acetate. The minimum content of linalyl acetate (29,4 per cent.) corresponds to an ester number of 84, or a consumption of 6 cc. semi-normal solution for 2 grams oil.

**Oil of Lemon** (*Citri essentia*). $d_{15^\circ} = 0{,}858$ to $0{,}861$; dissolves clear or with a slight turbidity in 5 parts alcohol; makes a clear mixture with carbon disulphide in every proportion[1].

[1] The solubility tests have little value for lemon oil, but a statement of the rotatory power would be very useful in this place; good lemon oil at 20° should have an optical rotation of at least $+ 58^\circ$, and at most $+ 65^\circ$.

**Menthol.** Needle-shaped, colourless crystals; almost insoluble in alcohol, ether, and chloroform[1]; melting point 42° to 43°; boiling point 212°[2]; the solution of 0,1 gram menthol in 1 gram glacial acetic acid should not colour when three drops sulphuric acid and one drop nitric acid are added; when evaporated on the water bath, 0,1 gram menthol should leave no weighable residue.

[1] This should clearly be: almost insoluble in water, readily soluble in alcohol, ether, and chloroform.

[2] The determination of the melting point would suffice for judging the menthol.

**Oil of Mustard** (*Sinapis essentia*). Colourless or yellowish; $d_{15^\circ} = 1{,}020$; boiling point 149°[1]; very sparingly soluble in water, readily soluble in alcohol, ether, and carbon disulphide.

For the rest the tests agree with those of the German Pharmacopoeia, excepting that a somewhat higher minimum content of isothiocyanallyl is required.

[1] In this case also certain fluctuations in the specific gravity and boiling point should be admissible, and we therefore suggest the following test: $d_{15^\circ} = 1{,}016$ to $1{,}025$; mustard oil should boil chiefly between 147° and 152°, and the first as well as the last portions of the distillate should have no pronounced difference in the specific gravity from mustard oil itself.

**Oil of Orange-blossoms** (*Aurantii florum essentia*). Yellowish, becoming brown on exposure to the light, slightly fluorescent. $d_{15^\circ} = 0{,}870$ to $0{,}880$; soluble in 1,5 to 2 vol. 80 per cent. alcohol to a clear liquid with a blue-violet fluorescence; cloudiness on further addition of solvent.

The determination of the saponification number: 20 to 55, would still be desirable.

**Oil of Peppermint** (*Menthae essentia*). Colourless of yellowish; $d_{15^\circ} = 0{,}900$ to $0{,}920$; soluble in an equal vol. alcohol; the solution of 0,1 gram oil in 1 cc. glacial acetic acid should acquire after some time a blue to blue-violet colour when 1 drop nitric acid is added.

According to the above, both English and American oils are allowed.

**Oil of Rose** (*Rosae essentia*). Crystalline, light yellow mass. Soluble in an equal vol. chloroform, from which it is partly again precipitated by a large excess of alcohol; when the molten oil is cooled to 18° to 20° transparent crystals in the form of needles or leaflets separate out.

**Oil of Rosemary** (*Rosmarini essentia*). Colourless or yellowish: $d_{15^\circ} = 0{,}900$ to $0{,}920$; soluble in one-half part by weight of alcohol.

**Oil of Rue** (*Rutae essentia*). Colourless or yellowish: $d_{15^\circ} = 0{,}833$ to $0{,}840$; congealing point 8° to 10°; soluble in 2 to 3 parts 70 per cent. alcohol.

**Methyl ester of Salicylic Acid** (*Salicylate de méthyle*). Colourless; $d_{15^\circ} = 1{,}1819$ [1]); boiling point 220°; saponification number at least 360; sparingly soluble in water, soluble in alcohol and ether; identity-reaction with ferric chloride.

[1]) The specific gravity of pure methyl salicylate lies a little higher, i. e. between 1,185 and 1,190 (15°).

**Oil of Sandalwood,** East Indian (*Santali essentia*). Light yellowish; $d_{15^\circ} = 0{,}975$ to $0{,}985$; boiling point 275° to 295° [1]); soluble in 5 parts 70 per cent. alcohol; santalol-content at least 90 per cent.; 10 grams oil, 18 grams acetic acid anhydride, and a small quantity of fused sodium acetate are boiled for one hour and a half, the mixture is then washed with distilled water and soda solution, and dried with anhydrous sodium sulphate; 5 grams of the acetylised oil are saponified with 40 cc. normal potash solution by boiling for 15 minutes, and thereupon the non-combined alkali titrated back after addition of 2 drops phenolphthalein solution. For this purpose not less than 14,5 cc. nor more than 16,6 cc. normal acid should be required [2]).

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[1]) The boiling point is not required for this purpose.

[2]) With regard to this treatment, we would make the following remarks: for the acetylisation equal volumes (10 cc.) of oil and acetic acid anhydride are sufficient;

they are boiled for one to one and a half hours with the addition of a small quantity of fused sodium acetate. After boiling, the acetylisation mixture is first of all left to cool; a small quantity of water is then added, and the whole heated for 10 to 15 minutes on a water bath, in order to decompose the excess of acetic acid anhydride. It is again left to cool, the oil separated from the aqueous liquid in a separating funnel, and washed with water until it shows a neutral reaction. The oil thus treated, after being dried with dehydrated sodium sulphate, is ready for the further treatment. For the saponification, alcoholic potash solution is more suitable, as it saponifies better than the aqueous liquor, a matter of great importance for santalyl acetate which is comparatively difficult to saponify. For the same reason, one hour's heating on the water bath is advisable.

The statements regarding the consumption of alkali are not correct; the saponification numbers 262,08 and 285,6 which result from it, refer to an alcohol of the formula $C_{10}H_{18}O$ (linalool, geraniol, etc.) whereas santalol has the formula $C_{15}H_{24}O$ (compare Report October **1900**, 58). A santalol-content of 90 to 100 per cent. corresponds to the saponification numbers 195,5 to 213,7, equal to a consumption of normal liquor of 17,46 to 19,08 cc. with 5 grams oil.

**Oil of Savin** (*Sabinae essentia*). Colourless or yellowish; $d_{15} = 0{,}910$ to 0,930; soluble in one-half volume by weight of alcohol.

**Oil of Wild Thyme** (*Serpylli essentia*). Colourless or yellowish; $d_{15^\circ} = 0{,}890$ to 0,920.

**Thymol.** Colourless, transparent crystals; very sparingly soluble in water, readily soluble in alcohol, ether, chloroform, and the aqueous solutions of caustic alkalies; heavier than water¹); melting point 50° to 51°; boiling point 230°.

For the rest the test corresponds to that of the German Pharmacopœia.

1) Molten thymol floats on water.

**Oil of Turpentine** (*Terebinthinae essentia*). Colourless; $d_{15^\circ} = 0{,}850$ to 0,870¹); boiling point 155° to 162°; soluble in 12 parts alcohol, the solution should show no acid reaction.

1) The limits in this case might be narrower: $d_{15^\circ} = 0{,}860$ to 0,870.

Wilbert¹) discusses the essential oils from the point of view of the United States Pharmacopœia. In view of the fluctuating composition and the large differences in the constants of natural oils, and also with reference to their generally higher prices, Wilbert, following the example of the German and Swedish Pharmacopœias, advocates the introduction of the active principles of the oils, such as benzaldehyde, eugenol, methyl ester of salicylic acid, or also of the synthetic oils, such as synthetic neroli oil.

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1) Amer. Journ. Pharm. **75** (1903), 155, 218.

# Novelties.

Professor Dr. E. Strasburger, of Bonn, while on a visit to the Riviera this spring, was kind enough to call our attention to some plants growing there which in the fresh state are extremely fragrant. At our request Professor O. Penzig, of Genoa, very willingly took the trouble of procuring us fairly large quantities of these herbs in a half dried condition, and he has thereby enabled us to make some trial distillations. We avail ourselves of this opportunity to express again to both gentlemen our very sincere thanks for the pains they have so kindly taken.

Although the distillations have given no results which are useful for practical purposes, as the aroma was totally destroyed during the drying and the distillation, and the distillates in no case showed the characteristic odour of the fresh plant, we desire to mention here the properties of the oils obtained.

**Oil from Psoralea bituminosa L.** (Papilionaceæ). This plant has a strong asphalt-like odour, especially when it is rubbed. At one time the leaves were official as *Herba trifolii bituminosi,* and were used as a remedy in all sorts of affections. When distilling 20,5 kilos dried herb, we obtained 10 grams = 0,048 per cent. of an oil which at ordinary temperature was semi-solid, but which no longer possessed in the least degree the bituminous odour of the crude material. It was possible to separate from it fatty acids whose melting points lay between 38° and 40° (laurinic acid?). The specific gravity of the oil was 0,8988 at 25°; acid number = 57,18; ester number = 12,25.

**Oil from Inula viscosa[1]) Desf.** (Compositæ). The plant which has a sticky feeling to the touch, is found throughout the Riviera, and fills the air with its resinous balsamic odour. In popular medicine the fresh leaves are used against snake bite, and in Euboea the fresh herb is added to wine, probably in order to impart to the latter the resinous taste which is much admired there. 20,8 kilos herb yielded on distillation 13 grams = 0,062 per cent. of a dark brown, viscid oil with a not very pleasant odour, from which at ordinary temperature paraffin separated out in abundance. The fatty acids isolated from it were liquid. The specific gravity at 25° was 1,006; acid number = 164,63; ester number = 15,77.

**Oil from Helichrysum angustifolium Sweet.** (Compositæ). A herb with a pleasant odour, widely distributed in Southern Europe, where it covers extensive areas. It grows for example in heaps on

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[1]) This plant as well as the one mentioned before are illustrated in: O. Penzig, Flore colorée de poche du Littoral Méditerranéen. Paris 1902.

the Monte Portofino near Genoa, whence the material worked up by us was also derived. We obtained from 20,2 kilos herb 15,3 grams = 0,075 per cent. of a yellow-brown oil of the specific gravity 0,9182 at 15°; $\alpha_D = + 0° 40'$; acid number = 14,4; ester number = 118,16. In 90 per cent. alcohol it dissolved at first clear, but the solution subsequently became cloudy with abundant separation of paraffin. The paraffin had the melting point 67°.

Two species of *Cistus*, whose leaves we have distilled on account of their fragrancy, also originated from the Mediterranean Countries, — in this case from Spain. Both oils are distinguished by an aroma like ambergris, and in this respect they resemble an oil which we produced a long time ago from *Ladanum*, the resin of another species of *Cistus*.

**Oil from Cistus monspeliensis** (Cistaceæ). Yield 0,015 per cent.; $d_{15°} = 0,9786$; $\alpha_D = + 1° 40'$; acid number = 15,7; ester number = 31,51. The light brown oil separates off between 20° and 25° abundant quantities of paraffin of the melting point 64°.

**Oil from Cistus salviifolius** (Cistaceæ). Yield 0,024 per cent.; $d_{15°} = 0,9736$; $\alpha_D = + 17° 20'$; acid number = 16,86; ester number = 22,73. This oil is yellowish green, and behaves like the one mentioned before with regard to the separation of paraffin.

**Spanish Oils of Orange-blossoms.** We are indebted to a Spanish firm for the receipt of two Spanish oils of orange-blossoms, one being a distillate from the blossoms of the bitter orange, and the other from the sweet orange. The properties of these two oils were as follows: —

Néroli Bigarade. $d_{15°} = 0,871$; $\alpha_D = + 10° 54'$; acid number = 1,37; ester number = 37,67; methyl ester of anthranilic acid: 0,5 per cent.; soluble in 1,5 vol. 80 per cent. alcohol and more; the dilute solution shows fluorescence and is rendered cloudy by paraffin. Although the odour of the oil is exactly like that of the French distillate, the delicacy of the aroma is far behind that of the latter.

Néroli Portugal. $d_{15°} = 0,8571$; $\alpha_D = + 42° 47'$; acid number = 1,6; ester number = 6,86. The oil does not dissolve in 80 per cent., but dissolves readily in 90 per cent. alcohol. The alcoholic solution shows fluorescence, and after a time a minute separation of paraffin. Whilst French néroli Portugal, according to Theulier¹), is free from methyl ester of anthranilic acid, we found in the Spanish oil 0,3 per cent. of this ester, which we identified further by the benzoyl compound melting at 100° to 102°.

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¹) Bull. Soc. chim. III. **27** (1902), 278.

From Japan wo received the two following interesting novelties:

**Kobushi Oil.** The oil obtained from the fresh leaves and branches of the Kobushi tree (*Magnolia Kobus* D. C.) in a yield of about 0,45 per cent., has a bright yellow colour, and possesses the following properties: $d_{15^\circ} = 0{,}9642$; $\alpha_D = -1^\circ 6'$; acid number $= 1{,}5$; ester number $= 8{,}87$; soluble in 1,2 vol. 80 per cent. alcohol; the greatly diluted solution shows opalescence. The odour of the oil reminds of sassafras oil, and gives rise to the presumption that it contains a large proportion of safrol; the oil also contains among others small quantities of citral. The species of magnolia which yields this oil occurs chiefly in the central districts of Japan; the distillation of the oil takes place from July to September.

**Yomugi Oil** (Japanese oil of *Artemisia vulgaris*). This oil is derived from *Artemisia vulgaris* L., has a bright green colour, and a powerful cineol odour. The constants of the oil are as follows: $d_{15^\circ} = 0{,}9101$; $\alpha_D = -13^\circ 16'$; acid number $= 1{,}56$; ester number $= 29{,}81$. The oil does not completely dissolve in alcohol, as the dilute solution shows opalescence or cloudiness even when absolute alcohol is employed.

The presence of cineol in the oil was proved by the iodol compound; thujone is probably also present.

The oil may possibly be fairly similar to that which is produced from our native *Artemisia vulgaris.*

**Oil of Ajowan herb** has recently been distilled by ourselves. The yield of oil from the fresh herb cultivated here by us, was 0,12 per cent. The light brown oil had a specific gravity of 0,8601 (15°) and an optical rotation of $+0^\circ 41'$; it is soluble in about 6 vol. 90 per cent. alcohol, with abundant separation of paraffin. Contrary to the oil from the fruit, the oil from ajowan herb contains but very little thymol (about 1 per cent.). Among other constituents, the preliminary examination showed small quantities of phellandrene.

## Notes on recent scientific work concerning terpenes and terpene derivatives.

In his annual report on the progress made in the domain of essential oils, A. Hesse[1]) communicates a method for the determination of phenols and phenolic acid esters on the lines of his determination of methyl ester of anthranilic acid. The oil to be

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[1]) Chem. Zeitschrift **2** (1903), 403, 434, 464, 497, 534.

examined is dissolved in three parts anhydrous ether, and semi-normal alcoholic potash solution is added. If phenols etc. are absent, no separation takes place after adding a certain quantity of potash; but if phenols or salicylic acid ester are present, the mixture becomes cloudy, and the potassium compounds are separated off in fine crystals. The phenol-content can be readily determined by decomposing the filtered and washed compounds with acids (preferably carbonic acid). If it is desired to estimate the alkali titrimetrically in the precipitated compound, — especially in smaller quantities —, it is necessary to avoid carefully too large an excess of potash liquor. The advantages of this method (which is being submitted to a thorough study) are, according to Hesse, that the risk of saponifying the esters present is diminished, and further that the determination is made with two miscible liquids, that is to say, different from the usual method of extracting the oil with aqueous solution.

In the same place Hesse mentions the high content of methyl ester of methyl anthranilic acid in an oil from mandarin leaves, which was found to be 65 %, against a content of 50 % mentioned by Charabot[1]). There was further observed the presence of a very small quantity of a base with a nicotine-like odour, which could not be saponified. It is a remarkable fact that the ester does not occur in the leaves of the closely allied lemon tree.

In the same journal Hesse discusses[2]) the more recent observations made in the industry of essential oils. During the last few years the technology of odorous substances has applied itself preferably to the imitation of valuable natural oils, and in many instances has been able to show good results in this domain. This imitation is based in the first place on the exact knowledge of the composition of the oils, — compositions which frequently are most complicated. In spite of the highly improved methods of examination, the chemical investigation of many precious oils has hitherto not been successful in isolating the characteristic bearers of the odour, which mostly occur only in extremely minute quantities; for this reason the fundamental hypothesis of the synthesis of complex odoriferous bodies, the determination if possible, quantitative of the composition of an oil, can be accomplished only in the rarest cases. The industry of the artificial oils has been promoted (in Germany) by the granting of so-called application-patents, which protect partly the imitation of the natural products, and partly the application of individual constituents which have been detected scientifically. The facts have shown that the natural oils have by no means been supplanted

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[1]) Compt. rend. **135** (1902), 580. Report April **1903**, 38.

[2]) Chem. Zeitschrift **2** (1903), 697, 728.

by their synthetic products: on the contrary, both branches of manufacture move hand in hand, and interchange their experiences. Quite recently, science has turned towards the study of the oil-formation in the plant itself, a task which especially Charabot and his co-operators have taken in hand, and which has frequently been referred to in these Reports. The methods of production of the odorous substances from the blossoms have also been examined scientifically by Hesse himself, and he was then able to etablish the remarkable fact that some blossoms, such as the jasmine and tuberose, yield after the gathering, in the *enfleurage* process, from nine to twelve times the amount of odorous substance which they contain when being gathered. In view of these yields, showing in what rational manner the unknown inventors of these processes (based on purely empirical methods) unconsciously worked, Hesse pronounces himself in favour of the employment of the extraction or *enfleurage* methods, as against the distillation process mostly used in Germany.

## Pharmacologico-physiological notes.

H. Hildebrandt[1]) reports on the pharmacological action of some species of "camphors". Whilst the use of thujone effects an increased pressure of the blood, continuing for ten minutes, fenchone does not act in this manner. Both bodies reduce the frequency of the pulse but increase its height. With thujone the number of pulsations increases again later on. Camphor, when administered in this condition, has a very stimulating effect on the musculature of the heart.

The same investigator has supplied a contribution to the study of the biological behaviour of some compounds occurring in essential oils[2]). He endeavoured to ascertain whether there existed a difference, from a biological point of view, between geraniol and nerol[3]). The physical constants of geraniol and those of nerol (which latter it has not yet been possible to produce free from geraniol) show such slight differences, that a definite differentiation of the two alcohols by means of their constants is not possible. With regard to the chemical behaviour, as far as it has been studied up to the present, there are no doubt differences which seem to justify the assumption that in the so-called nerol apart from geraniol another alcohol also is present. The biological examination showed that nerol and geraniol, when injected in white mice in minute doses of 0,05 gram, produced in a very few minutes

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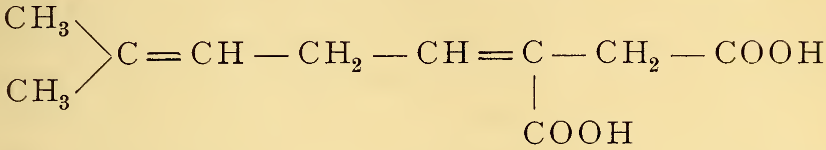
[1]) Arch. exp. Pathol. and Pharmak. **48**, 451, according to report Chem. Centralblatt **1903**, II. 132.

[2]) Zeitschrift für die gesamte Biochemie **4** (1903), 251.

[3]) Hesse and Zeitschel, Journ. f. prakt. Ch. II. **66** (1902), 481. Report April **1903**, 53.

toxic symptoms which showed no noticeable difference in their effect and intensity. Cyclogeraniol behaved differently; this only produced a state of deep stupor when administered in a dose four times as large.

The administration of geraniol and citral to rabbits yielded, as a first and principal product of assimilation, a dibasic acid[1]) $C_{10}H_{14}O_4$ of the melting point 192° to 194°, for whose constitution the formula



may be accepted as the most probable one. Cyclogeraniol and cyclocitral did not yield this acid, but only combined glycuronic acids were detected in the urine of the animals. When nerol was administered, abundant quantities of glycuronic acids could also be detected, in addition to small quantities of the dibasic acid, whose presence can be explained by the geraniol-content of nerol. According to these experiments the author considers nerol a body differing from geraniol.

H. Winterberg[2]) makes some communications on experimental examinations of the effect of camphor on the heart and on the vessels of mammals. According to these, camphor, when introduced direct into the circulation, exerts a transitory stimulating action on the vasomotor centre, which manifests itself in a transient, unimportant increase in the pressure of the blood. But as the principal action on the vessels, a peripheral vascular dilatation with diminished pressure of the blood was observed. Camphor does not promote the action of the heart, but neither have small and medium doses any injurious effect on it.

Jakobj[3]) has studied the pharmacological action on frogs and mice, of the following cyclic isoximes and of some compounds closely related to the latter: pentanone, hexanone, pentanone isoxime, hexanone isoxime, methyl pentanone isoxime, $\alpha$- and $\beta$-methyl hexanone isoximes, lævomenthone isoxime, tetrahydrocarvone isoxime, bihydrolævomenthone isoxime, benzoyl bihydrolævomenthone isoxime, isofenchone oxime, thujamenthone isoxime, trimethyl cyclohexanone isoxime. It was thereby found that all cyclic isoximes, if they produce any effect at all, belong to the group of medullary spasm-toxins represented by picrotoxin and camphor. All other compounds without the CO- or CH-group in the

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[1]) Arch. f. experim. Pharm. u. Path. **45** (1901), 121. Report April **1902**, 84.

[2]) Pflüger's Arch. **94**, 455. Report Chem. Centralblatt **1903**, I. 848.

[3]) Nachr. K. Ges. Wiss. Göttingen **1902**, 313. Report Chem. Centralblatt **1903**, I. 1092.

ring, proved to be typical paralysing toxins, with which a spasm-producing action could not be observed. The activity of the isoximes increases with the size of the ring, and also with the entry of a methyl-group. Specially powerful is the action of bodies with propyl-groups, particularly of those in which (as in isofenchone oxime) the propyl group is not attached to the ring, but inserted in it. Bihydrolævomenthone oxime and lævomenthone isoxime have a paralysing effect in frogs, but in mice they act as spasm-toxins without producing symptoms of paralysis. A practical application of these isoximes by way of collapse-remedies can scarcely be taken into consideration. These compounds may, however, possibly be employed in cases where it is intended to obtain a general, more powerful respiration.

## Phyto-physiological notes.

Carl Detto in his thesis[1]) deals with the importance of the essential oils in Xerophytes (plants of a very dry habitat). The author considers that the researches of various investigators have adequately confirmed the supposition that the essential oils of the internal gland organs of numerous families of plants (*Simarubaceae, Canellaceae, Piperaceae, Lauraceae,* etc., with secretion cells — *Hypericaceae, Rutaceae, Myrtaceae,* etc. with secretion openings; *Umbelliferae, Araliaceae, Anacardiaceae, Burseraceae,* etc. with ducts) form a means of protection against animal enemies. On the other hand, he occupies himself in detail with the significance of those essential oils which are formed in a readily volatilisable state in the external glands of organs, especially of the leaves. Here Detto opposes the view represented more particularly by Tyndall, that to the essential oils belongs the task of reducing the loss by perspiration, — on the one hand by the powerful absorption-capacity of their vapours for heat, and on the other hand by the formation of vapour itself, as a heat-abstracting process which diminishes the rapidity with which water evaporates.

On the strength of his study of the literature on the subject, and in consequence of numerous experiments made by himself from a phyto-geographical, anatomical, physical, and physiological point of view, the author comes to the conclusion that the absorption-capacity of the essential oils for heat which Tyndall had laid down, is of no importance whatever for the plant, and that a reduction of the perspiration by the action of the oil-vapours up to an œcologically active level, could only take place with simultaneous injury to the perspiring organs. On the contrary, the exogenous essential oils, apart from the odorous substances of the blossom, should also be considered as protective agents against insects, snails, grazing cattle, and other

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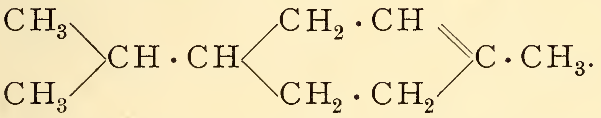
[1]) Carl Detto, Thesis, Jena 1903.

animals. This view, which had also been advocated already by other investigators, is supported by numerous examples and feeding-tests with the plants in question. For further particulars we must refer to the original work.

## Hydrocarbons.

F. W. Semmler¹) recommends sodium and alcohol as reducing agents for terpene derivatives, for the purpose of avoiding rearrangements in the molecule. The use of these agents has the desired effect not only in the case of aldehydes and ketones, but also in hydrocarbons which contain a conjugated system of double-linkings in the molecule²). The absence of such linkings also explains, why limonene and terpinolene cannot be reduced by means of sodium and alcohol. With phellandrene, however, the reduction succeeds when the ethyl alcohol is substituted by amyl alcohol. The reduction-product, a dihydrophellandrene $C_{10}H_{18}$, boils at 171° to 172°. Its physical constants are: $d = 0{,}829$, $\alpha_D = + 25°$, $n_D = 1{,}4601$.

The oily glycol $C_{10}H_{20}O_2$ formed by oxidation with permanganate is readily oxidised further into acetic acid and $\beta$-isopropylglutaric acid (m. p. 100°). According to this, the following constitutional formula would belong to dihydrophellandrene:



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\! CH \cdot CH \!<\!\! \begin{matrix} CH_2 \cdot CH \\ CH_2 \cdot CH_2 \end{matrix} \!\!>\! C \cdot CH_3.$$

Starting from the hydrochloride of the hydrocarbon, a dihydrolimonene is obtained in the following manner: The hydrochloride obtained by the introduction of dry hydrochloric acid in a solution of limonene in carbon disulphide, is dissolved in alcohol in the cold; sodium is added, and care is taken, by cooling the solution in ice, that the temperature during the reaction does not rise to above + 10°. The resulting dihydrolimonene boils at 173° to 174°. $d = 0{,}839$, $n_D = 1{,}463$, $\alpha_D = + 40°$. This reduction-method can be applied universally, and renders it possible to arrive from unsaturated compounds over their hydrohalogen addition-products to saturated hydrocarbons. In the same manner it is possible to produce from alcohols or aldehydes and ketones, the corresponding hydrocarbons by substitution of the oxygen by halogens. In an analogous manner there is formed from tanacetyl alcohol, or from tanacetyl chloride, the dihydrotanacetene $C_{10}H_{18}$ of the following constants: b. p. 164° to 166°, $d = 0{,}810$, $n_D = 1{,}451$.

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¹) Berichte **36** (1903), 1033.
²) Report April **1902**, 88.

The property which many terpenes possess of forming xanthogenic acid esters, which on being heated yield the original hydrocarbon, lends itself, according to Tschugaeff, especially to the isolation of terpenes and the production of those bodies in the pure state, as, in consequence of the absence of acids and alkalis, a rearrangement and formation of isomeric hydrocarbons is improbable.

Kondakow[1]), however, starting from anomalies which had been observed in regenerating bornylene from the xanthogenic acid ester, concluded that by this method no uniform bornylene is obtained, but that a portion passes over into camphene, as, contrary to pure bornylene, it yielded an ester when boiled with zinc chloride and glacial acetic acid, and also, when treated with hydrochloric acid gas in a solution of petroleum ether and of glacial acetic acid, yielded a mixture of the hydrochlorides of bornylene and pinene. Kondakow and Skworzow[2]) observed similar conditions when regenerating thujene according to Tschugaeff's method. The crude hydrocarbon boiled within very wide limits, and could be separated by methodical fractionating into portions of widely differing rotatory powers. Tschugaeff[3]) does not accept Kondakow's view that the high decomposition-temperature of the bornyl and thujyl xanthogenates favours the formation of isomeric forms, and he attributes the formation of the camphene or of the isobornyl acetate from the bornylene, to the esterification method employed. In opposition to these statements Kondakow maintains his opinion, and he points out many discrepancies in Tschugaeff's arguments. The controversy appears to show that the production of terpene hydrocarbons by the xanthogenate method, which at first appeared quite plain, does not lead to the uniform products which its discoverer assumed.

Pinene. The behaviour of pinene towards bromine, which had already been examined repeatedly, has once more been studied by P. Genvresse and P. Faivre[4]). Wallach[5]) as long ago as 1891 had conclusively settled the question of the addition-capacity of pinene for bromine, by converting the pinene in the then still unknown crystallised pinene dibromide of the melting point 169° to 170°. This reaction, conducted by Wallach in a dry solvent, proved the divalent character of pinene as compared with halogens. Genvresse and Faivre arrived at the same result when they allowed bromine

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[1]) Journ. f. prakt. Chemie II. **67** (1903), 280.

[2]) Journ. f. prakt. Chemie II. **67** (1903), 573.

[3]) Report of the proceedings of the Russian Phys.-chem. Soc. **1903**, No. 4, 81.

[4]) Compt. rend. **137** (1903), 130.

[5]) Liebig's Annalen **263** (1891), 1.

to act on pinene in the presence of water; they obtained, in addition to cymol, also the crystallised pinene dibromide whose melting point was found at 167° to 168°.

A. Denaro and G. Scarlata[1]) allowed monochloracetone and d-pinene to act on aluminium chloride whilst cooling in ice, and thereby obtained, as in the case when acetone acted on d-pinene in the presence of aluminium chloride, a colourless oil of the composition $C_{10}H_{16}O$, and the boiling point 290°. When iodine acts on d-pinene, there is formed the iodine derivative $C_{10}H_{14}I_4$, which when heated with sodium ethylate in a water bath, yields a tri-iodethoxy pinene ($C_{10}H_{14}I_3OC_2H_5$). By reduction it is converted into a mono- and a much more unstable di-iodethoxy pinene $C_{10}H_{14}IOC_2H_5$ and $C_{10}H_{14}I_2OC_2H_5$.

For the purpose of producing terpinol[2]), the authors recommend to allow a solution of 20 parts zinc chloride in 10 parts water to act on 100 parts terpin hydrate, and to distil with steam. By the action of two molecules hydriodic acid on terpin hydrate and treatment with caustic potash they obtained terpinylic acid, whilst monochloracetone yielded cajeputol (eucalyptol), boiling point 174°, in addition to terpinol (b. p. 168°).

By the reaction of chromyl chloride on pinene in a solution of carbon disulphide, Henderson, Gray and Smith[3]) obtained in addition to resinous products, a volatile oil, in which were detected a saturated aldehyde $C_9H_{15} \cdot CHO$ an unsaturated ketone $C_8H_{14} : CO$, and small quantities of a chlorinated body. The aldehyde melted at 32° to 33°, boiled at 205° to 207°, at 755 mm pressure, and was readily converted on oxidation with dilute nitric acid or an aqueous solution of permanganate into an acid $C_9H_{15} \cdot COOH$ of the melting point 117°, which was difficultly soluble in water, readily in alcohol, and slightly volatile with steam. The ketone was oily, and boiled at 206° to 207°, at 774 mm pressure; it yielded an oily oxime, and a semicarbazone melting at 226° to 228° with decomposition. With sodium hypobromite, bromoform and p-toluylic acid were obtained.

Camphene. Zelinski and Alexandroff[4]) had obtained from Russian oil of turpentine, by repeated treatment of the first runnings with solution of permanganate, a lævo-pinene of high rotatory power, $[\alpha]_D = -70^\circ 45'$, which strange to say yielded no nitroso-chloride.

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[1]) Preliminary communication. Gazz. chim. ital. **33** I. (1903), 393. Rep. Chem. Centralbl. **1903**, II. 571.

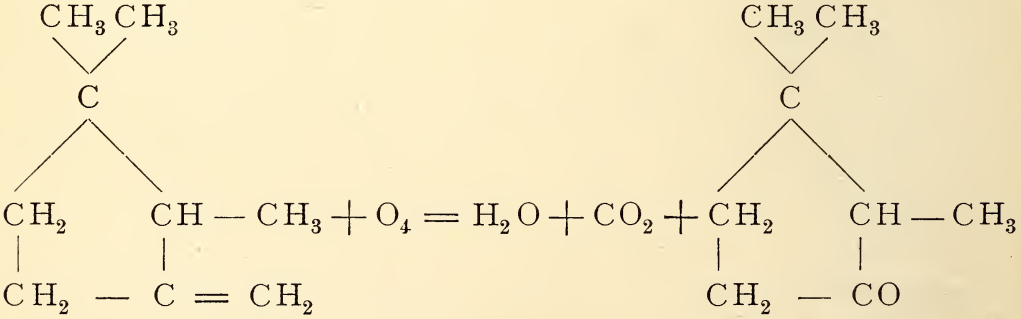
[2]) The compound "terpinol" does not exist. (Wallach, Liebig's Annalen **230** (1885), 271). It was found to be a mixture of terpineol and terpenes.

[3]) Proc. chem. Soc. **19** (1903), 195.

[4]) Chem. Ztg. **26** (1902), 1224.

Schindelmeiser¹) succeeded in isolating from Siberian pine needle oil, which is very closely allied in its physical and chemical properties to Canadian hemlock oil and American oil from the needles of *Picea nigra,* by freezing out the first runnings, a strongly lævorotatory camphene of the melting point 40°, whose molecular rotatory power amounted to — 94° 30′. Its hydrochloride melted at 150°; a nitrosochloride could not be produced. Schindelmeiser considers his camphene as identic with the not yet pure hydrocarbon of Zelinski and Alexandroff.

L. Bouveault and G. Blanc²) report on two new hydrocarbons isomeric with campholene and camphene. According to the authors there is obtained from dihydro-β-aminocampholene³) by means of methyl iodide and potassium hydroxide in alcoholic solution, the quaternary trimethyldihydro-β-campholene ammonium iodide $C_8H_{15}CH_2 \cdot N(CH_3)_3I$, in beautiful crystals which melt at 270° with decomposition. Silver oxide converts the compound into the corresponding hydrate, which, like the chloride and the sulphate, dissolved in water with extraordinary rapidity. The hydrate is an indistinct crystalline mass. On distillation it is split up into trimethyl amine and the hydrocarbon $C_9H_{16}$, trimethyl-1, 1, 2-methylene-3-cyclopentane. In consequence of the simultaneous formation of the tertiary base $C_8H_{15}CH_2N(CH_3)_2$ the yield of hydrocarbon is but small. This body, a mobile liquid with a turpentine-like odour, boils at 138° to 140°, and readily resinifies on exposure to the air. Contrary to the isomeric campholene, it does not form a solid derivative with hydriodic acid. Potassium permanganate oxidises it into the ketone 2, 3, 3-trimethyl cyclopentanone of Noyes⁴):



The base, which is also formed in the distillation of the hydrate, is a mobile liquid with a fish-like odour, and the boiling point 191° to 192°. Its hydrochloride has the melting point 166° to 167°.

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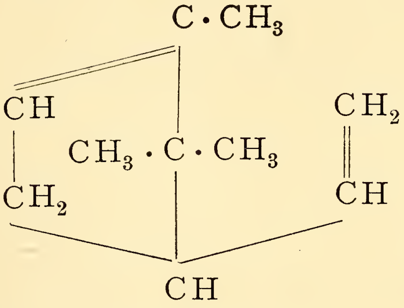
¹) Chem. Ztg. Rep. **27** (1903), 73; Chem. Centralbl. **1903**, I. 835.

²) Compt. rend. **136** (1903), 1460.

³) Bull. soc. chim. III. **23** (1900), 107.

⁴) Berichte **33** (1900), 54.

The other hydrocarbon, trimethyl-1, 1, 5-ethenyl-2-cyclopentene-4, 5, isomeric with camphene, is produced in an analogous manner from *α*-camphylamine. The quaternary ammonium iodide $C_8H_{13}CH_2 \cdot N(CH_3)_3I$, melts with decomposition at 285°. This hydrocarbon is a mobile liquid with a camphene-like odour, and the boiling point 157° to 158°. The tertiary base $C_8H_{13}CH_2 \cdot CH_2N(CH_3)_2$ which is formed in an analogous manner to the one mentioned above, has a fish-like odour, and boils at 215°. Its hydrochloride crystallising in leaflets melts with decomposition. The following diagram represents the constitution of trimethyl-1, 1, 5-ethenyl-2-cyclopentene:



Phellandrene. In order to clear up the constitution of phellandrene, Semmler[1]) oxidised the crude hydrocarbon (from eucalyptus oil) at reduced temperature with a quantity of potassium permanganate corresponding to 4 atoms oxygen. On then distilling the oxidation product with steam, he obtained an oil containing cineol and cymol. In the residue there was present a mixture of non-crystallising acids, which could be separated by means of copper acetate. From the insoluble copper salt, *α*-oxy-*β*-isopropyl glutaric acid $C_8H_{14}O_5$ was obtained, which on further oxidation with peroxide of lead yielded l-isopropyl succinic acid $C_7H_{12}O_4$ with the following constants: boiling point = 138° to 140° (at 19 mm); $n_D = 1{,}4519$; $\alpha_D = -3°$; $d_{20°} = 1{,}105$; mol. refr. = 34,7.

The soluble copper salt was that of an *α*-oxy-isopropyl adipic acid $C_9H_{16}O_5$ which was oxidised by peroxide of lead into l-*α*-isopropyl glutaric acid $C_8H_{14}O_4$, whose physical constants are: boiling point = 155° to 160° (at 19 mm); $n_D = 1{,}4613$; m. p. = 94° to 95°; $d_{20°} = 1{,}088$; mol. refr. = 39,2.

The mixture of the crude acids could also be separated in this manner, that it was further oxidised direct with peroxide of lead, and the acid mixture thus obtained precipitated at boiling heat with calcium chloride. Calcium isopropyl succinate thereby separated off in an insoluble state.

Semmler concludes from these results, that crude phellandrene consists of a mixture of two hydrocarbons. If two double linkings

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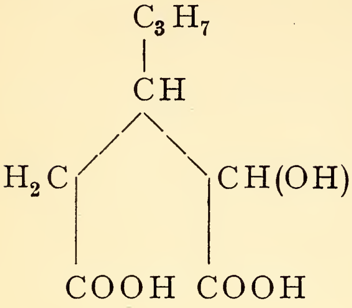
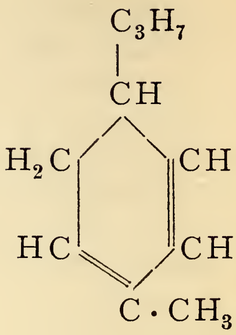
[1]) Berichte **36** (1903), 1749.

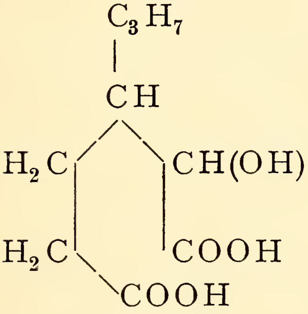
are assumed, whose presence the author considers as proved, α-oxy-isopropyl glutaric acid



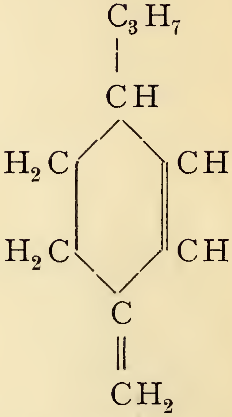
corresponds to "normal" phellandreme



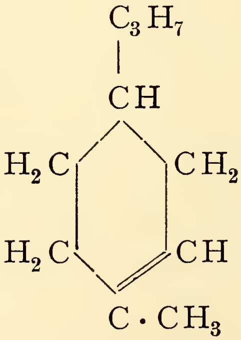
and α-oxy-isopropyl adipic acid



to "pseudo" phellandrene

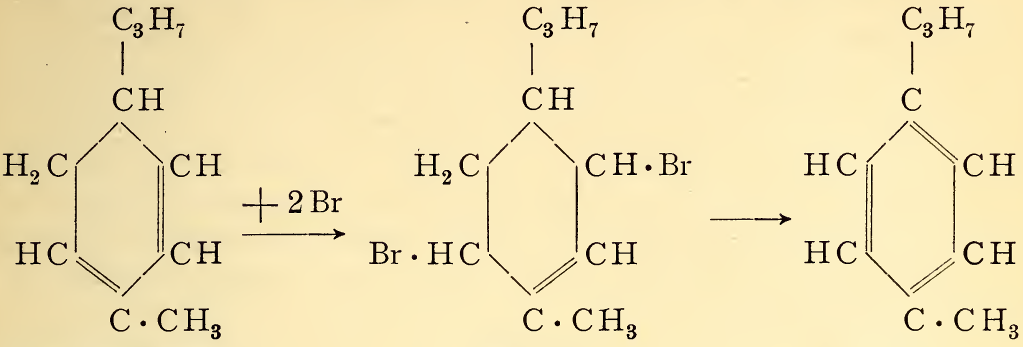


In agreement with this view of the constitution of phellandrene is the reduction with sodium and amyl alcohol. Here there is formed the hydrocarbon

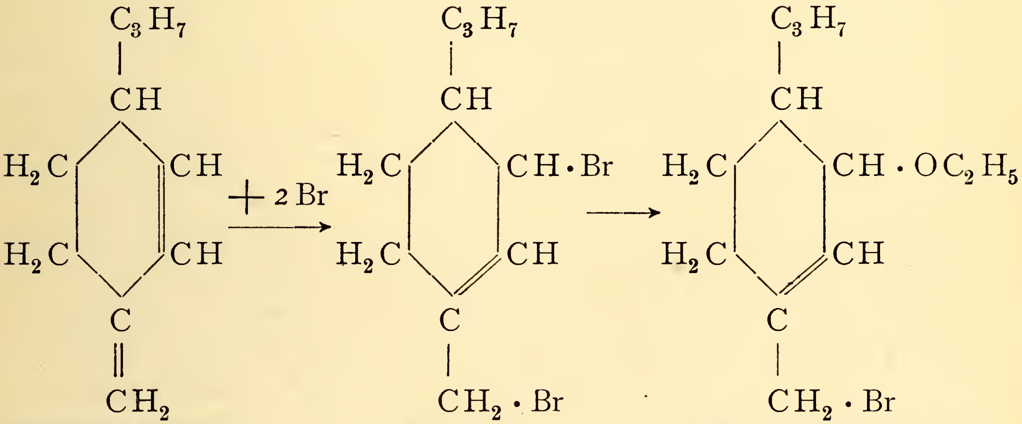


which must be formed from both the normal and the pseudo phellandrene, as both contain the two double linkings in close proximity, i. e. a conjugated system.

The behaviour of phellandrene dibromide also agrees with the accepted formula. If, namely, it is poured into alcoholic potash, there are obtained, on the one hand cymol, on the other a body containing bromine and oxygen, which has probably the formula $C_{10}H_{16}Br(OC_2H_5)$. This process may be represented by the following diagrams:



normal phellandrene — dibromide — cymol



pseudo-phellandrene — dibromide — body $C_{10}H_{16}Br(OC_2H_5)$

From the phellandrene formula shown, the author still deduces the formulae of phellandrene nitrite and nitrophellandrene, on the further examination of which he is still engaged.

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Menthadiene. Wallach had on a previous occasion[1]), by distilling dihydrocarvylamine hydrochloride, obtained a mixture of cymol and terpinene. But when Harries[2]) recently distilled the phosphate of this base, a new menthadiene was formed, which contained only traces of cymol.

Harries produced the carvoxime which served as crude material, by mixing 100 grams carvone with a solution of 50 grams hydroxylamine hydrochloride in 400 cc. methyl alcohol, and leaving this mixture standing for 3 to 4 days at the temperature of the room. It was then poured into double the volume cold water, when the oxime immediately separated out in the form of crystals, in the theoretical yield of 98 to 99 per cent. The carvoxime was converted by Wallach's[3])

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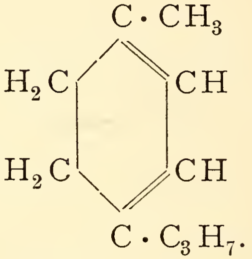
[1]) Liebig's Annalen **275** (1893), 125.

[2]) Liebig's Annalen **328** (1903), 322.

[3]) loc. cit.

method into dihydrocarvylamine, and the phosphate of the base then distilled dry *in vacuo*[1]). The hydrocarbon thus obtained was still contaminated with terpinene, which, however, could be separated off as nitrite by nitrous acid. The new menthadiene $C_{10}H_{16}$ further purified by distillation over sodium, has the following properties: boiling point: 174° to 176° (766 mm); optical rotation: — 3° (tube 200 mm long); $d_{27^\circ}^{27^\circ}$: 0,8441; n: 1,48451. The optical rotation is in the author's opinion probably due to a small admixture of limonene, whilst the menthadiene itself is inactive. The latter is rapidly destroyed by chromic acid mixture, but otherwise is very stable. The author assigns to it the following formula:



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**Pulegene.** In his sixty first Treatise on terpenes and essential oils[2]) **Wallach** reports on pulegenic acid and its derivatives.

Pulegenic acid $C_{10}H_{16}O_2$ is formed when pulegene dibromide is boiled with a solution of sodium[3]) in methyl alcohol as much as possible free from water. By converting its chloride with aqueous ammonia, the amide (melting point 121° to 122°) is obtained, whilst conversion with aniline in ethereal solution yields the anilide (melting point 124°).

The ester of pulegenic acid is very difficult to saponify. If it (3 molecules) is oxidised with a 1 per cent. solution potassium permanganate (2 molecules), a bioxyester (melting point 118° to 119°) is formed, which very easily saponifies already during the recrystallisation. If the liquor obtained on saponification of the ester is acidified, there is obtained, not the dioxyacid, but immediately the oxylactone $C_{10}H_{16}O_3$, which has been described previously[4]), and which is formed by oxidation of pulegenic acid.

The lactone $C_{10}H_{16}O_2$ from hydrochlorpulegenic ester, which has also been described some time ago[5]), can be obtained in a more simple manner by boiling pulegenic acid with dilute sulphuric acid. It melts at 30° to 31°, and boils at 126° to 128° (at 12 mm). The same lactone is also obtained when hydrobromic acid is attached to pulegenic acid,

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[1]) Liebig's Annalen **328** (1903), 90.
[2]) Liebig's Annalen **327** (1903), 125.
[3]) Report April **1896**, 53.
[4]) Liebig's Annalen **327** (1903), 125.
[5]) Report October **1898**, 59.

and the reaction-product is boiled with alcoholic potash. The pulegenic lactone $C_{10}H_{16}O_2$ differs from pulegenolide $C_{10}H_{14}O_2$[1] inasmuch as it does not, like the latter, yield an oxyacid capable of existence. From this it may be concluded that pulegenic acid lactone is a $\gamma$-lactone.

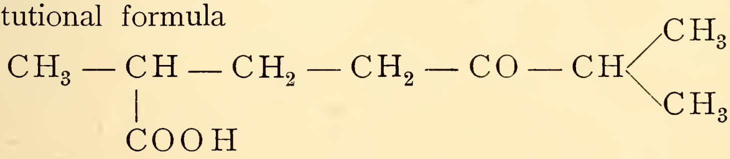
Pulegenic acid readily passes over in the distillation, by splitting off carbonic acid, into the hydrocarbon pulegene, which has the following physical constants:

boiling point 138° to 139°; $d = 0{,}761$; $n_{D_{22^\circ}} = 1{,}4380$.

Under certain conditions which must be strictly adhered to, it is possible to obtain from pulegene a nitroso-chloride (melting point 74° to 75°) which with piperidine is converted into pulegene nitrolpiperidide $C_9H_{16}NO \cdot NC_5H_{10}$ melting at 106° to 107°. If hydrochloric acid is abstracted from the nitroso-chloride by means of sodium methylate, the oxime $C_9H_{14}NOH$ of pulegenone $C_9H_{14}O$ is obtained. This ketone is split off from the oxime by dilute sulphuric acid. It boils at 189° to 190°, has the specific gravity 0,914, and at 20° the refraction index 1,4645. Its semicarbazone melts at 183° to 184°. Pulegenone absorbs on reduction four hydrogen atoms, and passes over into dihydropulegenol $C_9H_{18}O$. This alcohol can be oxidised by chromic acid into dihydropulegenone $C_9H_{16}O$, which has a menthone-like odour, and possesses the following constants:

boiling point 184° to 185°; $d = 0{,}8875$; $n_{D_{20^\circ}} = 1{,}440$.

The oxidation of dihydropulegenone, undertaken for the purpose of clearing up the constitution, yielded two ketone acids of the same composition $C_9H_{16}O_3$, one of which is converted by further degradation with sodium hypobromite into the dibasic $\alpha$-isopropyl glutaric acid $C_8H_{14}O_4$ (melting point 94° to 95°), but of which the other is identic with the ketone acid obtained by the oxidation of pulegene. This acid is formed by shaking pulegene with a five per cent. solution of potassium permanganate. It forms a yellowish oil boiling at 164° at 15 mm pressure, and yields a semicarbazone as well as an oxime. Its products of degradation, obtained by means of chromic acid, are acetone and $\alpha$-methyl glutaric acid. From these results Wallach concludes that the constitutional formula



$$CH_3 - \underset{\displaystyle COOH}{\underset{|}{CH}} - CH_2 - CH_2 - CO - CH \begin{matrix} \diagup CH_3 \\ \diagdown CH_3 \end{matrix}$$

belongs to the ketone acid.

In this connection Part IV of the Treatise contains discussions on the constitution of pulegenic acid and its derivatives. On the strength of the experimental material, the author establishes the following atomic groupings:

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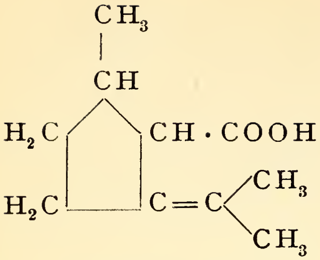
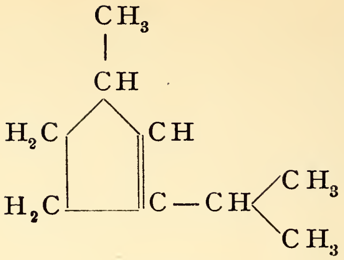
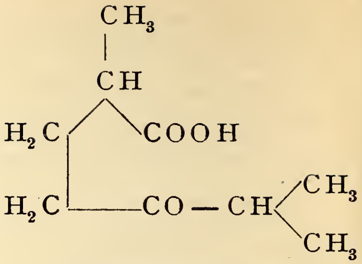
[1] Report October **1898**, 59.



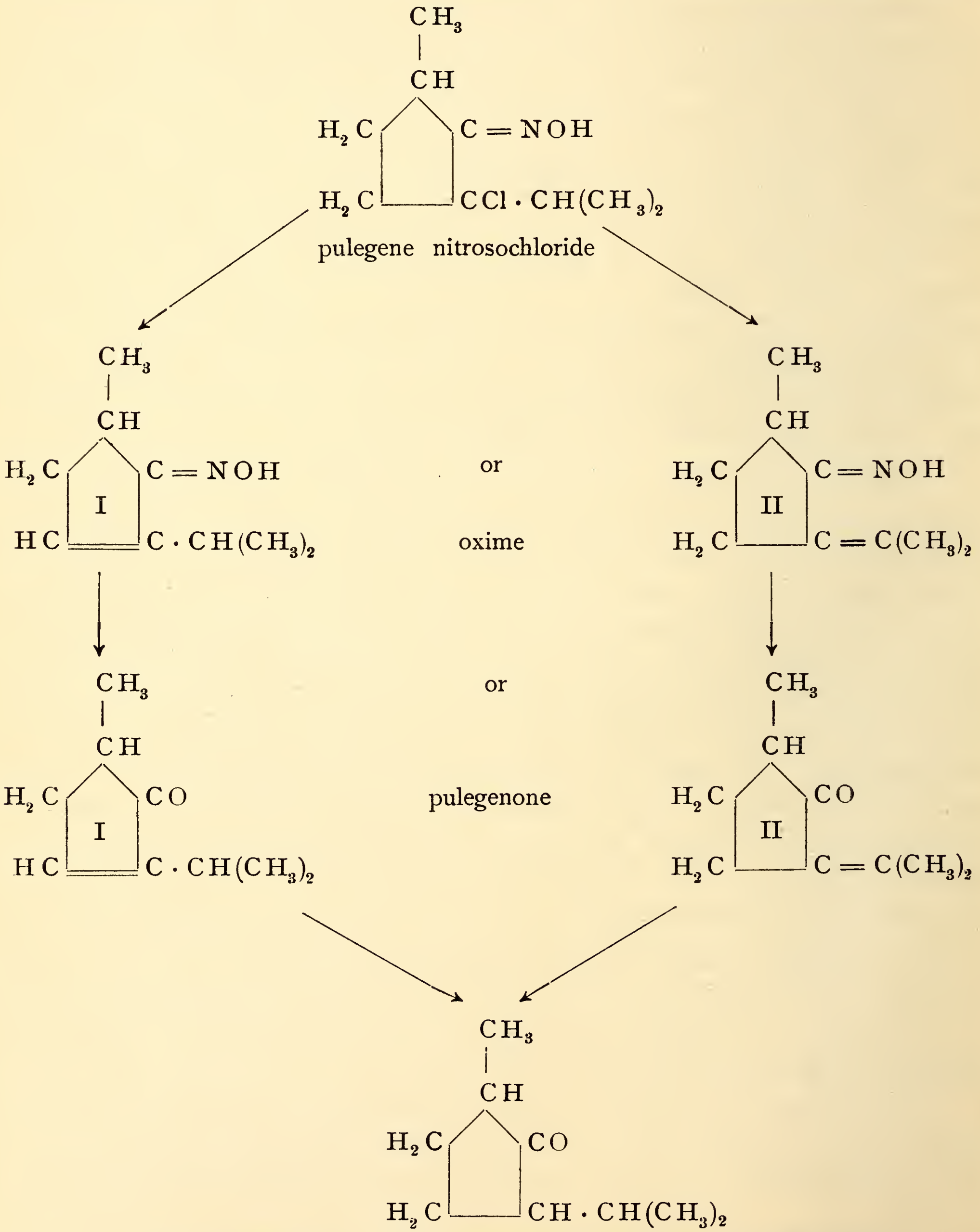
pulegenic acid



pulegene

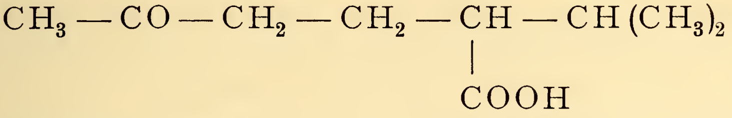


ketone acid $C_9H_{16}O_3$



Dihydropulegenone $C_9H_{16}O$ = methyl(1)-isopropyl(3)-pentanone(2).

With this formula of dihydropulegenone its behaviour is in perfect agreement. From it can be formed, not only the above formulated ketone acid $C_9H_{16}O_3$, but also one of the formula:



$$\mathrm{CH_3-CO-CH_2-CH_2-\underset{\substack{|\\ COOH}}{CH}-CH(CH_3)_2}$$

which should further yield isopropyl glutaric acid. For pulegenone Wallach accepts in the first place formula I, as formula II agrees with that of camphorphorone, whose properties, however, do not correspond to those of pulegenone. On the other hand, dihydropulegenone, must be identic with dihydrocamphorphorone, — a matter which has been proved as a fact.

Sesquiterpenes. With the study of sesquiterpenes Schreiner occupies himself in a number of essays[1]) which have been handed in as a thesis to the University of Wisconsin in June 1902. After a detailed historical retrospect of the discovery and classification of terpenes in general, and more particularly of sesquiterpenes, the author discusses his division of these hydrocarbons into five classes (already previously published by him[2]) according to the number of carbon-rings and of double linkings. This work is followed by a special part containing a detailed discussion of the individual representation of this class of bodies, their presence, and their physical and chemical behaviour. In Schreiner's opinion, the large number of the less exactly identified sesquiterpenes may probably be reduced to a small number of a few isomers, as was the case with the terpenes after Wallach's pioneer's work.

Caryophyllene. Up to the present, nothing was known of the constitution of caryophyllene, and of the hydrate formed from it by the addition of water according to Bertram's method. It may be concluded from the molecular refraction, that the molecule of the sesquiterpene must contain at least two double linkings. Semmler[3]) now has recently selected both bodies as subjects for examination, and he has attempted to produce reduction-products of them. Caryophyllene cannot be reduced by sodium and alcohol. On the other hand, the hydrate, which this investigator considers a tertiary alcohol owing to its behaviour on oxidation with chromic acid mixture, is converted into a saturated hydrocarbon $C_{15}H_{26}$, when heated with zinc dust in a sealed tube. Its physical constants are as follows:

$$\text{b. p. } 138^\circ \text{ (19 mm)};\ d_{20^\circ} = 0{,}918;\ n_D = 1{,}4925.$$

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[1]) Pharm. Arch. **6** (1903), 24, 33, 56, 65, 81.

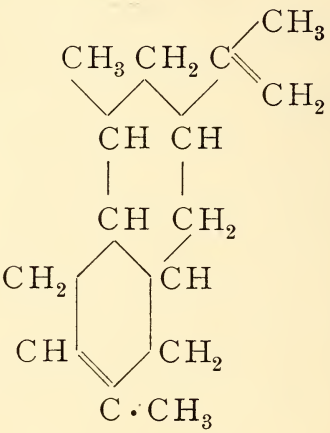
[2]) Ibidem **4** (1901), 141, 164; Report April **1902**, 85.

[3]) Berichte **36** (1903), 1038.

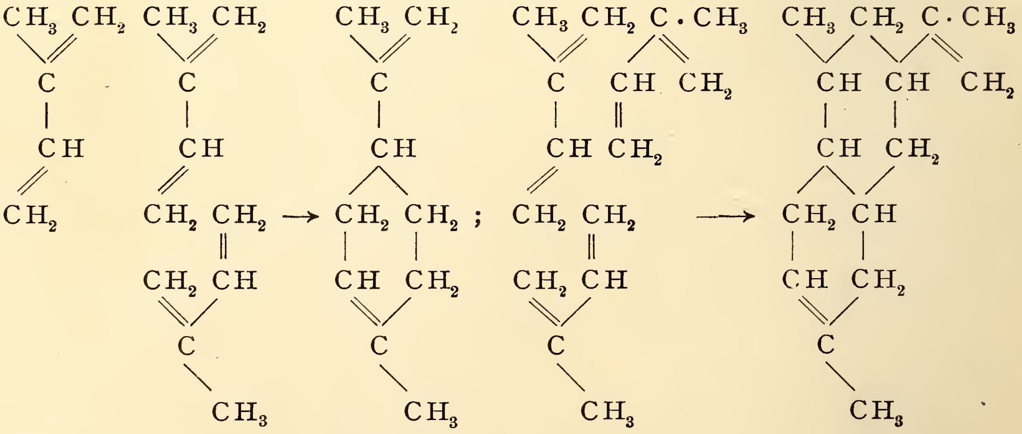
The author calls this body “dihydro-isocaryophyllene”, in view of the fact that caryophyllene has yielded no reduction product, and that the formation of the reduction product $C_{15}H_{26}$ takes place from caryophyllene hydrate, whose constitution is not analogous to that of caryophyllene. It would therefore be more correct to designate caryophyllene hydrate as iso-caryophyllene hydrate.

For the rest, dihydro-isocaryophyllene is also obtained when isocaryophyllene hydrate is treated with phosphorus pentachloride, and the product $C_{15}H_{25}Cl$ thus formed (which has the melting point 65° and the boiling point 295°) is reduced with sodium and alcohol whilst cooled in ice.

From experiments which will be published later on, Semmler concludes that the constitution of the sesquiterpene $C_{15}H_{24}$ can be reduced essentially to the following type:

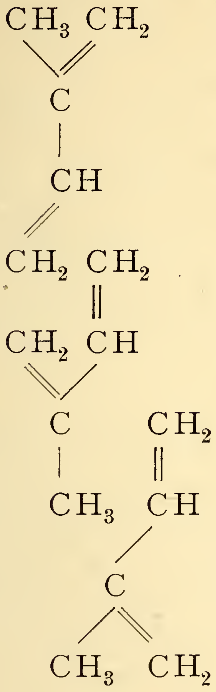


This would be a derivative of a hydrated naphthalene, whose formation, in view of the relations existing between the terpenes (and consequently the sesquiterpenes) and isoprene, might be explained as follows:

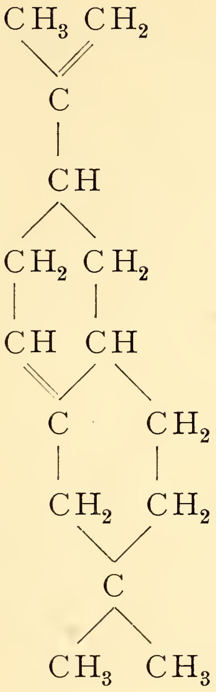


1 isoprene 2 isoprene limonene 3 isoprene sesquiterpene

Judging from the results hitherto obtained, there would be only a small group of sesquiterpenes in which the individual isoprene molecules might be grouped as follows:

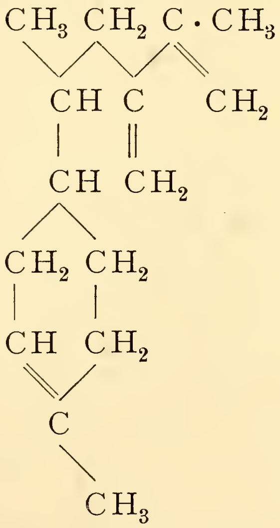


3 isoprene



sesquiterpene

The sesquiterpenes with a remarkably small specific gravity may possibly be either completely olefinic compounds, or terpenes, in which the second ring is not yet closed. The structure of the latter might be conceived somewhat in the following manner:



sesquiterpene with three double linkings.

These views harmonise with those held by Schreiner.

Cadinene. In a note in the "Archiv der Pharmacie" **241** (1903), 148, E. Deussen expresses the opinion that E. Grimal[1]) has stated in his work on the oil of Atlas cedar that dextro-cadinene was not known previous to this examination. With reference to his work on West Indian Sandalwood oil published in the "Archiv der Pharmacie" **238** (1900), 119, and **240** (1902), 288, E. Deussen points out that he had isolated dextro-cadinene already previously from this oil by fractional distillation. We would here remark that this reproach made by Deussen against Grimal is not justified, for Grimal only says that up to the time of his examination only lævorotatory halogen-derivatives were known both of the dextro- and of the lævorotatory cadinene, and that a regenerated dextro-cadinene hat not yet been produced, — a statement which is in complete agreement with the actual facts.

From the Errata of the "Comptes rendus" **136** (1903), 336, we find that the constants of the dihydrochloride and dihydrobromide of d-cadinene given in E. Grimal's work, should be corrected as follows: For the dihydrochloride the rotatory power in chloroform solution has been found as $[\alpha]_{D20^\circ} = + 8^\circ 54', + 8^\circ 51', + 8^\circ 59'$, and for the dihydrobromide the mean of several determinations in acetic ether solution $[\alpha]_{D20^\circ} = + 25^\circ 40'$.

## Alcohols.

Fenchyl alcohol. As appears from earlier work done by Kondakow and Lutschinin, lævo-fenchyl alcohol from dextro-fenchone yields with $PCl_5$, $PBr_5$, or with hydrohalogen acids, in addition to various hydrocarbons, also a mixture of haloid anhydrides which differ in their behaviour when split up with alcoholic potassa. From one of these mixtures Kondakow was able to separate a solid chloride which was extremely stable against the above-mentioned reagent, and which he jointly with Schindelmeiser[2]) has made the subject of a detailed examination. The fenchyl chloride was produced by repeated treatment of fenchyl alcohol in a solution of petroleum ether with $PCl_5$, at a temperature below 0°. It showed the melting point 75°, and at 11 mm pressure the boiling point 81° to 82°. Alcoholic potash only split off hydrochloric acid at 180°, with formation of a high-boiling lævo-fenchene of the b. p. 159° to 161°, and of small quantities of a lævo-fenchyl alcohol of the boiling point 197° to 201°. With strong hydrochloric acid the chloride yielded a dihydrochloride of the melting point 49° to 51°, which with alcoholic potassa at 125° formed an inactive hydrocarbon $C_{10}H_{16}$, boiling at 180°; the latter

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[1]) Compt. Rend. **135** (1902), 582, 1057.

[2]) Journ. f. prakt. Chemie II. **68** (1903), 105.

gave the sylvestrene-reaction (blue coloration of a drop of oil on adding glacial acetic acid and concentrated sulphuric acid), — although with a violet hue. The authors suspect in this terpene Baeyer's carvestrene, and attribute the differences which still exist between these two bodies, to deficient purity of the preparation obtained by Baeyer. On the strength of their observations Kondakow and Schindelmeiser draw up for this hydrocarbon various formulae of a metamenthadiene, and refer to the newly-discovered relation between fenchone and metacymol derivatives. The formation of dihalogen compounds with halogen to the tertiary carbon atom, brings the authors back to the presence of a tertiary isofenchyl alcohol, from which as crude material they hope to obtain a higher yield of the carvestrene-like terpene.

## Ketones.

Camphor. There has recently appeared from the pen of the Helsingfors Professor Ossian Aschan, a monographic representation of the theoretical results of the camphor-research[1]). It gives a concise but excellent historical review of the fundamental work in this domain, so closely allied to the terpene chemistry, — work, which in the course of time has led to more than 30 different camphor formulæ. On the strength of the facts resulting from this work, all the formulæ are criticised, from which criticism issues as the sole expression which meets all requirements and observations, Bredt's formula which has been universally recognised as correct. Of the derivatives closely related to camphor, the author discusses camphene and bornylene and their respective constitutions, which since Wagner's work have gained renewed interest for the camphor-research of the last few years.

Methyl cyclohexanone. Contrary to the work done by Bouveault and Tétry[2]) and by Speranski[3]), who in the oxidation of cyclic ketones, such as menthone, pulegone, and $\beta$-methyl hexanone, obtained exclusively $\beta$-methyl adipic acid, Markownikoff[4]) established the occurrence of $\alpha$-methyl adipic acid in addition to the $\beta$-modification; both isomers occur in equal quantities. Markownikoff attributes the negative results of Bouveault and Tétry to the fact that they incorrectly judge the different degrees of solubility of dianilides of the

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[1]) The constitution of camphor and its most important derivatives. Brunswick 1903. Fr. Vieweg & Sohn, publishers.

[2]) Bull. Soc. chim. III. **25** (1901), 441. Report October **1901**, 66.

[3]) Journ. russ. phys.-chem. Ges. **34** (1902), 10. Report October **1902**, 97.

[4]) Journ. russ. phys.-chem. Ges. **35** (1903), 381; Chem. Centralbl. **1903**, II. 289.

two acids. In a special work[1]) the same investigator gives detailed characteristics of β-methyl adipic acid and of d-pyrotartaric acid anhydride, which he obtained in addition to a series of other acids in the oxidation of menthone with permanganate.

**Phenols and phenol ethers.** The behaviour of unsaturated phenol ethers whose side-chain is saturated with bromine, has been examined by Pond and Siegfried[2]). As had already been previously established by Auwers and Müller[3]), it was found that the brominated propyl-group can only yield glycol ether in the case of free phenols. In phenol ethers, on the other hand, of which the authors examined in detail monobromisosafrol and -isoapiol dibromide, it could be proved, in agreement with previous results, that only the bromine atom which stands in the α-position towards the benzene-ring, can be readily exchanged for other atom-groups, but not the comparatively stable β-bromine atom.

Hell and Bauer[4]) make some communications on aromatic propene compounds. They allowed sodium ethylate to act on brominated unsaturated phenol ethers, and were able to establish that in the case of monobrom-para-anethol dibromide there is first formed a brominated propyl ether, which when heated splits off alcohol, and yields a β-brompropenyl compound. With excess of sodium ethylate there are obtained from the brominated propyl ether, unstable propenyl ethers which are readily converted by acids into ketones. Of a different behaviour are monobrom-ortho-anethol dibromide (from methyl salicylic aldehyde according to Grignard's reaction), and dibrominated phenyl propene (from benzaldehyde, after the same method). With these bodies the formation of a brominated propyl ether could not be observed; moreover, when treated with an excess of ethylate, they did not yield propenyl ethers, but the o-anethol derivative yielded an allylene derivative, whilst in the case of phenyl propene dibromide the reaction remained in the first phase (β-brompropenyl benzene). In the para- and ortho-anethol dibromides disubstituted in the nucleus, the reactivity of the bromine atoms of the side-chain is considerably reduced. The peculiar progress of the reaction in these bodies, which reminds of certain transpositions of the pseudobromides, induces the authors to accept for their bromides

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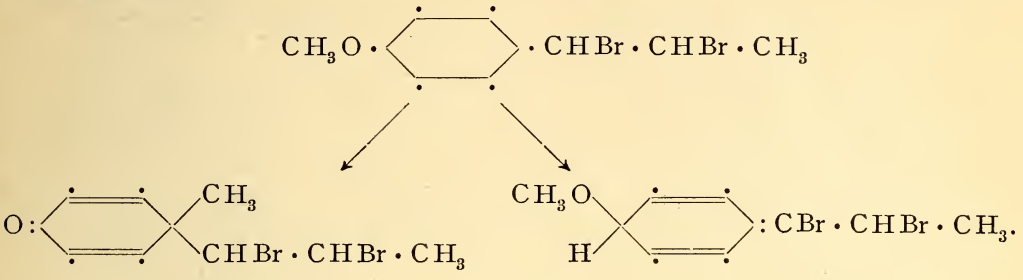
[1]) Journ. russ. phys.-chem. Ges. **35** (1903), 287; Chem. Centralbl. **1903**, II. 287.

[2]) Journ. Americ. Chem. Soc. **25** (1903), 262.

[3]) Berichte **35** (1902), 114. Report April **1902**, 95.

[4]) Berichte **36** (1903), 206, 1184.

quinone-like formulæ, in which the methyl of the methoxyl-group, or respectively an H-atom in the $\alpha$-position of the side-chain, enter into the para-position:



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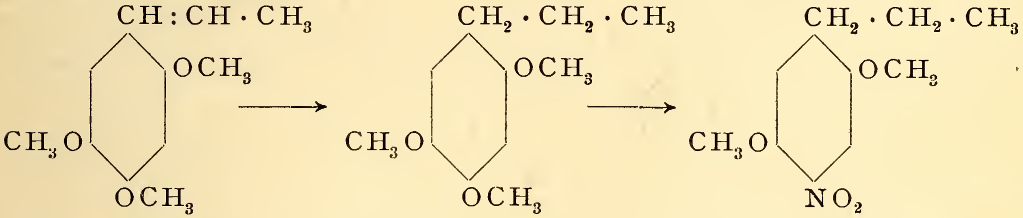
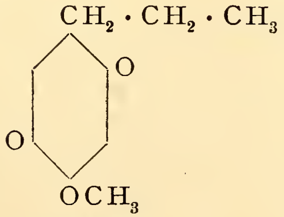
Apiol. Products due to the action of nitric acid on phenol ether have recently served H. Thoms1) for establishing the constitution of apiol. For the more detailed study of the interesting examination we must go back to an earlier work by H. Thoms and J. Herzog2). In the latter these chemists showed that dihydroasarone, when treated with nitric acid, yields, in addition to a known quinone, also a nitro-body, in which the nitro-group occupies the para-position towards the propyl-group. There has consequently taken place an elimination of the methoxyl-group situated in 1, 4-position towards the propyl-group in the dihydroasarone molecule:



asarone dihydroasarone nitro-product (1) propyl-(2, 5) dimethoxy-(4) nitrobenzene

and



quinone.

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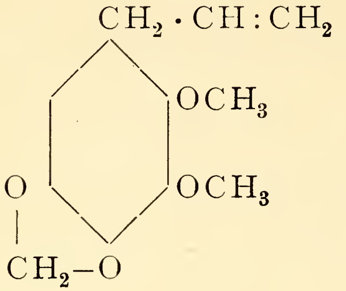
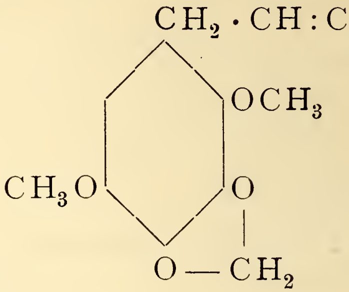
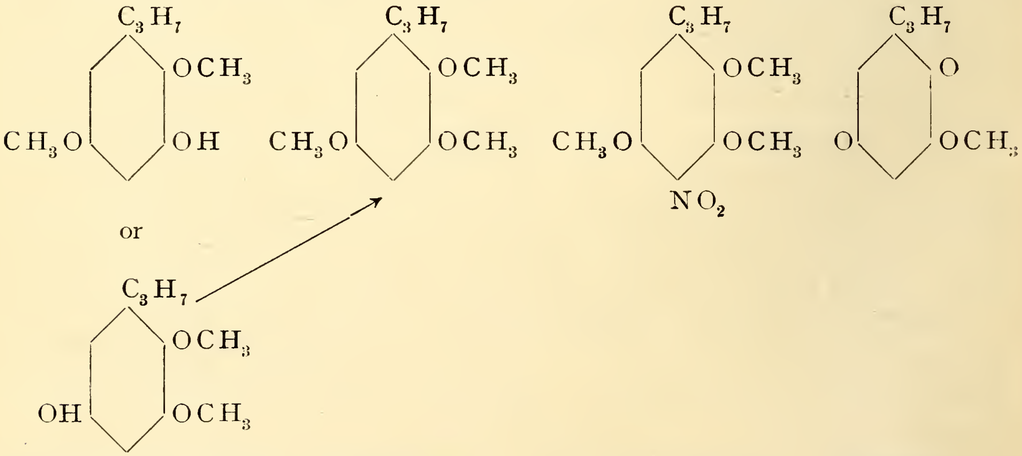
1) Berichte **36** (1903), 1714.
2) Ibidem **36** (1903), 854.

For the purpose of ascertaining the constitution of apiol, for which, according to the work by Ciamician and Silber[1]), hitherto only the following two formulæ came under consideration:





Thoms started from isoapiol, or respectively from a degradation-product of this body, a propyldimethoxy phenol. The methyl ether of this phenol, when treated suitably with dilute nitric acid, yields a nitro-product in addition to a quinone. Contrary to the process mentioned for dihydroasarone, no elimination of a methoxy-group has here taken place, but the entry into the free para-position towards the propyl-group has occurred. The quinone which occurs in addition, is isomeric with the one formed from dihydroasarone. The following formulæ may illustrate this more clearly: —



propyldimethoxy phenol methyl ether nitro product quinone

By means of these results the question of the constitution of propyldimethoxy phenol (and consequently also of apiol) could be decided. For this purpose there were produced, by substitution of the hydrogen atom of the OH-group by an ethyl- and a propyl-group, a propyl-dimethoxy-ethoxy-benzene, and a propyl-dimethoxy-propyloxy-benzene, and each of these compounds was converted by means of nitric acid

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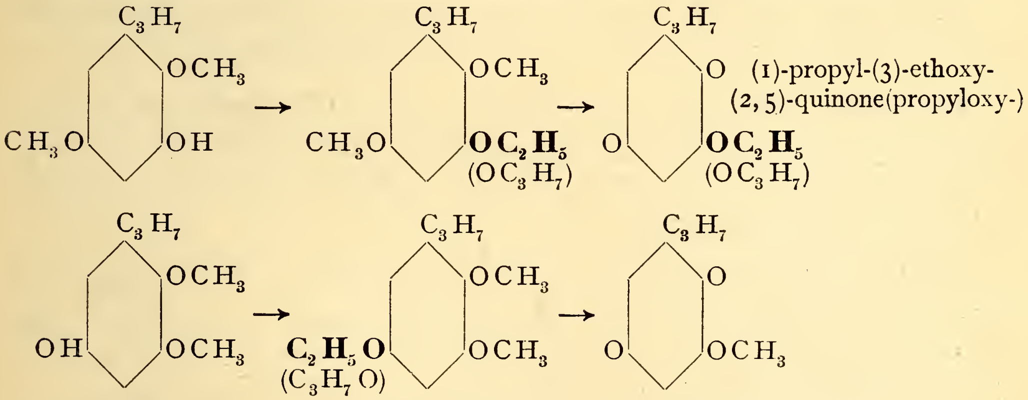
[1]) Berichte **23** (1890), 2293.

into the quinone or the hydroquinone respectively. In this manner two different bodies were obtained. Now, in order to solve the question of the constitution of the above-named phenol, it only required the following consideration: assuming that the phenol were a (1)-propyl-(2, 3)-dimethoxy-(5)-oxy-benzene, and the OH-group therefore in 1,5 position towards the propyl-group, it would follow that from the (1)-propyl-(2, 3)-dimethoxy-(5)-propyloxybenzene and -(5)-ethoxy benzene, when treated with nitric acid, one and the same quinone, (1)-propyl-(3)-methoxy-(2, 5)-quinone were formed, for the quinone-formation is brought about with elimination of both alkyl-groups occurring in the para-position. Assuming, on the other hand, that the phenol in question were a (1)-propyl-(2, 5)-dimethoxy-(3)-oxy benzene, it would follow that from the (1)-propyl-(2, 5)-dimethoxy-(3)-ethoxy benzene and the (3)-propyloxy benzene two different quinones, or hydroquinones respectively were formed, viz. (1)-propyl-(3)-ethoxy-(2, 5)-quinone, and (1)-propyl-(3)-propyloxy-(2, 5)-quinone. Now, as the latter case agreed with the actual facts, it was thereby proved that the phenol is a (1)-propyl-(2, 5)-dimethoxy-(3)-oxy benzene. Apiol is consequently a (1)-allyl-(2, 5)-dimethoxy-(3, 4)-methylenedioxy benzene.

The following formulæ explain the course of examination:



propyl-dimethoxy-phenol

propyldimethoxy-ethoxy benzene (propyloxy-)

(1)propyl-(3)-methoxy-(2, 5)-quinone

**Aubépine (Anisic aldehyde).** This body is obtained as a by-product, and its value is consequently problematical. Although our quotations have been much reduced, the use of this article remains to a certain degree limited, as the perfume-compositions for which it is employed as a base do not belong to the most popular articles of perfumery.

**Citral.** The value of this preparation moves up and down with that of lemongrass oil. A reduction is for the present out of the question. Products of less purity than ours are plentiful in the trade, and for this reason the constants should also be carefully compared when a comparison is made of the prices.

**Coumarin, crystal.** There are signs that the ring which had been formed by some makers, in order to raise the selling-prices, exists no more. Those who joined the combination have undoubtedly overestimated their power. Since our new installations have been completed, we are again in a position to supply this preparation promptly in any quantity.

**Eucalyptol.** Under this designation there exists in the trade a quality which is quoted 5 marks per kilo, and which is occasionally contrasted with ours. This, however, is nothing but a fractionated eucalyptus oil, and strictly speaking does not deserve to be called eucalyptol.

Pure eucalyptol such as ours should solidify at — 1° to a crystalline mass, and should be optically inactive. A preparation possessing these properties cannot be supplied at the above-named price.

We would ask that samples may be forwarded to us in doubtful cases, so that we may express our opinion on them.

**Geraniol.** We again call attention to this beautiful product which does not yet meet with the demand which it deserves; for rose-soaps we recommend it mixed with Réunion geranium oil, whose pungent radish-like odour it softens.

**Heliotropin.** We have to record a further fall in prices, and desire to state here, that, as we were the first firm to produce this body in Leipzig on a commercial scale, we naturally claim a share of the business, and will not allow anyone to dispute us this.

In accordance with a frequently expressed wish, we introduced some months ago a product which is purified by a special process, and we shall be pleased to submit samples of this quality for comparison.

**Linalyl acetate.** This principal constituent of the oils of bergamot and lavender is in great demand for fine concentrated compositions, in which ready solubility is an important factor, and we keep it in stock in large quantities.

**Menthol, recrystallised pure.** In the course of the last six months a very brisk trade has again been carried on in this important product, a trade of which we were able to secure an important share owing to abundant supplies purchased at favourable prices. The prices of crude menthol in Japan were maintained for several months at 22/- to 23/- per lb. On the other hand, the article for prompt delivery was here very scarce and in strong demand up to about the middle of August, when old supplies from Japan came on the market, and at the same time offers for early shipment of the new harvest were made. The new season's prices started at 18/-, and gradually declined to 14/-, but the last-named quotation has only been maintained for a short time, as the movement in American oil has not left the price of menthol untouched. The Japanese are holding back, and the opinion of the article is generally very favourable.

This product is constantly growing in importance. In future, as before, we shall be able to meet all competition, and we solicit enquiries, as in view of the frequent fluctuations in prices, the quotations on our lists cannot always be taken as a guide.

**Menthyl acetate.** A body, newly taken up by us, which has a pleasant refreshing odour. In view of the general demand for new preparations, this one may possibly be a welcome addition. A fairly brisk demand has recently also sprung up for menthyl valerianate (see p. 132 of this Report), whose medicinal action appears to be worthy of further examination.

**Musk, artificial "Schimmel & Co."** (*Trinitroisobutylxylene*). Under this designation we have, after expiration of the respective patents, introduced a product which contains 100 per cent. musk, and which is free from any artificial admixture. This musk is consequently ten times richer than the hitherto-known musk "Baur", which according to the statements of the manufacturers themselves, contained only 10 per cent. musk and 90 per cent. admixture (antifebrin).

Our musk has a specially fine odour, which very closely approaches that of natural musk. For this reason it comes a little higher in price than other makes. It dissolves, in the proportion of 1 in 200, in slightly warmed alcohol of 90 per cent., and also in the essential oils which are employed for the same purpose.

We recommend this excellent preparation for comparative trials, and are convinced that it will be preferred over any other.

**Safrol.** The value of this article has lately undergone no change, as the price of the raw material has rather hardened owing to the introduction of the camphor-monopoly in Japan. The Japanese safrol-competition does not appear to have come to anything up to the present. The rational manufacture is as difficult as the sale on a large scale; this may have been found out in Japan. For the rest, the importance of this article has been overrated. Although it may play a certain part in various industries, it is entirely out of the question that a factory which only produces safrol and its by-products, can possibly prosper.

**Terpineol.** Since the price of American turpentine oil has risen to 90 marks per 100 kilos cif. Hamburg, the production of terpin hydrate comes so much more expensive, that an advance in the price of terpineol is justified. It will come as soon as the old stocks have been used up.

**Thymol.** The demand for this powerful antiseptic was so brisk owing to the exceptionally low prices, that we have only been able to meet it by working overtime. The value of the raw material remains low, as before.

**Vanillin.** The decline in the value has not only come to a standstill, prices show even an advance. They may have to be raised still further, should those of clove oil, which forms the material for vanillin, continue to rise.

It is well known that the vanilla fruit, in the state in which it is gathered, does not in the least possess the characteristic odour of vanilla. It only acquires this odour by suitable treatment. H. Lecomte[1]) has now studied the conditions which bring about the formation of vanillin, which imparts the wonderful perfume to the fruit. According to the researches of the above-named scientist, there exist in the vanilla plant two ferments, which differ in a marked degree from each other in their functions. The one, an oxydase, is present in the individual organs of the plant, such as the leaves, shoots and their aqueous extracts, in the green and ripe fruit which has not yet been worked up, and in the prepared commercial fruit. Lecomte detected it in these organs of plants of different origin, by means of G. Bertrand's reactions. At the same time, the presence of manganese salts was observed in all products, which renders it not impossible that they stand in some relation to the above-named ferment. The second ferment is contained in the sap of the vanilla, and produces as a hydratising ferment (in the manner of diastase bringing about the conversion of starch into grape sugar), the formation of a substance which shows the same reactions as those which have always been met with in the vanilla plant. With regard to the mechanical treatment of vanilla, it would appear in the first instance as if it counteracted the function of the ferment. It consists, as is well known,

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[1]) Journ. de Pharm. et Chim. **17** (1903), 341.

of the immersion of the fruit during twenty seconds in water of 85° C., a manipulation which might bring about the destruction of the ferment. But the author has convinced himself that a temperature of about 50°, such as the interior of the fruit probably only reaches during the short duration of the process, really promotes the function of the oxydase.

Both ferments, the oxydase as well as the one possessing the hydrolytic action, appear to be necessary for the formation of vanillin in the plant, and their action may possibly be explained thus: During the preparation, the coniferin produced by the plant is split up into glucose and coniferyl alcohol. This process would explain also the constant occurrence of grape-sugar in vanilla. The oxydase would then oxidise the coniferyl alcohol into vanillin.

**Schimmel & Co.**

# On the Pharmaco-therapeutics of the *Aethereo-Oleosa*

by

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Director of the Institute for Pharmacology and Physiological Chemistry,
University of Rostock.

# Table of Contents.

## 1. Introduction.

When, more than a quarter of a century ago, I selected oil of turpentine as the object of my first two scientific investigations[1]), drugs and galenic preparations containing essential oils enjoyed a high reputation in the medicinal treasure. But there came a time, when a desire arose to place the medicinal treasure on a more scientific basis. From that moment the alkaloids, the glucosides, an enormous number of compounds of iron, mercury, and iodine, the artificial febrifuges, artificial narcotics, and artificial antiseptics, played such an important part in pharmacological instruction that no time was left for the discussion of the old plants containing essential oils, and of the preparations made from them. The teachers of this branch of knowledge mentioned perhaps once or twice, at the end of the lecture: "There are unfortunately in the medicinal treasure still a large number of antiquated remedies which have been derived from popular medicine, but which are nearly all superfluous and antiquated. I may be excused from enumerating and demonstrating these". But this they merely said as a matter of form for the sake of doing their duty.

In spite of being thus degraded to the position of a pariah in the eyes of Science, the *aethereo-oleosa* have continued to play a useful part in the practice of our daily life, and in the last decade they have become even more important. This advance was due to the fact that Chemistry, independent of Medicine, turned its attention towards the production and the study of the individual substances contained in the essential oils, and only thereby rendered the analysis of their actions possible. Up to that time it was no doubt known in Pharmacology "that the essential oils could not all be tarred with the same brush"; — but all the rest, apart from the experience gained at the sick-bed, stood on an uncertain foundation. At the present day, when most of the essential oils which here come under consideration have been accurately

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[1]) Beiträge zur Terpentinölwirkung. Erster Teil. Zeitschrift für die gesamten Naturwissenschaften für Sachsen und Thüringen. Edited by Professor Giebel, Vol. **49** (1876), 1. — Beiträge zur Terpentinölwirkung. Zweiter Teil. Thesis. Halle o./S. 1877.

examined chemically, and when a book of reference[1]) embracing the whole of our knowledge on this subject is available, in which not only the chemist, but also the physician can readily find his way, we may perhaps venture, without exciting the displeasure of the theorists, to enquire in which groups of pharmaco-therapeutics *aethereo-oleosa* are still frequently made use of by non-antiquated practitioners. A summary of all individual remedies and actions is here naturally not contemplated; I would rather refer the reader once and for all to my detailed "Text-book of Pharmaco-therapeutics"[2]), or my equally detailed "Text-book of Intoxications"[3]).

## 2. Group of Odour-Corrigents.

In this group, so extremely important for the practice of our daily life, an enormous change has occurred in the course of half a century in the respect that the manufacture of the perfumes for diseased and healthy persons is no longer carried on in chemists' shops according to recipes by physicians, but on the contrary takes place in special factories, in an absolutely ideal and perfect manner, with the help of all conceivable auxiliaries. Although we physicians may preach ten times "mulieres bene olent, si nihil olent", the weaker sex will continue to buy perfumes and to enjoy them. We must be content if only poisonous substances are not allowed to be added to these mixtures. But we will never consent to the so-called improvement of the air in the sick-room by fumigating powders and fumigating essences; on the contrary, we will make it clear to the rising generation, with our utmost energy, that constant renewal of air is the best odour-corrigent of the sick-room. In the same manner, patients who suffer from bad-smelling breath should not go to perfumery shops, but to the dentist, or to the specialist for the nose or the lungs. Even for healthy persons, perfumes are only admissible in homœopathically minute doses. Only quite recently a report passed through the daily press that the Empress of Russia used yearly many thousands of roubles' worth of odeur de violette, essences of jonquil, tuberose, elder, jasmine, and narcissus, of which such large quantities were sprayed each day in her rooms that her maids of honour "not unfrequently became unwell, and had to be taken out into the fresh air". If this paragraph should be true, we could only shake our head and wonder that Her Majesty's physician

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[1]) The Volatile Oils, by E. Gildemeister and Fr. Hoffmann. Written under the auspices of Messrs. Schimmel & Co., Leipzig. Authorized translation by Edward Kremers. Milwaukee, Pharm. Review Publ. Co. 1900, 733 pp. with 4 maps and numerous illustrations.

[2]) Stuttgart, published by F. Enke, 1898.

[3]) Stuttgart, published by F. Enke, 1893. Second Edition (Part One) 1902.

tolerates such abuse. Of Queen Wilhelmina the same newspaper-paragraph mentions that every morning there is added to her bath a pint of Eau de Cologne. The notion of many great ladies, that they can improve, or even only preserve, their complexion by such additions, is of course wrong. The mother of the King of Spain prefers to Eau de Cologne an Eau d'Espagne, unknown to Science. Eau de Cologne, whose exact composition is naturally kept secret, has been introduced from time to time into chemists' shops by some Pharmacopœias as *Aqua coloniensis*, or *Spiritus coloniensis.* Nowadays our Pharmacopœia Germanica no longer attempts to compete with genuine Eau de Cologne. Naturally, fashion also reigns in the realm of perfumes and prefers at one time heliotrope, and at another ylang-ylang, Jockey club, or elder-blossom, and then again tuberose, jasmine, violet, musk, etc.

It is a remarkable fact that chemistry has recently detected in perfumes some substances, which in concentrated form lose their odour completely, and further, even such which have a nasty smell when concentrated. As a proof of the last-named fact I would mention that oil of jasmine-flowers contains the malodorous substance indol, and Abyssinian civet the evil-smelling skatol 1). Indol and skatol are two characteristic products of putrefaction of the intestines, and skatol possesses in an exquisite degree the specific odour of fæces.

We are nowadays able to compose artificially from the individual components the perfume, for example, of the oils of orange-blossoms, ylang-ylang, jasmine, etc., and even to produce perfumes which do not occur in nature. Vanillin, heliotropin, irone, ionone, coumarin, nerolin, terpineol, benzaldehyde, and nitrobenzene, are chemically uniform substances of extraordinary aroma, which can partly be produced artificially. Most plants, however, are not satisfied with one single substance, but produce several; and even at different periods of vegetation the composition of the odorous principle in one and the same plant frequently varies considerably. According to Semmler, all organic perfumes known up to the present can be reduced chemically to four fundamental types.

But unfortunately the structure of many, partly most ancient, and especially animal perfumes, such as musk, ambergris, castoreum, and civet, is still unknown. It follows that with these also, there is enough work for chemistry for many decades to come. What is bought under the name of *Moschus arteficialis*, are trinitrobutyl derivatives of toluol, xylol, and allied substances. These interesting compounds have no doubt a striking musk-like odour, but they have most certainly a totally different composition, and their physiological action is wholly different from that of animal musk. Our knowledge of vegetable musk, i. e. of oil of ambrette-seeds (from *Abelmoschus moschatus* Moench

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1) Compare our Berichte October **1900**, p. 99, and October **1902**, p. 112.

Malvac.) and of oil of sumbul (from *Euryangium Sumbul* Kauffmann Valerianac.) is unfortunately also extremely limited, although *Radix sumbul* in Russia is even official, — or at least was so in my time.

The essential oil which in many respects is the most important of all, is and remains rose oil, superior to all vagaries of fashion. The German Industry could enjoy no greater triumph than that the German rose oil of Schimmel & Co. surpassed in value the Persian and Turkish oils. Some of the odorous constituents of rose oil, for example geraniol, citronellol, citral, and others, can also be separated from other essential oils. On the pharmacological action of all these substances our knowledge is still full of blanks. But it suffices for the physician to know, that the aroma of roses, properly diluted, is harmless for most people.

For perfuming iodoform, characterised by its intensive, disagreeable odour, various *aethereo-oleosa*, as for example coumarin, are suitable, — that is to say, so long as the preparation remains in the box. But as soon as it is placed on a human wound, the iodoform odour always soon becomes perceptible. For this reason this remedy is now no longer perfumed. — For perfuming soaps, especially those manufactured from the not very pleasantly smelling cocoa-nut oil, the addition of safrol commends itself. Oil of bitter almond, and nitrobenzene, are also frequently used for the purpose of imparting odour to soaps. Naturally, all other perfumes can be added as well. In order to reduce the expense, many soap-manufacturers perfume their soaps only externally. In such soaps the perfume very rapidly disappears in use. With regard to tooth-powders and tooth-pastes, I would refer to my book "Arzneiverordnungslehre" [1]).

## 3. Group of odorous Taste-Corrigents.

There is no strict line of demarcation between the odour-corrigents and the odorous taste-corrigents for the remedies which are intended for internal administration.

By far the greatest importance as an odorous taste-improving substance for the science of prescribing remedies, has the peppermint and the many preparations made with it. Oil of peppermint, contained in this botanically ill-defined and by no means uniform species of plant, varies considerably in its quantitative composition according to its origin. In the medical literature of the last decade it is repeatedly either stated direct, or at least to be read between the lines, that the authors consider menthol as the only substance in this oil which is worthy of consideration. This, however, is by no means the case; as a corrigent of taste and odour, the oil plays a more important part than menthol.

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[1]) Third edition, with 207 illustrations. Stuttgart 1900.

For this reason the former is mostly present in the patented and much advertised liquid dentifrices; but its action tends to inflame the sensitive mucous membrane of the mouth, and it should therefore not be left at random to every patient — especially the female patient — to be used *ad lib.* The pharmacological examination of the question, which of the substances contained in the oil is so often badly tolerated by the mucosa of the mouth, is not yet closed, but I have the promise of an article on the subject from Neisser's Clinic at Breslau, for the "Zeitschrift für Krankenpflege" edited by me.

Of other remedies of our class, which may come under consideration as corrigents for liquid dentifrices, I would mention oil of orange-blossoms, oil of bitter orange, oil of cinnamon, and especially oil of cloves, which in the 4th edition of the German Pharmacopœia is designated as eugenol, although it does not by any means consist exclusively of eugenol. It would therefore be more correct if the name *Oleum caryophyllorum* were completely deleted, and that of eugenol substituted. In the same manner the German Pharmacopœia is pleased to denote *Oleum carvi* as synonymous with carvone, and *Oleum anisi* as synonymous with anethol, whereas in reality the situation is the same as with oil of cloves. As taste-corrigents for remedies in powder-form, the oil-sugars, i. e. essential oils triturated with sugar, are in demand, especially *Elaeosaccharum menthae piperitae, anisi, carvi,* and *vanillae.* In the last-named preparation vanilla is triturated as such with sugar.

As corrigents of odour and taste simultaneously, for solid food as well as beverages, the *aethereo-oleosa* have played for thousands of years a most important part. We now know that even the most nutritious food, if taken without spices, easily becomes distasteful and does not agree with us. That the line between kitchen and chemists' shop is hard to draw, especially in the case of strong spirituous liquors, is well known. Of non-spirituous liquors of the present class I would mention particularly the highly-important ginger-beer.

Of the internal remedies which require perfuming, the best-known is cod-liver oil. It would appear to me that in this case the aroma of freshly roast coffee is the best corrective. The quantities of poisonous furful alcohol, detected in it by E. Erdmann¹), are much too insignificant to prejudice us against this cheap and readily obtainable aromatising agent. For deodorizing anæsthetic ether, Fr. Fischer²) most strongly recommends pine-needle oil, *Oleum pini pumilionis*, 1 drop to 10 grams ether. I personally prefer the addition of an equal quantity of limonene. I return to this substance further down.

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¹) Arch. f. exp. Path. u. Pharm. **48** (1902), 233.

²) Münch. med. Wochenschr. **1903**, No. 10, p. 445.

## 4. Group of Stomachics, Digestants, and Carminatives.

Between taste-corrigents and stomachic tonics there exists no clearly defined limit. Thus, Tappeiner for example includes the preparations from the rind of the bitter orange among the corrigents, whilst I am in the habit of dealing with them among the stomachics. Apart from the *aethereo-oleosa,* only the *amara* play an equally large part in the group of stomachic remedies. Many drugs belonging to the latter, however, contain not only essential oils, but also at the same time bitter remedies; these are called aromatico-amara. If it is desired to put the words stomachics, digestants, and carminatives into English, they should be translated as remedies which in some respect or other are useful for the gastro-intestinal canal with regard to the digestion. It is mostly a question of stimulating the appetite, increasing the gastro-intestinal secretion, and promoting the motions of the intestine. Even if we had no other indications for the *aethereo-oleosa* than those just mentioned, it would already be necessary, thanks to these, to work up yearly many tons of drugs, for the number of otherwise quite healthy persons who, partly from habit, partly from insufficient gastro-intestinal functions, take almost daily kitchen or chemist's preparations from bitter orange, wormwood, ginger, calamus, cinnamon, caraway, aniseed, dill, parsley, coriander, etc. is quite enormous. It is scarcely necessary still to mention *Schnaps*, or liquors such as Boonekamp, Angostura bitter, Benedictine, Chartreuse, Curaçao, etc., etc. Of course, all the essential oils contained in these are poisonous, unless only very small doses are taken. Thus we saw how recently in France before the Academy of Medicine, a very interesting debate¹) took place on the toxic character of such liquors, when especially th ehabit of the Frenchmen of drinking absinthe was strongly attacked. According to Boudran, an adult person can only just tolerate the following quantities (in cc.) of essential oils, diluted: Oils of rosemary 56,7, fennel 33,3, peppermint 28,3, juniper 19,7, lemon 12,4, bitter almond 12,3, aniseed 10,0, caraway 9,5, wormwood 5,3, star-aniseed 4,9, cloves 3,3, cinnamon 3,3, and calamus 2,6. According to these figures, it would be necessary to caution even more strongly against the use of calamus-*schnaps* than against absinthe. However, the method of examination employed by Boudran, according to which the action was deduced from the chemical behaviour towards potassium permanganate, is quite arbitrary, and in no way conclusive. For instance, in a case described by Benjamin²), a person took for the purpose of suicide a dose of 150 grams oil of caraway, of which, according to Boudran, only 9,5 cc. are tolerated, and whose carvone

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¹) Séance du 10 juin **1902**. Compare Boudran, Bullet. des sc. pharmacol. **1902**, p. 236. — Syndicat central des Négociants en liqueurs et spiritueux de France et des Colonies. Réponse au Rapport du Dr. Laborde sur les liqueurs.

²) Schmidts Jahrbücher **278** (1903), 133.

Hildebrandt[1]), with regard to its toxic character, places close to the extremely dangerous pulegone. And yet the would-be suicide came off scot-free. As to oil of wormwood, in an experimental examination[2]) made under my direction many years ago, I have had gathered together particulars of the severe attacks on the use of absinthe, which were made even at that time; but from the experiments on animals which we then made, I have not been able to come to a definite confirmation of the justice of those attacks. But now, after having further examined this question for more than two decades, I am decidedly on the side of the opponents to absinthe. The same position is taken by the most recent investigator of the absinthe-question, S. D. Laloue[3]). The study of the effect of oil of calamus can only now be commenced, since Rud. Beckstroem[4]) has solved the chemical preliminary question of the composition of this oil. Of the substances interesting to us, which were thereby detected, I would enumerate eugenol, calameone, and asarone which hitherto had only been known as a constituent of the oils of *Asarum europaeum* and matico. These three substances may probably determine the toxic quality of calamus oil.

Among the thirst-quenching and appetite-stimulating beverages, which, cooled in ice, are sold in summer in the United States very generally at the street-corners, and also by chemists, not a few contain safrol, which belongs to the essential oils. We pharmacologists cannot caution sufficiently strongly against the possible introduction of this mischief in Europe, for safrol, even greatly diluted, is a powerful and dangerous irritant for the kidneys, which may no doubt be prescribed medicinally, but should never be taken *ad libitum* as a condiment. For the same reason I am bound, — though otherwise a friend of colonial enterprise — to reject the liqueur from massoy-bark, which is introduced by some colonial firms, as it also contains safrol.

It will be readily understood that the group of stomachic liqueurs contains numerous proprietary preparations possessing (according to the advertisements) some wonderful action. Of these I mention as an example Kiesow's Essence of Life, which, according to G. Arends[5]), contains, in addition to other substances, five essential oils possessing stomachic qualities.

In the foregoing paragraphs, two effects of essential oils on the intestinal canal have not yet been mentioned, viz., the one as an addition to cholera-drops, and the other as an addition to remedies for worms. Both will be treated in subsequent groups.

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[1]) Ztschr. f. physiol. Chem. **36** (1902), 441, 452.

[2]) C. Fr. Bohm, Über die Wirkungen des ätherischen Absinthöles. Thesis, Halle o./S. 1879.

[3]) Contribution à l'étude de l'essence d'absinthe etc. Paris, 1902.

[4]) Über die Bestandteile des Kalmusöles. Thesis, Basle, 1902.

[5]) Neue Arzneimittel u. pharmaz. Spezialitäten (Berlin 1903) p. 254.

## 5. Group of Uterine remedies, Emmenagogues, and Abortifacients.

The common people had already discovered centuries ago that a few *aethereo-oleosa* not only act on the gastro-intestinal canal, but also on other organs in the abdomen, such as on the organ which secretes the bile, i. e. the liver, and particularly on the urogenital apparatus. This explains how it is that in all countries individual remedies containing essential oils (and always remedies of a heroic character) have been in use for the purpose of bringing about the menses, or for expelling the fœtus, and that these remedies are probably still being used, in spite of all remonstrances by the medical profession. Whether there is among these remedies a single one that can be applied without injuring the patient, is a question which scientific pharmaco-therapeutics is up to the present unable to answer. But every practitioner must know the injurious effect of these remedies whose use is generally concealed from him. They are savin, thuja, European pennyroyal, rue, and arnica.

The twigs of the savin-tree, *Summitates sabinae*, represent of this group the remedy which is best known to the medical profession, as they are still official in most countries. Its toxic character is due to sabinol, a substance which Hildebrandt¹) has recently submitted to a most careful study. In cats and dogs it brings about the discharge of blood in the urine, irritation of the genitalia, the formation of methaemoglobine, somnolence, etc. C. G. Santesson²), when microscopically examining rabbits poisoned with this substance, found fatty degeneration of the liver reminding of phosphorus poisoning. My assistant Dr. Jürss discovered the same alteration of the liver in animals poisoned with thujone. Thujone is the active constituent of the oils of tansy, *Thuja occidentalis, Artemisia absinthium*, and other plants which do not interest us here. For oil of European pennyroyal, a number of experimental examinations are available. According to all these, there can no longer be any doubt whatever, that pulegone, detected by Beckmann and Pleissner³), which in addition to menthol and menthone is present in this oil, according to Falk⁴), Lindemann⁵) and G. Martins⁶), causes, in a much

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¹) Zur gerichtsärztlichen Kenntnis des Sadebaumöles. Sonderabdruck aus dem offiziellen Berichte der XVII. Hauptversammlung des Preuß. Medizinalbeamtenvereins, Jahrgang 1900. — Über Synthesen im Tierkörper II. Verbindungen der Kampfergruppe Nr. 1: Sabinol, der Terpenalkohol des *Oleum sabinae.* Arch. f. exp. Path. u. Pharm., Vol. **45** (1901), 110.

²) Einiges über die Wirkung des Sabinaöles. Skandin. Arch. f. Physiol. **11** (1900), 228.

³) L. Tétry, Bull. Soc. Chim. III. **27** (1902), 186. — M. Pleissner, Liebigs Annalen **262** (1891), 1.

⁴) Ther. Monatshefte **1890**, 448.

⁵) Arch. exp. Path. u. Pharm. **42** (1899), 356. — Ztschr. f. Biologie **39**, 1. — Zieglers Beiträge **27** (1901), 484.

⁶) Arbeiten des Kaiserl. Ges.-Amtes **15** (1899), 443.

larger degree than the plants mentioned before, phosphorus-like fatty degeneration of the liver and other organs. Oil of European pennyroyal has, particularly in England, in attempts at abortion frequently caused severe intoxication, and even death[1]). It is derived from various plants and different countries. There are four commercial qualities of our oil: the Spanish is derived from *Mentha pulegium*; the American from *Hedeoma pulegioides*; the Russian from *Pulegium micranthum*, and the Canarian from *Bystropogon origanifolius*[2]). The physiologico-chemical behaviour of pulegone in the organism has been studied by Lindemann and Hildebrandt[3]).

Oil of rue has frequently been used for purposes of abortion, especially in France. Its chemical composition was again examined only last year, by C. Mannich[4]), and also by Power and Lees[5]). According to these authors, the oil is a mixture of more than ten different substances, of which methyl nonyl ketone and methyl heptyl ketone are no doubt the most important; of the former, according to Gildemeister and Hoffmann, the oil may contain as much as 90 per cent. Pharmacological examinations of this body by H. Paschkis and Fr. Obermayer[6]) are the only ones at present available. According to these, methyl nonyl ketone has a powerful reducing action on the pressure of the blood, with which the abortient effect may be connected. The oil as such acts moreover as a strong local irritant, which may equally lead to abortion.

The use of arnica flowers for the purpose of expelling the fœtus has again been observed medically not later than last year[7]). The infusion from 20 grams flowers was already sufficient to make a girl extremely ill. We find in literature proofs of the abortifacient use of this remedy, which go back for a period of several centuries. The symptoms occurring after taking the infusion, such as hæmatemesis, show that arnica oil exerts a powerful local stimulation, a fact also proved by other observations. We return to this remedy when dealing with the cutaneous stimulants.

The apiol of the oils of parsley and dill has been recommended by J. Roussel in doses of 0,2 gram, dissolved in oil, for promoting the discharge of the menses in amenorrhœa; but this statement requires further confirmation.

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[1]) The Lancet, 10th April, 1897.

[2]) Report Schimmel & Co., Oct. **1902**, p. 82.

[3]) Ztschr. f. physiol. Chem. **36** (1902), 456.

[4]) Ber. d. d. pharm. Ges. **12** (1902), 267.

[5]) Chem. Centralbl. **1903**, I, 29.

[6]) Pharmakol. Untersuchungen über Ketone und Acetoxime. Sitzungsber. d. kaiserl. Akad. der Wiss. zu Wien, Mathem. Klasse. Vol. **101**, Part. 3, May 1892.

[7]) Deutsche Medizinal-Zeitung **1902** (Nr. 90).

## 6. Group of Diuretics.

I do not know whether, apart from the experimental work made by Alexander Raphael[1]) in my Institute, any other examination dating from the last decade, on the diuretic action of essential oils, is in existence. I am just now having the results obtained at that time checked over again. There is no doubt that oil of juniper-berries possesses a considerable diuretic action. Raphael prefers *Oleum baccarum juniperi sine terpeno* (0,4) to that containing terpenes; but in any case the conclusion may be drawn from his experiments that the action is not solely due to the terpene. Raphael also found that terpine hydrate (1,0 gram) promotes the secretion of urine, whereas with oil of turpentine this action was not clear. The same author also found that the oil of parsley-seed (0,4 gram) had on himself a diuretic action. He recommends the administration in "pearls". The action continues for many hours. Oil of jaborandi leaves (*Oleum foliorum jaborandi*), oil of lovage (*Oleum radicis levistici*), and angelica oil (*Oleum radicis angelicae*), when administered to Raphael in the same dose and manner, also proved to be diuretics. Raphael also tested juniper oil and oil of parsley on patients, and found them useful. It goes without saying that not every patient should be submitted to such experiments, for the point of attack of the above-named remedies does not lie in the heart and in the vascular system, as with digitalis, but in the kidney itself, whose secernent parenchyma is stimulated by those bodies, the same as by calomel. For calomel exactly-defined indications and methods of administration have been evolved, which have rendered this remedy absolutely indispensable; in the same manner a sphere of indications, if only limited, may be discovered and permanently maintained for the above-named essential oils, or for the active principles contained therein, if they are carefully tested in many Clinics. By way of appendix we must here also refer once more to the safrol from sassafras oil, already mentioned on page 115. There can be no doubt that its secretion-stimulating action on the kidney is the only factor, which has led to the adoption of the wood of sassafras roots in antisyphilitic wood-beverages. Whether safrol in such dilution excels the above-named substances as a diuretic, without producing a toxic effect, will have to be finally proved in Clinics by careful experiments. A further diuretic constituent of wood-infusion, *Lignum guaiaci*, does not itself contain any essential oil or even traces of it; but another kind of guaiacum wood is found (derived from *Bulnesia sarmienti* Lor.), which gives a

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[1]) Über die diuretische Wirkung einiger Mittel auf den Menschen. Works of the pharmacolog. Institute of the Imperial University of Dorpat, edited by Rud. Kobert. Vol. X (Stuttgart 1894), p. 81.

rich yield of essential oil. The only physiological experiments with this oil and with guaiol, contained in it, originate from my pupil W. Frieboes[1]). As experience shows that the kidney reacts with a more powerful secretion of urine to the administration of a mixture of diuretic substances, than to a much larger quantity of the individual bodies, it is expedient, to some extent as a substitute for the old diuretic infusion, to introduce into commerce a ready-made mixture of essential oils, which can be very conveniently administrated in very small capsules (i. e. in so-called pearls), and which greatly surpass the various infusions in activity and exact dosage. I recommend as such a mixture of equal parts of *Oleum juniperi, Ol. levistici, Ol. angelicae, Ol. fol. jaborandi, apioli, safroli, guaioli, terpineoli, borneoli.* Of this mixture capsules containing 0,1 gram are introduced into commerce as *Capsulae olei diuretici* (Kobert). They should be taken several times daily in quantities of two to four capsules, where it is desired either to drain the body (dropsy), or to flush the urinary passages more abundantly (catarrh of the bladder, stone-forming deposit of the urine, tendency to decomposition of the urine, etc.). It is recommended to let the patient at the same time drink any liquid which is agreeable to him. The volatile constituents of the internal antigonorrhoeic remedies, such as oil of copaiba, oil of cubebs, oil of matico leaves[2]), East Indian Sandalwood oil, and the oil of Atlas cedarwood recommended by Trabut[3]), also have unquestionably a diuretic, and at the same time antibacterial, action. Whether they have any other action as well is a question which in this place does not interest us.

## 7. Group of Diaphoretics.

Since many centuries hot infusions of lime-blossoms and of elder-blossoms have been used in popular medicine to stimulate the secretion of sweat. Most investigators are of opinion that the effect here is simply obtained by the hot water. Of course no sensible person will deny that hot water by itself brings about perspiration. Moreover, it was proved already 70 years ago that lime-blossoms in the most favourable case yield only 0,038 per cent. oil, and elder-blossoms even less, and it is consequently highly improbable that the homœopathic doses of these oils which can possibly be contained in a few cups of such

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[1]) Beiträge zur Kenntnis der Guajakpräparate. Prize Essay of the med. faculty of Rostock. With a preface by Rud. Kobert. 10 figs. in the text. Stuttgart 1903.

[2]) This oil varies considerably in its composition. Compare Gildemeister and Hoffmann, The Volatile Oils, p. 325.

[3]) Bullet. des sc. pharmacol. May **1900**.

tea, may participate in the action. The reverse test, however, i. e. the experiment with these oils first in larger, then in smaller doses, has, so far as I know, not yet been made by anyone, and we can therefore pronounce absolutely no opinion on their real action. In Russia a diaphoretic tea is used which has a much more agreeable taste, and which I would prefer under any circumstances to the two above-named sorts. This is raspberry tea, prepared by pouring boiling water on dried raspberries. With regard to oil of raspberries, of which, in addition to sugar and fruit-acids, traces are present in this infusion, I can find nothing in the whole literature.

## 8. Group of Antihydrotics.

Even at the present day many practitioners still prescribe, in the profuse perspiration of patients suffering from tuberculosis of the lung, cold infusion of sage, to be taken shortly before going to sleep. An exact experimental test of this treatment is not, however, available. In view of the fact that oil of sage contains borneol and thujone, it may be assumed that it increases the pressure of the blood, and stimulates the tone of the vessels, and the perspiration. Picrotoxin, which undoubtedly excites the centres of the medulla oblongata, is looked upon occasionally as an antihydrotic if taken in small doses, and camphoric acid is very generally in use for the same purpose. All three remedies, however, have not the slightest antihydrotic action in the healthy, — rather the reverse. All three are used with advantage only for phthisics, and that only for those large defects or infiltrations in the lung, where usually during the night an insufficient arterialisation of the blood takes place. With such patients, all substances which excite the centres of the medulla oblongata, such as camphor, borneol, ammonia, picrotoxin, etc., have a favourable effect on the respiration and circulation, and thereby indirectly counteract perspiration. Experiments with oil of sage on animals have been made not only by Cadéac and Meunier, but also by Lalou[1]). These experiments show that larger doses of oil may produce thujone-intoxication. For use at the sick-bed, however, only very small doses come under consideration.

## 9. Group of Antiseptics.

There can be no doubt whatever that many essential oils up to a certain point possess antimicrobic properties. If the mucous membrane of the intestine of a newly-killed animal is scraped, as I have

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[1]) L. c. page 201.

often been compelled to do for the purpose of chemical examination, and if this pulpy mass is carefully kept only for one day at the temperature of the room, an intensive, evil-smelling putrefaction with formation of bubbles (marsh-gas, carbonic acid, etc.) takes place. If, however, the mass is mixed with water which, mixed with oil of turpentine, has been standing for some time in sunlight and been frequently agitated, the minute quantities of ozonised oil of turpentine which the water has been capable of dissolving are sufficient to arrest as desired the evil-smelling putrefaction of the mass scraped from the intestinal mucous membrane. That real ozone does not actually take part in this process, as is generally believed, I have been able to prove in a detailed examination of the turpentine-oil water, made jointly with my pupil Ernst Pallop¹). The German Patent No. 138638 granted to Dr. H. Noerdlinger in 1901, makes use of the above-mentioned action for the purpose of disinfecting waste water. The vaporisation of so-called ozonised oil of turpentine in the sick-room, according to Schrohe²), may perhaps also be based upon the idea of such an antibacterial action. The long-known excellent deodorising action which the oils of turpentine and myrtol, when administered or inhaled, exert on the effluvia from the lung of patients suffering from bronchitis putrida and gangrene of the lung, takes place in an analogous manner. I have taken pains, in the course of last year, to substitute limonene for oil of turpentine which the patients do not willingly take or inhale, and I have been able to confirm that this chemically uniform substance, which has an agreeable odour and taste, was readily used by all patients, and left nothing to be desired in its deodorising action. For the purpose of sterilising the cavity of the mouth of healthy persons and patients, both before and after meals and also before and after the night-rest, many substances have in the course of time been proposed, but very few proved to be not only permanently harmless, but also pleasant in use and yet active. Among these I would mention the methyl salicylate of oil of wintergreen, from *Gaultheria procumbens* L. (Ericaceae) and *Betula lenta* L. (Betulaceae), which is now also produced synthetically on a large scale, and has already been adopted officially in many countries. In the mouth it is a pleasant disinfectant; internally in doses of one gram it is used with advantage in acute articular rheumatism. Piperonal, which has already previously been examined by Heffter, and now again by my pupil Kleist³), possesses a very pleasant odour (it is for this reason also called heliotropin), and in addition, according to Frignani and Wimmer, also considerable

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¹) Über die Wirkung des sog. ozonisierten Terpentinöles. Thesis, Dorpat 1889.
²) Therapie der Gegenwart, **1902**, Nr. 8.
³) See our Report, April, **1903**, 133.

antiseptic properties, whilst it is moreover quite non-toxic. As it has further an antipyretic action and is inexpensive, it might deserve much greater attention on the part of physicians as a mouth-wash, febrifuge, etc. than has been the case hitherto. The antiseptic action of menthol and thymol would make these remedies appear suitable especially as additions with a not obtrusive odour to tooth-powder and liquid dentifrice.

Since 15 years I have added these two substances (each 1,0 gram to 30 powder) to all tooth-powders prescribed by me, in lieu of peppermint oil and of camphor so popular in England, and I have never had reason to complain about it. For restricting putre-faction in the gastro-intestinal canal, thymol and menthol are also useful. This explains why there is scarcely one kind of cholera-drops not containing oil of peppermint. In how far both substances, after internal administration, are also active against microbes of the urinary canal, requires further examination.

The use of balsams and essential oils in catarrhs of the urinary canal, as mentioned above (page 118), should have a diuretic effect, and thereby more frequently flush the diseased parts of the urinary passages, and prevent prolonged stagnation of the urine. But these remedies are also used with the view of obtaining an antiseptic action. The idea upon which this is based is this, that these remedies, which are secreted from the kidney like menthol and thymol, in the form of combined glycuronic acids, are decomposed when in contact with urine containing bacteria, and at the moment of decomposition exert an antiseptic action. That this action also extends to gonococci, has been demonstrated by Neisser. But further experiments on this subject, which is of such great importance for every physician, are desirable. R. Boehm[1]) mentions among the internal antigonorrhoeic remedies gurjun balsam (*Balsamum dipterocarpi*), as having an action very similar to that of copaiba balsam. It contains about 65 per cent. essential oil. For the purpose of sterilising catgut, many surgeons use essential oils. Only recently W. Fedorow[2]) has expressed the opinion that the turpentine-oil and cajeput-oil methods are to be preferred to all other sterilising methods of catgut. The antiseptic properties of terpineol, vanillin, etc. have already been referred to in the April number of these Reports (page 80). Some experiments by my pupil H. Kleist, on the action of microbes on certain derivatives of anthranilic acid, have also been communicated there in the original (page 111 et seq.)

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[1]) Lehrbuch der allgem. u. spez. Arzneiverordnungslehre. Third edition, completely revised. Jena, 1903.

[2]) Russky Wratsch, 1902, Nr. 30.

## 10. Group of Leukotactics.

As indirect antiseptics, or leukotactics, I desire to discuss a group of substances which effect a "healthy leukocytosis", and which send forward the increased number of white blood-corpuscles occurring in that process as combatants against the toxic substances and the invading microbes. The first experiments on the action of essential oils on the number of leukocytes circulating in the blood, originate from E. Hirt (1856) and from C. Binz and his pupils H. Meyer and V. V. Grisar. In addition to these, I have made (at first still under H. Koehler), partly alone, partly with S. D. Marcusson[1]) and with Bohm[2]), counting tests of the most primitive character with the blood of animals to which essential oil had been administered. The experiments made by R. Winternitz[3]) are greatly perfected in their technique. According to all the above-mentioned authors, most essential oils or their components (excepting menthol and camphor), produce leukocytes, and that with subcutaneous injection in the first instance locally (so-called sterile suppuration). Attempts have been made to utilise this, for example with oil of turpentine in appendicitis[4]). Too large doses of this oil, however, when repeatedly administered, produce amyloid degeneration. H. Schulz[5]) and Brummer, on the other hand, go much too far when they think they have observed on themselves all sorts of disturbances after merely fractions of one drop of turpentine oil. In France, *Tinctura thujae* is used as a leukotactic remedy.

The leukotactic action of Balsam of Peru led Landerer to the introduction of injections of this substance into the blood as a remedy against tuberculosis. Later on, this investigator passed from the balsam to the active substances of the latter and, as is well known, now continues these injections, not without favourable result, with chemically pure compounds of cinnamic acid. It is impossible to quote the very large number of publications which exist on this subject. — Finally I would briefly mention the Peru cognac, or "perco", much advertised as a remedy against tuberculosis.

## 11. Group of Antiparasitics.

It is advisable to divide this group, which attack animal parasites, into two subdivisions, viz., external and internal.

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[1]) Das Pfefferminzöl, Thesis, Halle 1877.

[2]) Compare citation on page 115.

[3]) Über Allgemeinwirkung örtlich reizender Stoffe. Arch. exp. Path. u. Pharm. **35** (1895), 77.

[4]) Moritz Mayer, Erfahrungen über Terpentinöl und verwandte Mittel bei Blinddarmentzündung. Münch. med. Wochenschr. **1902**, No. 32.

[5]) Ein Beitrag zur Kenntnis der Terpentinölwirkung. Münch. med. Wochenschr. **1900**, No. 28.

### a) As external antiparasitics,

*aethereo-oleosa* come especially under consideration in the treatment of psoriasis. In previous times this treatment was carried out with balsam of Peru or styrax, but in the course of the last decade there have here also been made systematic trials to test the usefulness of such individual substances contained in balsam of Peru, which can be produced artificially — this being chiefly due to the constantly increasing price of good balsam of Peru. Of these substances, the benzyl ester of benzoic acid has up to now been examined most in detail. It is dissolved in soaps or fatty oils in the proportion of 25 per cent. and applied by inunction. The modern treatment of psoriasis with the ester has over the old method the great advantages of neatness, purity, and accurate dosage, but the disadvantage that only one substance acts on the mites, whilst in the other a mixture of active substances is present.

Protection against fleas and bugs is now as before afforded by Persian or Dalmatian insect-powder, for the manufacture of which are used the blossoms of various species *Pyrethrum* s. *chrysanthemum.* Its activity is due, in addition to other substances, also to the essential oil. More detailed trials on the question whether the oil alone is useful, are absent, but they would seem necessary, as many persons suffer from severe irritation of the skin after using the powder. If the oil should be found to be better tolerated by the human skin, and at the same time have an equally powerful action on the parasites, the manufacture of the oil would be remunerative. But if, on the other hand, the inflammation of the skin should be attributable to the oil, the latter could no doubt be removed[1]). The tincture which is now occassionally used, has a value by no means equal to that of a solution of the oil in alcohol. *Blumea densiflora* D. C., used in India instead of insect-powder, contains an essential oil, like the closely allied species *Bl. lacera* D. C. and *Bl. balsamifera* D. C. The oil of the last-named species is rich in borneol; those of the other two should be submitted to a chemical analysis, the same as that of our oil of insect-powder.

Against head- and body-lice the peasant has for ages used aniseed and parsley-seed. The pure essential oils of these and similar plants, or the substances anethol and apiol obtained from them, are also useful for these purposes. For the head they are employed in the form of pomades and hair-oils, which need only contain one to five per cent. essential oil. Many practitioners prefer pomade of balsam of Peru.

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[1]) I am aware that E. Hirschsohn (Pharm. Ztschr. f. Russl. **29** [1890], 209) found insect powder still active after having rendered it odourless by drying it thoroughly at 120 degrees C. But this does not absolutely prove that the essential oil of this remedy is totally inactive. Moreover, I myself found an essential oil of insect powder of a well-known firm by no means inactive.

Against crab-lice, the inunctions with such a lice-oil can only be recommended as a subsequent treatment, after having been preceded by an inunction with grey ointment.

Since patients are now frequently allowed to lie on open balconies, in halls, and even entirely in the open air, we use much more often remedies for banishing gnats, crane-flies, and stinging flies, than was previously the case. Fairly useful for such purposes are pieces of filtering paper, saturated with oil of cloves, and placed on a plate not far from the patient. But many patients find the odour of the oil in the long run inconvenient. For healthy persons who go out for walks in the gnat-season, rubbing the hat with a gnat-pencil may be useful. Such pencils consist mostly of a solid fat to which has been added anise oil, oil of cloves or anethol, eugenol, or some other strong-smelling essential oil.

Clothes and collections are protected by camphor, naphthalene, oil of cajeput, or benzaldehyde and prussic acid. It has lately become known, through H. v. Soden and Rojahn[1]), that naphthalene, long known as a coal-tar product, also occurs in essential oils, for example in that of clove-stems.

### b) Of internal antiparasitics, those which interest us most in this case are worm-remedies, anthelmintics.

Against *Oxyuris vermicularis*, enemas of infusions of garlic, ramsons, chive, onion, asafœtida, are in many cases sufficient.

Against *ascaris*, the remedy now mostly used is santonin lozenges. But I must not refrain from mentioning that electuary of zedoary-seed, which was formerly employed, was very useful (although it has an unpleasant taste), as it brought into the field against worms both santonin and oil of zedoary-seed, in about equal proportions. This oil, acting chiefly through its cineol-content, and in this respect resembling oil of eucalyptus, supports, according to my observations, the action of santonin. These observations agree with the experience of veterinary surgeons. Whilst, namely, for horses or cattle, for expelling *ascaris*, 10 to 25 grams santonin are required (according to Froehner)[2]), which with a santonin-content of 2 per cent. would equal a quantity of 500 to 1250 grams worm-seed, there are, as a matter of fact, not more than 100 to 250 grams seed required. That the worm-treatment can be assisted by oil of zedoary seed is perhaps also proved by the fact that there exists a species of artemisia which contains an essential oil but no santonin, and which, according to old as well as recent

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[1]) Pharm. Ztg. **1902**, p. 779.

[2]) Lehrbuch der Arzneimittellehre, VIth ed. Stuttgart 1903, p. 478.

reports¹), can be used successfully as a vermifuge. This is *Artemisia herba-alba* Asso. Now, as there is no lack of observations of santonin-poisoning in children, whilst cineol in comparison is harmless, it seems advisable to substitute cineol again for santonin. Of course, there is no objection to replace cineol by other essential oils or by substances prepared therefrom provided these are found to have vermifuge properties and at the same time are harmless. The experience of veterinary surgeons, namely, shows that, for example, *Herba tanaceti* is also a vermifuge. This contains an alkaloid and an essential oil²). A mixture of the two, in the form of an extract, has recently been placed on the market, and is well worth a trial. Oil of tansy contains, as its most important constituent, tanacetone (s. thujone). As shewn by the experiments by Jürss, mentioned below, it is poisonous when administrated in large doses, and these must therefore be avoided. In how far small doses are capable of exerting a vermifuge action, is a question which needs to be settled. Spinola's worm-cakes, frequently used by farmers for sheep, contain a mixture of tansy and calamus-root in equal proportions. It is not yet known in how far calamus oil has a vermifuge action. In the United States and in Brazil a worm-seed oil is used, not without success, which is obtained from *Chenopodium ambrosioides* L. (Jesuit's tea), *Chenopodium anthelminthicum* L., and *Chenopodium suffroticosum* W. The constituents of these oils should be submitted to a chemical and pharmacological test. In the United States, oil of chenopodium, which is there known as worm-seed oil, is included in the Pharmacopœia. Against *taenia*, *bothriocephalus*, and *ankylostoma*, a mixture of substances is recommended, of which extract of fern and thymol are the two most important. Formerly it was stated that the only active constituent of extract of fern was filicic acid, or the mixture of substances sold in the trade as filicic acid. More than ten years ago I³) have already shown that filicic acid by itself, even in doses of one gram, does not act as a vermifuge in man, but only becomes capable of such action when dissolved in a small quantity of fatty oil and mixed with a little essential oil, — as is the case with the extract. I based my statements regarding the strengthening of the action by the essential oil upon experiments made with essential oil of filix on lower animals of various kinds. Since, due to R. Boehm's merits, several butanones have been detected in fern, and have been recognised as active, F. Kraft⁴) has recently designated

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¹) M. Battandier, Journ. de Pharmacie et de Chimie I. **23** (1891), p. 380; see also the verbal report by Professor E. Grimal, Algiers.

²) For a short examination of the oil by myself, see the Berichte d. deutsch. pharm. Ges. **39** (1902).

³) Über die wirksamen Bestandteile im Rhizoma filicis maris. Pharmac. Post **1892**, Dec. issue; and Sitz.-Ber. der Dorparter Naturforscherges. **1892**, 167.

⁴) Pharm. Ztg. **1903**, p. 272.

filmarone as the only active butanone, which Boehm had overlooked. Without at all having read my work, he characterises my view that the specific substance of the fern, which is insoluble in water, must be diluted in a small quantity of fatty oil, and mixed with essential oil, as a "long since abandoned hypothesis". Only during the last few months I have treated two children for tapeworm with the adult dose of filmarone (without oils), with all possible precautions, and have been unsuccessful in both cases. With this unfavourable experience the reports agree, which are made from all sides, that in *ankylostoma* also the butanones alone do not act sufficiently. On the other hand, I have before me reports from totally different quarters, mentioning that the combination of butanones (dissolved in a small quantity of fat) with essential oils[1]), leaves nothing to be desired in certainty of action.

As extract of fern contains only a very small quantity of essential oil, it is replaced by other vermifuge essential oils, — with which I entirely agree. Those hitherto mostly used are oil of turpentine and thymol, — which does not say that the others mentioned above may not perhaps act better than oil of turpentine. Thymol by itself also has an expelling action in *ankylostoma*, but it does not act with sufficient certainty in all cases. — In how far the small quantity of essential kousso oil contained in fresh kousso has a share in the vermifuge action, has not yet been investigated; but this much is certain, that the substance, when old and stale, does not expel the worm. Possibly the treatment may here also be greatly improved by the admixture of a vermifuge oil. The treatment with kamala, by itself uncertain, might, in combination for example with cineol, give better results than without this addition.

## 12. Group of Antidotes.

With narcotic poisons, such as chloral hydrates, trional, and morphia, injections or solutions of camphor are suitable in case the patient is found completely insensible and without reaction. The camphor-injections may also be found useful in the collapse-stage during the deprivation-treatment for morphinism. J. Hoffmann[2]) has, as a matter of fact, only seen favourable results from the internal administration of camphor during such treatment. In acute phosphorus-poisoning, if the phosphorus has already been resorbed from the gastro-intestinal canal, we can no longer do any good with the usual

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[1]) Compare E. Schmidt, Chem. Centralbl. **1903**, II. 390; H. Goldmann, Deutsche Ärzte-Ztg. **1903**, No. 5; Baker, Brit. med. Journ., 28. March **1903**; Nagel, Deutsche med. Wochenschr. **1903**, p. 545; Pharm. Ztg. **48** (1903), 436.

[2]) Therap. Monatshefte **1902**, No. 7.

antidotes, such as sulphate of copper and permanganate of potash. In such desperate, but by no means rare cases, the only antidote which comes under consideration is the so-called ozonised oil of turpentine, which forms with the phosphorus the so-called turpentine-phosphorous acids studied by myself jointly with my pupil O. Busch[1]). We found that these acids are less toxic than phosphorus. As such a careful investigator as Stich[2]) had completely denied the existence of these acids, I determined to have Stich's statement, that these acids be only a mixture of phosphorus with oil of turpentine, submitted to a test. This task has just been completed by my pupil August Fischer[3]). The result obtained by him shows that the so-called turpentine-phosphorous acid is not a mixture of phosphorus and oil of turpentine (as Stich maintains), but on the contrary that, as Busch had already assumed, it represents a mixture of several compounds of phosphorus (differing in their phosphorus-content), with oil of turpentine. This admitted, the treatment of acute cases of phosphorus poisoning with ozonised oil of turpentine remains fully justified. I propose to study the action of turpentine-phosphorous acids on animals once more with my pupil R. Glette.

## 13. Group of Dermerethistics.

There is no reason to assume that the application of remedies provoking irritation of the skin is out of date, because they have been borrowed from popular medicine, and are looked at askance by some theorists. On the contrary, in practice we very frequently use the *aethereo-oleosa* belonging to this class, and obtain excellent results in the following indications.

In order to produce in cold feet the pleasant feeling of warmth, and to stimulate the circulation in them, mustard-baths and rubbing with spirit of juniper and especially spirit of mustard, are useful. After the mustard-bath the feet, which have become red as a lobster, are given a douche of cold water, rubbed slightly, and then put into clean dry stockings and shoes; this produces an exceptionally pleasant feeling which continues for a long time. An examination of the toxic effect of oil of mustard was made at one time by myself and R. Heinz[4]).

When the skin is badly nourished, atropic, dull, and pale, as occurs so often in scrophulous and rhachitic children in addition to a high

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[1]) Experimentelle Versuche über die Wirksamkeit des Terpentinöls als Antidot bei der akuten Phosphorvergiftung. Thesis, Dorpat 1892.

[2]) Pharmac. Ztg. **47** (1902) 567; Münch. med. Wochenschr. **1902** No. 32, p. 1347.

[3]) Beiträge zum Phosphornachweis. II. Einiges über die terpentinphosphorige Säure. Pflüger's Arch. f. d. ges. Physiologie **97** (1903), 591.

[4]) Das ätherische Senföl. Thesis, Halle o. S., 1878.

degree of anæmia, it is advisable to give a course of warm baths, to which has been added calamus-root, spirit of calamus, spirit of mustard, spirit of camphor, or eau de Cologne; these baths are willingly taken by the children, and they improve in a striking manner the condition of the skin, and indirectly also the composition of the blood.

In neuralgic affections below the skin (trigeminus-, intercostal-, ischiadicus-neuralgia), in muscular rheumatism, chronic articular rheumatism, in dry pleurisy, and in pericarditis, the legion of stimulating remedies which are rubbed on are turned to account. They very often contain oil of turpentine, oil of rosemary, camphor, oil of mustard, etc. A turpentine-ointment sold on a large scale bears the proud name of "King's Ointment" — *Unguentum basilicum*. Not infrequently such mixtures are sold largely as proprietary medicines. For example, "*Kloster-Balsam*" (friar's balsam?) is nothing but a vaseline-ointment containing turpentine.

R. Heinz[1]) has supplied an experimental work on the local inflammation-producing action of oil of turpentine. The different varieties of oil of turpentine, such as pine-needle oil, oil from fir-cones, etc. differ in odour, but not in the action. The same applies to pine-needle oil from *Pinus montana*, to which I will return lower down. All the constituents of the various oils of turpentine appear to have a share in the local stimulating action, and the use of the individual and comparatively expensive constituents would therefore not be of much advantage. Oil of rosemary, whose toxic symptoms I have at one time studied jointly with P. Schreiber[2]), consists of pinene, camphene, cineol, camphor, and borneol. In the form of nerve-ointment, *Unguentum rosmarini compositum*, it is still in demand. The composition readily explains the local stimulating effect of oil of rosemary. Tincture of arnica, which, unfortunately, is still popular with ladies, and the butter-like oil of arnica-blossoms which it contains in very small quantity, and which has not yet been examined chemically, are the worst of all skin-stimulants; Hebra has already cautioned against their use in emphatic language, as they frequently produce severe inflammation of the skin. Less harmful are the oils of marjoram and of balm. The oils of cumin (*Cuminum cyminum*) and of fever-few (*Matricaria parthenium*) have no connection with the womb (as might be assumed from the German names *Mutterkümmel* and *Mutterkraut*), but are at most only used as popular remedies, for rubbing on, when mixed with nutmeg-balsam. It is highly questionable whether they have any value whatever. Many of the local stimulants also belong at the same

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[1]) Studien über die Entzündung seröser Häute. Münch. med. Wochenschr. **1900**, No. 7.

[2]) Das Rosmarinöl. Thesis, Halle o. S., 1878.

time to the group of anæsthetics, that is to say, they first excite the extremities of the sensory nerves, and then paralyse them. The same is the case with nerve-ointment. This explains why opodeldoc is such a favourite in painful contusions and rheumatic affections. A few of our remedies exert in slight cases of frost-bite (chilblains) an action which at the same time again excites the contractibility of the principal vessels which have lost their tone through the frost-bite. For this reason camphor is a never-absent constituent of frost-bite ointments. In burns or scalds, it is usual to add peppermint oil to the burn-ointment consisting of linseed oil and lime-water, because it reduces the sensation of burning and heat.

In cases of apoplexy, mustard-paste is applied to the sole of the foot for withdrawing the flow of blood. The derivative action commences as soon as the feet assume a red colour.

As remedies for stimulating the mucosa of the mouth, and the gums in case they are anaemic and badly nourished, dentifrices and mouth-washes containing *Spiritus cochleariae* play the most important part. It is a remarkable fact that oil of peppermint (but not menthol) has a reverse action, and is consequently employed where it is intended to bring about contraction of the vessels, when the gums are pathologically reddened.

## 14. Group of Excitants.

I consider camphor the most valuable excitant which we possess, as its stimulating action is not only confined to the centres of respiration, blood-pressure, and reflexes, but also promotes the activity of the heart. In severe cases of tuberculosis of the lung, where the pulse is small and feeble, the blood-pressure low, and respiration defective, I have very often observed the beneficial effect of injections of oil of camphor. But also in various conditions of debility, in collapse, fainting, narcotic poisoning, camphor is a serviceable remedy, and in proper dosage harmless. In view of its insolubility in water, it is obvious that attempts should have been made to find soluble derivatives of this substance. Campho-carbonic acids, which have been studied especially by J. W. Brühl[1], yield alkaline salts soluble in water. A series of detailed experiments made jointly with my pupil A. Lapin[2], unfortunately gave the unexpected result that campho-carbonate of sodium is inactive, even in doses of one gram, and passes without change through the organism. Professor K. Gottlieb[3], who checked

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[1] Berliner Berichte **24** (1891), 3382 and 3708; **26** (1893), 290; **35** (1902), 3510, 3219, 4030, 4113; **36** (1903), 668 and 1305.

[2] Zur Pharmakologie der Kampfergruppe. Thesis, Dorpat (then already renamed Jurjew) **1893**, p. 51.

[3] Berichte **35** (1902), 3518.

these experiments, could only confirm our results. The esters of camphocarbonic acids have a feeble stimulating action, but up to now have not been employed. On the other hand, camphoric acid, *Acidum camphoricum,* has justly been incorporated in the medicinal treasure, as, in addition to a faint camphor-like action, it has undoubtedly the effect of counteracting sweating in phthisics. (Compare p. 120.) As several essential oils contain borneol, I also examined this substance with Lapin[1]). We were able to determine that it also represents a stimulant of the central nerve-system and the heart. If Borneo-camphor were less expensive here, borneol might possibly be able to compete with ordinary camphor. We also found a characteristic camphor-action in the acetic ester of borneol[2]). This is explained by the fact that this ester in the organism splits off borneol. The action of menthol[3]), which was examined at the same time for comparison, was totally different, inasmuch as the central nerve-system was rapidly paralysed by this substance. But the terpenes[4]), which, in addition to menthol, are contained in oil of peppermint, act as excitants, as we have also proved.

Whether the cramp-exciting action of thujone may be used therapeutically, is an open question.

## 15. Group of Sedatives and Narcotics.

Ointments and liniments containing oil of peppermint (already repeatedly mentioned above) have only a local cooling and pain-allaying action on inflamed parts of the skin. The remaining cooling ointments (*Unguenta refrigerantia*) exert their refrigerating action by evaporation of water, but they mostly also contain a substance having the character of an essential oil. Thus, the favourite cold cream (*Unguentum leniens*) belonging to this class contains rose-water. Whether, when a warmed pouch with aromatic herbs (*Species aromaticae*) is placed on the swollen cheek in toothache, such a quantity of essential oil penetrates into the skin, that it can thereby affect the inflammation or the pain, is a matter which cannot be decided, as the heat which is emitted acts at the same time. But it is a fact that common people still cling to this treatment in toothache, mumps, swollen lymphatic glands, etc.

Of internal sedatives, I have at all times recommended valerian to the audience at my lectures, as a by no means antiquated or valueless remedy. Like alcohol, valerian has also an exciting as well as a sedative action. In the form of an infusion (from *Radix valerianae*), or drops (*Tinctura valerianae*), this non-toxic remedy produces in the

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[1]) Compare also Lapin p. 108.
[2]) l. c. p. 108.
[3]) l. c. p. 124.
[4]) l. c. p. 200.

female sex in many cases a beneficient euphoria and removes a state of excitement. Only in recent times a commencement has been made to split up the individual components of the oil according to their action, and to manufacture from them artificial preparations. As such I would mention essence of valerian (*Spiritus valerianae compositus*), valerobromine (double salt of sodium bromide and sodium valerianate), valeridine (para-valeryl-phenetidine), validol (menthol ester of valeric acid), and valyl (valeric acid diethylamide). Asafœtida, much valued by the modern school, belongs according to its action also to this group, and deserves experimental examination. The proprietary remedy "pertussin" recommended as a sedative in severe attacks of whooping-cough of children, contains oil of thyme (in addition to bromide of potassium!). Cypress oil, which Schimmel & Co. introduced into commerce in 1894, appears to me a more valuable remedy against whooping-cough. The first author who recommended this oil is an Italian physician of the name of Bravo (not otherwise known to me); he used it already in whooping-cough in 1892. The method of application is as follows: The oil, diluted with alcohol in the proportion of 1 : 5, is sprinkled on the pillow and the shirt of the child suffering from whooping-cough, and thereby rapidly reduces the intensity and frequency of the attacks. The root of *Artemisia vulgaris*, acting through its content of essential oil, has already been recommended by Burdach against eclampsia of children. No less a person than Nothnagel has again brought this forgotten method to the light, and Boehm¹) also honours it by mentioning it again. It is therefore not out of place to submit these experiments with oil of artemisia and its constituents to a further test. As a sedative in painful difficult breathing, oxycamphor²) ($C_{10}H_{16}O_2$), and also its 50 per cent. solution called "oxaphor", come under consideration. Up to the present I have no information as to its toxicologic action.

It is generally known that occasionally traces of essential oils are added to chloroform and ether in order to perfume these substances. Less known is the fact that some essential oils can be added to chloroform in larger quantities, in order to obtain the stronger narcotic effect. As long ago as 1877³) I showed that the inhaling of oil of turpentine may produce profound narcosis.

F. Zahradnicky⁴), of Deutschbrod, has now employed a mixture of chloroform and oil of turpentine on man in 421 cases, for the purpose of producing narcosis before surgical operations, and not once

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¹) Lehrbuch der allgem. u. spez. Arzneiverordnungslehre. Third revised Edition, Jena **1903**, 210.

²) Berliner Berichte **35** (1902), 3811.

³) See the quotation on page 109.

⁴) Cbl. f. Chirurgie **1903**, Nr. 1, p. 32.

has he observed the occurence of unfavourable incidents. When repeating such experiments, I would recommend the use of the much more pleasantly smelling and chemically uniform body limonene, instead of oil of turpentine.

## 16. Group of Expectorants.

Among the remedies which dissolve the coagulating sputum in catarrh of the lung, pneumonia, emphysema, asthma, and tuberculosis of the lung, and which thereby promote its expectoration, anethol takes the first place. Only ammonia can be placed alongside it as of equal value. Both active remedies are contained in *Liquor ammonii anisatus,* which, however, acts much too powerfully to place it without risk direct in the hands of the public. A preparation which lends itself much more to the direct delivery to the public than the one just mentioned, is the good old Ringelmann's pectoral elixir, *Elixir e succo liquiritiae,* which in Russia is also called *Elixir regis Daniae.* As recently complaints have been made that the anethol in it in winter separates out in pieces, it is advisable to dilute this preparation once more, most suitably with glycerine *aa.* During the time I was Director of Brehmer's Sanatorium for pulmonary diseases at Görbersdorf, I have had the opportunity of prescribing this remedy very many times, and I can again state that it is very inexpensive, tastes well (under milk, sugared water, or Chinese tea), and moreover is very effective. Of course I should never dream of maintaining that it has a favourable effect on tuberculosis of the lung as such. Sanosin, the patent fumigating remedy recommended against tuberculosis of the lung by L. Danelius[1]) and unfortunately also by the President of the German Anti-Quackery Society, Professor Sommerfeld[2]), which is said to be a mixture of sulphur, carbon, and eucalyptus oil (from *Eucalyptus maculata* var. *citriodora*) has still to prove its usefulness. The objections made to it by Fraenkel[3]) are only too well founded. If the patients who come to Reichenhall fix all their hope there on pine-needle oil (from *Pinus montana*), this must undoubtedly have a very useful psychical effect on those who had up to then been without hope. But from a pharmacological point of view, *Oleum pini pumilionis* can only be considered as one of the oils of turpentine, and in aroma it is inferior to the equally active limonene, already referred to above in several places. The best method of application of oils of turpentine, and of limonene, myrtol, etc. in tuberculous patients, consists of sending the patients, on days

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[1]) Berl. Klin. Wochenschr. **1903**, No. 23, p. 524.
[2]) Pharm. Ztg. **1903**, No. 65, p. 653 and 655.
[3]) Berl. Ärzte-Korresp. **1903**, No. 32.

when the weather is very unfavourable, for a few hours in an inhalation-room, where large spray-diffusers, attached to the ceiling, minutely diffuse under high pressure water or a normal solution of common salt, to which traces of essential oil have been added. In such a room the patients walk chatting up and down, and from time to time make the prescribed deep inhalations. These have a deodorising and expectorating effect, in spite of the fact that only traces of oil are thereby brought into action. Systematic experiments on pure cultures of tubercle bacilli and other microbes found in the lung, made to test the antiseptic effect of essential oils, and of constituents of those oils, are urgently needed. It is hoped that this reference to them may lead to such experiments being made.

J. J. Weber, Leipzig.

# SEMI-ANNUAL REPORT

OF

# SCHIMMEL & Co.

(FRITZSCHE BROTHERS)

MILTITZ
NEAR LEIPZIG

LONDON ✻ NEW YORK.

APRIL/MAY 1904.

Dwellings of employees of Schimmel & Co., Miltitz near Leipzig.

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# Contents.

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## List of abbreviations.

$d$ = specific gravity at 15°, unless otherwise stated.

$d_{20^\circ}$ = specific gravity at 20°.

$d\frac{20^\circ}{4^\circ}$ = specific gravity at 20°, compared with water at 4°.

$\alpha_{D\,15^\circ}$ = optical rotation at 15°, in a 100 mm tube.

$[\alpha]_D$ = specific rotation.

$n_{D\,15^\circ}$ = index of refraction at 15°.

n = normal.

$\frac{n}{2}\left(\frac{n}{10}\right)$ = semi-normal or deci-normal (titrated solutions).

gm. = gram; cc. = cubic centimeter; mm. = millimeter.

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Temperatures are uniformly stated in **centigrade** degrees (°).

**Miltitz,** near Leipzig, April/May 1904.

We are unable to place on record any decided change in the general economic condition of the German Empire since the date of our last Report. The Chemical Industry shows the same picture of great prosperity as in the preceding years, as evidenced by the excellent results of the leading houses. The branch comprising the essential oils and artificial perfumes, in so far as we are able to judge about the network of wide-spread ramifications, also appears to have reason to be satisfied with the result of last year's working.

The warlike events in the Far East do not as yet appear to exert any pronounced influence on trade and industry. The incidents are localised in such a small area that outside this area they are hardly noticed. The German steamship-lines carry on their services without hindrance, under the protection of neutrality, and no pronounced influence on the value of Japanese products, in which we are largely interested, has up to now become apparent.

In the commercial intercourse with France, the difficulties in the clearance of terpineol and similar products make themselves felt very acutely. The French Tariff demands in the case of terpineol 1 fr. 60 c. for 2 litres alcohol which, in the opinion of the French Customs Authorities, are supposed to be used in the manufacture of this preparation.

This view is totally erroneous! Not a single drop of alcohol is used in the manufacture of this article, and the duty on it is consequently charged unjustly. It would only be necessary to refer the matter to a scientific expert, to demonstrate the correctness of our protests, — which in a general way is already proved by the price of the article. For how could 2 litres alcohol of a value of about 2/6 be taken into consideration, where the price of terpineol is only 4/-?

In Brazil a new Bankruptcy Act has come into force on 7th June 1903, in which the remarkable provision occurs (par. 134), that every merchant is compelled to submit every year his ledger (*diario*) to the judge, as soon as the balance sheet, as required by Art. 12 of the Commercial Law Code, has been entered, when the presence thereof on the day in question is to be certified by the judge by his visa and signature.

The trade with Roumania will derive facilities from the law of 15/28th June 1903, inasmuch as not only the duties on the essential oil employed in the manufacture of perfumes and soaps have been reduced, but also the analyses previously required have now been abolished. On the other hand of all other essences or essence-containing oils the importation is only allowed if previously two samples weighing at most 20 grams in all have been taken from these articles, sealed, and submitted to the Chemical Institutes of Bucharest or Jassy, according to the proximity of these places, and after a reply has been received from these Institutes respecting the character of the samples, and as to whether they can be admitted in accordance with the sanitary law and the administrative requirements of the country. Such essences and essence-containing oils must not be analysed by the chemists at the Custom houses, but only at the above-mentioned Institutes, to which the samples must be submitted with the request for prompt analysis. Under these conditions, the better-class German firms will probably not enter into keen competition for the Roumanian trade.

According to a communication contained in the "Deutsches Handels-Archiv", the Commercial Treaties of 1857 between the United Kingdom and Persia have been amended and amplified on the 9th February 1903, in consequence of which these two countries now grant to each other special advantages with regard to import duties. The export duty on Persian products is entirely abolished. Finally, the system of farming out the collection of the duties will be abolished in perpetuity, and instead of this, Custom houses will be established on all the frontiers. The Persian Government erects warehouses in which the British merchants are allowed to store the imported goods for 12 months without payment or dues of any kind.

The export to the United States was very brisk, but it may possibly be affected to some extent towards the middle of the year by the approaching Presidential election.

In the Argentine Republic trade is improving slightly after the not unimportant decline which the sale of our manufactures had suffered during the last few years.

Our relations with all other countries show no changes worth mentioning. As a Customs curiosity we may state that the Austrian chief Custom office at Bodenbach has recently thought fit to subject the article anethol, a specially purified anise oil, as an „artificial perfume“ to a duty of 75 gold florins per 100 kilos, whilst as an essential oil, which it indisputably is, the duty is only 15 gold florins per 100 kilos. We have naturally protested vigorously against this arbitrary action, and if need be will follow up this matter to the Supreme Court of Appeal.

A retrospect at the past half-year no doubt shows a number of rising quotations in various leading articles of our branch, but also some considerable declines in values. In the following pages of our Report we endeavour in an impartial manner to give reasons for both categories of movements, and, where they have been produced artificially, to attack them vigorously, hoping that we shall thus be able to render a real service to the public interested in our articles.

Our scientific laboratory once again provides matter for the Report by a number of interesting researches.

We would further mention here that we have acquired the patents belonging to Professor Dr. Dunbar, of Hamburg, for the serum against hay-fever, called "Pollantin", invented by him.

The manufacture of Pollantin is carried on under control of the inventor, in conjunction with the agricultural work of our firm at Miltitz.

**Almond Oil, bitter.** The raw material which comes under consideration for this oil, i. e. Syrian apricot-kernels, could be purchased favourably, and there was also a sufficient demand for pressed oil, so that the manufacture could be carried on by us on a normal scale. At the same time, the demand exceeded our output.

Two parcels of "genuine" oil of bitter almonds, which were offered to us for sale, showed a distinct chlorine-reaction and had been adulterated with chlorinated benzaldehyde. In one case the usual argument was brought forward, that the oil had been dried with common salt, and that the chlorine-content must be attributed to this. This argument has been answered by us in detail already years ago (Report April **1891**, 29), and we now repeat that the chlorine-content of oil of bitter almonds is solely due to the presence of organic chlorine products, and not to the minute traces of anorganic chlorides which might originate from the drying of the oil, and which, as a matter of fact, could not possibly be detected by the method of combustion employed by us.

To-day we absolutely maintain this view. The oil is an article of confidence, and it is a great mistake to let low prices be an inducement for buying.

**Almond Oil, pressed from apricot-kernels.** The prices of Syrian kernels, which in September last year set in at a low level, advanced already in the course of the last months of 1903 by about 15 %. As we ourselves had to pay these higher prices, we were soon forced to increase our lowest price for large parcels to

130 marks per 100 kilos. At this rate we believe to be able to meet all further demand until the time of the new harvest. The sale at this price, which is still exceptionally low, was very brisk in all directions.

**Almond Oil, pressed from sweet almonds.** The Sicilian and Bari fruit, which on account of the minute content of bitter almonds comes almost exclusively under consideration for our manufacture, could not yet be purchased at the former normal prices. With the latter we mean about 100 to 110 marks. But since forward transactions have gained the upper hand also in this article, it has become a tool in the hands of speculators, and the results of the harvests and other statistical considerations are only of secondary importance. The November issue of the "Deutsches Handels-Archiv" contains the following report from the German Consulate at Bari:

> "In the middle of March a few successive night-frosts destroyed the whole Apulian almond-crop; of about 120000 bales of a normal full harvest, only a few thousand bales were gathered in the course of the autumn. After the frosts, the prices continually moved upwards all through the year, and on the 10th September they reached their highest level at 219 lire per 100 kilos, gross weight for net, f. o. b. Bari, for first-class sweet Bari almonds, the principal brand of the district. Against this, the quotation in March, shortly before the frost, was 155 lire f. o. b. Bari. As the quantities available on the whole of the world's markets, for the season 1902, in the unanimous opinion of experts, approximately correspond to those of the season 1900, when prices of over 300 lire were reached, it was generally believed that the further movement in the prices would also be the same as in 1900.
>
> But it turned out to be otherwise. The depressed economical situation led to such a restriction in the demand, especially from Germany, the principal consumer of Bari almonds, and to such a flagging of all speculative enterprise on the part of German import firms, that the Bari market, operating with a stock of about 40000 to 50000 bales of the 1901 crop, was no longer able to hold its own against the universal reserve. A collapse followed, and the quotations fell rapidly and without interruption.
>
> At the end of March 1903 the quotation for spot was 160 lire per 100 kilos f. o. b. Bari, with practically no business."

Unfortunately we have not been able to obtain in good time a more recent authentic report on the state of the market.

Our quotations are calculated on the basis of new Sicilian almonds. We only ship oil which has been pressed quite freshly.

**Oil of Ambrette-seeds.** Offers of ambrette-seed have lately been more numerous than ever before. In addition to the seed from the West Indies and Java, large consignments have arrived from the Comores, which have depressed the prices considerably. If this overproduction should continue, the values will show a marked decline, as the consumption is limited.

In consequence of the above-mentioned facts, the prices of the two kinds of essential oil also suffered a decided drop.

Our distillates are of standard quality in every respect.

**Anise Oil.** Only after the second anise-market had been held at Alexejewka was it possible to take a clear view of the result of the last anise-harvest. This was generally considered to be a failure, both as regards quantity and quality of the seed, of which only one half has a normal, and the other half a mottled, brown appearance. In view of the exceptionally unfavourable weather-conditions, such a result could cause no astonishment.

In Roumelia, where the cultivation of anise appears to have increased considerably, the result of the anise-harvest has been very abundant.

This variety is becoming a competitor of the Russian anise, well worthy of consideration. The prices, at first low, were soon driven up by the prevailing conditions, and at present they no longer leave a profit, although fairly large stocks are apparently still in existence.

The principal centre of production appears to lie in Eastern Roumelia. The export of anise from Dedeagatsch, a small port of that province, amounted in 1902 to 355982 kilos. The shipments from Salonica, though, are probably much more important.

The larger parcels worked up by us gave satisfactory results.

The total export of anise from Bulgaria was in 1902: 472055 kilos, value 198786 francs.

Russia exported in 1902 a total of 262797 poods, value 541048 roubles, and in 1903, by sea, only 156000 kilos, against 296000 kilos in 1902.

The unfavourable situation in Russia was bound to react on the prices of anise oil and anethol, and this would probably have been the case to a much greater extent, if one had been dependent on the Russian seed alone. But this is not so, and everyone who is interested in anethol will rejoice in the fact that there are sufficient other sources from which an anethol, answering the highest requirements, can be produced, independent of the Russian market.

Our sales of anethol reached an exceptional height. Large contracts for the raw material enable us to accept orders for any quantity, for prompt or forward delivery.

The comsumption of ordinary anise oil is growing smaller and smaller, as in consequence of the important difference in price it shows no advantage when compared with the purer and finer anethol. If it is taken into consideration that anise oil, in addition to anethol, contains about 10% of foreign substances, it follows that as a matter of fact the yield of anethol is higher by the same percentage, and this agrees with the difference in the prices of these products.

The pseudo nitrosite of anethol has already been produced years ago by Tönnies[1]), but its constitution had been wrongly interpreted,

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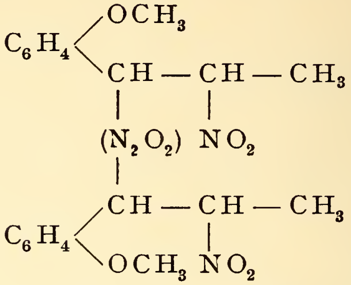
[1]) Berliner Berichte **11** (1878), 1511.

as Wieland[1]), in a work on pseudo nitrosites, has recently demonstrated. The latter attributes the following formula to the pseudo nitrosite of anethol:



It is formed when a solution of anethol in glacial acetic acid is treated at much reduced temperature with sodium nitrite. When boiled with alcohol, it becomes isomerised into the oxime of anisyl nitro-ethyl ketone (melting point 187°), whilst treatment of the pseudo nitrosite with alcoholic ammonia, or better with alcoholic caustic lye, in the cold, produces $\beta$-nitro-anethol (melting point 48°). If, in producing the pseudo nitrosite, the mixture is not treated at a temperature low enough, there is formed anisyl methylglyoximeperoxide of the melting point 97°; and if the reaction-temperature is allowed to increase to 50° to 60°, the amphi-dioxime of anisyl methyl-1, 2-diketone (melting point 206°) is also formed.

**Apopin Oil (Shu-yu).** In our last Report[2]) we published the translation of a treatise on this oil by Keimazu which had appeared in Japanese language. A further communication by the same author, published in the Journ. of the pharm. Soc. of Japan, No. 258, August 1903, is reproduced below, in abbreviated form, but in part literally translated:

I have already reported on my examinations of some constituents of shu-yu, and will now communicate some results of the continuation of this work.

### I. Detection of formaldehyde.

When washing the oil with water, I was struck by the strong pungent odour of the aqueous portion, the cause of which I was able to detect, by the usual reactions, as being due to the presence of formaldehyde. The fact that it was question of formaldehyde, and not of some other homologous aldehyde, was proved by the positive result of Rimini-Vitali's reaction.

### II. Detection of pinene.

The liquid obtained by the fractional distillation of shu-yu at 155° to 160°, has the specific gravity 0,8812 (16°), and the rotatory

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[1]) Liebig's Annalen **329** (1903), 225.

[2]) Report, October **1903**, 10.

power $+31^\circ 25'$ (100 mm tube). I suspected in it the presence of pinene.

The nitroso chloride produced by Wallach's method melted at 103°, in agreement with the melting point indicated by Wallach for pinene nitroso chloride. But as pinene cannot be detected simply by the nitroso chloride, it is necessary to produce also other derivatives from it. For this purpose the nitrol piperidide appeared to me the most suitable, and I produced this also according to Wallach. It melted at 118° to 119°, the melting point of pinene nitrol piperidide. From this I was able to conclude that the dextrorotatory pinene is present in shu-yu.

### III. Detection of a new terpene alcohol—apopinol.

The portion boiling at 195° to 202° is present in shu-yu in large quantity, and consists of one third of the entire oil. In my last report I stated that I was not at that time able to give more exact details respecting that portion, and that there might possibly be an alcohol, linalool, in question. I am now able to give further information on the subject.

From the above portion I distilled off another portion of the boiling point 197° to 199°, which had the following constants:

specific gravity (pycnometer): 0,8942° at 18°
opt. rotatory power: $+6^\circ 4'$ in 100 mm tube.

(In the description given in the previous report there are some errors; the present data are therefore more correct)

This substance is a colourless and transparent liquid, with an odour typical to shu-yu. Elementary analysis showed a body $C_{10}H_{18}O$.

Oxidation of the suspected alcohol with bichromate and sulphuric acid, according to the usual method, led to an oil which combined with a solution of sodium bisulphite, with formation of a crystalline body. The oil liberated from the addition-product boiled at 130° to 135° (55 mm pressure), and had the specific gravity 0,8942 (17°). Elementary analysis led to the formula $C_{10}H_{16}O$. The probability that it was here a question of citral, was confirmed by the fact that, when 10 grams of the substance to be examined was boiled with pyruvic acid and naphthylamine according to Döbner, there was obtained a condensation-product of the melting point 200° to 202° (Döbner 197°, Gildemeister 200° and higher). Other methods for detecting citral, such as formation of the semicarbazone or of the condensation-product with cyanacetic acid, were not applied.

### Naming the substance under examination.

It follows from the above examinations and the subsequent reactions, that it was here a question of a terpene alcohol, which on oxidation yields citral, as for example linalool. But in spite of the similarity in the oxidation-product and the boiling point, there are also properties which do not agree with those of linalool. Thus, in the first place the optical rotatory power; that of linalool has not been exactly determined, but it is with lævorotatory linalool at most 20° 7′, and with the dextrorotatory at most 15° 1′. Secondly, the acetyl derivatives. Linalyl acetate is the principal constituent (30 to 40 %) of bergamot oil, and has a typical aromatic odour; but the acetate of my oil has a totally different odour. In view of these facts, it would be more correct to take this substance as an isomer of the same series, such as geraniol or nerol (Hesse). I have given to our substance the name "apopinol".

When an ethereal solution of the alcohol was treated with metallic sodium, a sodium compound was formed which was soluble in ether and petroleum ether, and which could be obtained in the form of an amorphous yellow body by driving off the solvent by steam and removing the oily portion. The sodium-determinations made with the substance showed that only about 77 % of the theoretical sodium-content was present in the body.

This unsatisfactory result is essentially due to the property of the sodium compound of very powerfully attracting water and carbonic acid.

The acetylisation of apopinol succeeded both by boiling the fraction containing the alcohol with acetic acid anhydride and sodium acetate, and by dissolving the sodium apopinolate in ether and digesting it with acetic anhydride.

The resulting esters boiled at 134° to 140° (55 mm pressure) and 207° to 210° (at atmospheric pressure) respectively.

The figures of the analysis do not agree particularly well with those of an ester of the formula $C_{10}H_{17}O \cdot COCH_3$. From the difference between the figures found and calculated, and also from the sodium-determination of the alcoholate, I believe to be justified in assuming that 20 % of the oil remain unchanged during acetylisation; in the saponification of the ester the proportion of the quantity of caustic lye consumed to that required in theory was also 79,6 to 100.

The alkylation of apopinol was carried out by allowing methyl or ethyl iodide to act on dry sodium apopinolate. The methyl ether boiled at 188° to 190°, the ethyl ether at 195° to 196°. The analytical figures correspond fairly well with the calculated values.

The attempt to produce a urethane of apopinol led to no result; I only obtained diphenyl urea (m. p. 235°; corresponding nitrogen-determination), as probably water had been split off from the alcohol.

## Final conclusions drawn from my examinations of shu-yu.

I found in shu-yu formaldehyde, pinene, and a new terpene alcohol apopinol $C_{10}H_{18}O$, apart from the substances mentioned in my last communication.

This discovery of the aldehyde may probably lead to a simple differential diagnosis between shu-yu and camphor oil. For, according to Gildemeister, camphor oil only contains acetic aldehyde, — a fact which I myself proved in several samples of camphor oil. Although I do not know whether the formaldehyde in shu-yu is derived from the original material, or is formed by the method of production, its content in the oil is very considerable, and its detection very easy. Theoretically it is certainly possible that formaldehyde may occur as a product of decomposition together with the methyl alcohol, when the wood is dried, but yet we have hitherto never found it in pyroligneous acid which has repeatedly been examined by us. If it were once and for all established that all kinds of camphor oil only contain acetic aldehyde, we should now have a convenient method of detecting adulteration with shu-yu.

Now with regard to apopinol, the direct demonstration of its presence is not yet satisfactory, but by detecting citral I was able to assume its presence indirectly. It goes without saying that this apopinol is also valuable for the recognition of shu-yu.

I suspect that there are still some unknown terpenes also present in shu-yu, but I do not believe that they are of sufficient importance to be submitted to examination as important constituents.

In conclusion I beg to express my thanks to Prof. Shimoyama and Mr. Nagai for their guidance, and Messrs. Morita and Hagina for their assistance.

**Basil Oil.** *Ocimum viride* Willd., a species closely allied to the well-known *Ocimum basilicum*, which contains in the oil-glands of the leaves abundant quantities of aromatic essential oil, has in recent times been recommended as a protection against mosquitoes. According to Captain Larymore, as communicated by Shipley in "Nature", four plants placed round the bed afford greater protection than a mosquito-net. This effect is, however, denied by J. P. Quinton[1]).

An infusion of the leaves, taken hot, is used in Sierra Leone as a diaphoretic in high fever, and has given good results.

**Bay Oil.** The distillation of bay-leaves imported direct from the West Indies, is carried on by us on a large scale. A sample-consignment from Bermuda yielded an oil of a widely divergent character which cannot replace in practice the distillate from the West Indian material.

This oil, obtained in a yield of 1,33 %, showed the following constants: $d_{15^\circ} = 1{,}0301$; $\alpha_D = -3^\circ 4'$; $n_{D20^\circ} = 1{,}53012$; phenol-

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[1]) Annual Report on Government Gardens and Parks in Mysore for the year 1902/03, 11. This Report also contains a good picture of *Ocimum viride* Willd. and some parts of the plant.

content 61 %; soluble in 0,4 and more volumes 80 % alcohol; the dilute solution shows opalescence. Most striking are the considerably higher specific gravity and the ready solubility of the oil.

From an abstract from the „West Indian Bulletin"[1]) it appears that the island of Dominica is the centre of the bay oil and bay rum industries and trades. The manufacture of bay rum is carried on chiefly at St. Thomas, where the leaves are imported from St. John's, Dominica, and other islands. In recent years, however, the export from Dominica has fallen off considerably; for, whilst for example in 1898 the exports had a value of £ 1372, their value in 1902 was only £ 490. The cause of this decrease must be attributed to the fact that, since the annexation of Porto Rico by the United States, large quantities of bay leaves are shipped from Porto Rico to St. Thomas, where they are admitted free of import duty. But as the Porto Rico leaves are mainly the produce of "Bois d'Inde citron", and, owing to the taste and odour of lemon, are said to be useless for the preparation of the best qualities of bay oil and bay rum, it may be expected that the trade in bay leaves will soon again acquire its former dimensions, the more so, as the leaves from Dominica are the best.

**Oil of Boldo leaves.** The oil of boldo leaves which are used as a remedy in affections of the liver, has been submitted to a chemical examination by E. Tardy[2]). The oil, obtained by him, in a yield of slightly under 2 %, by distillation from the dried leaves, had a brownish-green colour and the specific gravity 0,876; $\alpha_D = -6^\circ 30'$. By extracting boldo oil with potash lye, the author obtained a small quantity of a phenol which was identified as eugenol by the vanillin odour occurring during the oxidation. An aldehyde isolated by means of bisulphite solution was found to be cuminic aldehyde. Of esters, a small quantity of acetic acid esters could be detected. When submitting boldo oil to fractional distillation (from 150° to 225°), Tardy found that the lowest-boiling portions were dextrorotatory; the following fractions showed a decreasing dextrorotation, and subsequently a constantly increasing lævorotation, which again diminished in the last fractions. In saturating the fraction passing over from 155° to 173° with dry hydrochloric acid gas, and subsequently fractionating the reaction-product in vacuo (3 cm), he obtained chiefly two portions which passed over respectively between 90° and 100°, and 125° and 135°; by submitting these to a low temperature they were obtained in crystalline form, and were identified by their melting points of 125° and 50° respectively as pinene monohydrochloride and dipentene dihydrochloride. It follows that boldo

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[1]) Chemist and Druggist **64** (1904), 188.

[2]) Journ. Pharm. Chim. VI, **19** (1904), 132.

oil contains a divalent terpene hydrocarbon which is dextrorotatory, and a tetravalent lævorotatory one. In the fraction of the oil passing over from 215° to 220°, Tardy detected terpineol. The fairly large residue, boiling above 225°, consisted mainly of sesquiterpenes, which had possibly been formed by condensation of the hydrocarbons, and which distilled over from 265° to 275°.

**Cajeput Oil.** According to Umney[1]) there have now for some years been cajeput oils on the market which do not answer the requirements of the British Pharmacopoeia. Whilst up to 1899 the specific gravity of cajeput oil was seldom found to be below 0,922, Umney recently determined this constant in several cases at 0,919. Whether the low specific gravities of recent imports are the result of using a different species of *Melaleuca* for the distillation, or whether the methods of distillation or rectification have been changed, is an open question. On the strength of his experiences, Umney proposes to adopt in the British Pharmacopoeia the limits of specific gravity of cajeput oil as 0,919 and 0,930. Umney detected as adulterants crude eucalyptus oil and petroleum which in one instance had even been artificially coloured with chlorophyl.

Parry[2]) agrees with Umney's above proposal; he considers an oil as genuine, if there are no other indications of sophistication, so long as the specific gravity does not fall below 0,919. A cajeput oil examined by Parry, which had the specific gravity 0,902, showed a marked phellandrene reaction, and had no doubt been adulterated with eucalyptus oil (from *Eucalyptus amygdalina*).

**Camphor oil.** The new Japanese Act regulating the monopolisation of the camphor and camphor oil production in Formosa and Japan, has now been published in the "Deutsches Handels-Archiv". It reads as follows: —

### Crude camphor and camphor oil monopoly.

(Japanese Gazette, 17th June 1903).

Par. 1. The Government has the right of monopoly for crude camphor and camphor oil.

Par. 2. Whoever produces camphor and camphor oil, must deliver the crude camphor and camphor oil to the Government.

The time and place of delivery are fixed by the Government.

Par. 3. The Government pays an indemnity for the crude camphor and camphor oil delivered. The amount of the indemnity is fixed by the Government, and must be published beforehand.

Par. 4. In so far as it is not a question of crude camphor or camphor oil sold by the Government, no one is allowed to have these articles in his

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[1]) Chemist and Druggist **63** (1903), 725.

[2]) Chemist and Druggist **63** (1903), 783.

possession, or to hold, transfer, hypothecate, or use them; nor to ship them abroad, or from Old Japan to Formosa, or vice versa. This does not apply, however, to the possession or holding prior to the date of delivery to the Government, or if this delivery has been delayed for legitimate reasons.

Par. 5. Camphor and camphor oil may only be exported, or shipped from Old Japan to Formosa, or vice versa, from the ports indicated by the Government.

Par. 6. Whoever desires to produce crude camphor or camphor oil, or to purify crude camphor, must fix the place of production, the number of furnaces, the weight and quantity of the estimated annual production, and also the date of the commencement of the manufacture, and must apply to the Government for permission therefor.

If it is desired to make a change on any of the points for which under the foregoing paragraph permission has been granted, or to discontinue the manufacture, permission must first be obtained from the Government.

Par. 7. When a person has taken over the manufacture of camphor or camphor oil by right of succession, he must give notice of the fact to the Government.

When a person otherwise than by way of succession desires to take over the manufacture, he must apply to the Government for permission.

Par. 8. No person carrying on the manufacture of crude camphor and camphor oil, is allowed to carry on at the same time the purification of crude camphor.

Par. 9. The Government has the power of limiting the production of crude camphor and camphor oil, in accordance with the relation between supply and demand of camphor and camphor oil.

Par. 10. When a person to whom permission for the manufacture of camphor and camphor oil has been granted, acts contrary to the provisions of the present Act or of the regulations issued in accordance with this Act, or when he does not fulfil the conditions which have been determined in advance, the Government has the right to withdraw the permission granted.

When in view of the situation in the district of the Savages, it is considered necessary for the purpose of maintaining public order, the Government may temporarily suspend the manufacture of crude camphor or camphor oil, or withdraw the permission to manufacture.

Par. 11. The producers of camphor and camphor oil must, in accordance with the regulations, enter in their business-books all facts concerning the manufacture.

Par. 12. The competent officials have the right to examine all business-books relating to the production of camphor and camphor oil, and to make an inspection of all places where camphor or camphor oil are, or are suspected to be, produced or stored, and further to take all other steps required for the exercise of control.

Par. 13. Camphor and camphor oil are as a rule sold at a fixed price, but where necessary the sale takes place by auction instead.

Par. 14. Crude camphor or camphor oil which have not been sold by the Government are subject to seizure by the Government when found in possession of any person who holds them without conscious infringement of the present Act. In such case an indemnity is paid in accordance with par. 3, unless it is a question of crude camphor or camphor oil which have been mixed with other substances.

Par. 15 to 23. (Articles dealing with penalties.)

Par. 24. With regard to the regulations required for carrying this Act into effect, the Governor General of Formosa decides in Formosa all questions which (in Old Japan) appertain to the department of the competent Minister.

### Supplementary Regulations.

Par. 25. This Act comes into operation on the 1st of October 1903.

The Regulations concerning the camphor and camphor oil monopoly in Formosa[1]) and also the Regulations concerning the manufacture of camphor and camphor oil in Formosa[2]) are abrogated.

Par. 26. Crude camphor and camphor oil which in Old Japan, at the time this Act comes into operation, are the property of producers of or dealers in camphor and camphor oil, must, in accordance with the present Act, be delivered to the Government in accordance with the regulations which shall be published hereafter.

Par. 27. The provisions of this Act do not apply to crude camphor and camphor oil, which in Old Japan, at the time this Act comes into operation, are the property of other persons than producers of or dealers in camphor and camphor oil.

Par. 28. Whoever, at the time this Act comes into operation, produces in Old Japan camphor or camphor oil, must obtain before the 1st November 1903 permission (for continuing his trade). Up to that date he may continue the production as hitherto.

Par. 29. Whoever, in accordance with the Regulations concerning the production of camphor and camphor oil in Formosa, has obtained permission, will be considered, until the expiration of the said permission, as having obtained it in accordance with the present Act.

It remains to be seen what the effect of this law will be on the trade in camphor and camphor oil. At present the situation is uncertain, but as the monopoly has now been introduced in both producing countries, its position will now be decidedly stronger than hitherto, and, in view of the great expense of the war, the intention will probably be to turn the monopoly to account by a considerable increase in the prices of camphor.

To whom the monopoly will be transferred is as yet uncertain.

It is not yet possible to say whether, and in how far, camphor oil will be affected by this state of affairs, but it appears practically certain that an attempt will be made to make as much profit as possible out of this product.

In the meantime, and until further notice, we supply at the prices quoted in our list. The sale of the three kinds carried by us was assisted so largely by the high prices of oil of turpentine, that we were unable to accumulate a stock, and even now we may occasionally have to ask for some delay in the delivery where it is a question of large parcels.

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We were recently able to demonstrate the presence of borneol in camphor oil. We succeeded in detecting it, when treating a camphor oil fraction of the boiling point 210° to 222° with phthalic acid anhydride. For this purpose the oil to which the same quantity phthalic

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[1]) D. Hand.-Arch. **1899**, I. p. 840.

[2]) Ibidem p. 841.

acid anhydride had been added, was heated on the water bath for 3 to 4 hours, with frequent shaking, and the phthalic acid compound formed was converted in the usual manner into the sodium salt of phthalic ester acid. When the strongly foaming solution of phthalic ester salt, which had been extracted 4 to 5 times with ether, was saponified, borneol was obtained, which could readily be abstracted from the alkaline liquid by steam distillation. The compound, repeatedly purified from petroleum ether, crystallised in hexagonal leaflets, and melted at 203°. Oxidation with chromic acid and glacial acetic acid, at the temperature of the water bath, led to camphor of the melting point 176°. The semicarbazone produced from the latter melted at 236°.

**Cananga Oil.** From the Head of the Government Medical Depot of Bangkok, Mr. H. Willems, we received a cananga oil which had been distilled from the fresh and dried blossoms of cultivated cananga trees. The physical constants of this pale-yellowish oil were as follows: $d_{15^\circ} = 0{,}9200$; $\alpha_D = - 51^\circ 40'$; acid number = 1,82; ester number = 34,17. In 10 volumes 90 % alcohol the oil was insoluble, but of 95 % alcohol 0,5 volume sufficed for making a solution, which, however, again became turbid when more alcohol was added. The odour of the oil showed a great similarity to that of ordinary cananga oil, but left something to be desired with regard to delicacy. This drawback, though, may in future possibly be removed by a more rational method of production.

According to Mr. Willems, the Menam valley appears to be very suitable for the cultivation of the cananga tree. Experiments in this direction have already been made, and have also been extended to other cananga varieties which, according to Siamese taste, produce a finer odour; but these species do not blossom so abundantly.

**Caraway Oil.** The stocks of last year's seeds from the districts preferred by us, have dwindled considerably, and the prices have recently hardened by about 1 florin per 100 kilos. Probably little will change until the autumn, as sufficient stocks of the ordinary commercial quality are said still to exist. With regard to the quantity sown, nothing can as yet be said, owing to the delay in the tilling of the fields due to the frost. Some small parcels of good value were placed on the market from Sweden, but in that country the producers are only with difficulty becoming accustomed to the low prices.

**Cassia Oil.** During the last six months only unimportant fluctuations have taken place in the price of this important article. Only within the last few weeks the value has exceeded the normal limit of 3/- per lb., and in the high-quality oils a scarcity has become perceptible which may easily bring about a further rise of a few pence.

The export of cassia and star-anise oils in 1903 shows a striking decline, which is difficult to explain. According to the statistics available, the shipments from China were: —

| | | | |
|---|---|---|---|
| in | 1903 | 2082 | piculs |
| against „ | 1902 | 3635 | „ |
| „ | 1901 | 6423 | „ |
| „ | 1900 | 4201 | „ |
| „ | 1899 | 3374 | „ |
| „ | 1898 | 4461 | „ |
| „ | 1897 | 4967 | „ |
| „ | 1896 | 4177 | „ |
| „ | 1895 | 2931 | „ |
| „ | 1894 | 4439 | „ |

If the situation is judged by these figures, the conclusion would be favourable for the future of these two Chinese oils.

In the examination of cassia oils we have recently had repeated opportunities of observing that in China the admixture of small quantities of colophonium to the oil is again being practised. The oils in question were suspected chiefly on account of the somewhat larger distillation-residue (above 11 $^{0}/_{0}$), as well as the higher acid number; some of them also formed fairly considerable precipitates when the alcoholic solution (1 in 3) was decomposed with alcoholic saturated solution of acetate of lead¹), whereas in the case of pure oil no precipitate is produced. We can strongly recommend for this purpose the test with alcoholic solution of lead acetate, but we would call attention to the fact that the solution does not keep, and is best prepared fresh on each occasion.

As in spite of this, the examined oils showed a fairly high aldehyde-content, and the adulteration therefore appears to be only in the early stages, we have so far taken no objection, but in future every oil of this character will be rejected.

A short time ago Hanus²) published a very exact method for the quantitative estimation of cinnamic aldehyde, — a determination which up to now has only been carried out by the bisulphite method indicated by us. His process is based on the separation and the determination by gravimetrical analysis of the cinnamic aldehyde as semi-oxamazone, and it is carried out as follows: —

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¹) Hirschsohn's reaction. Comp. Gildemeister and Hoffmann, "The Volatile Oils" p. 388.

²) Zeitschrift für Untersuchung der Nahrungs- und Genußmittel sowie der Gebrauchsgegenstände **6** (1903), 817.

0,15 to 0,2 gram cinnamon oil is decomposed in an Erlenmeyer flask of about 250 cc. capacity with 85 cc. water¹), and finely divided by shaking. Next, about one and a half times the quantity of semi-oxamazide²) which has been dissolved in hot water is added; the mixture is well shaken for about 5 minutes, and then left standing for 24 hours with occasional shaking; especially during the first three hours the liquid must be agitated repeatedly. The semi-oxamazone separated out in the form of small flakes, is filtered through a Gooch tile prepared with asbestos and dried and weighed, and is then washed with cold water, and dried at 105° up to the constant weight, which operation is completed in 4 to 5 hours.

The percentage of cinnamic aldehyde is obtained by means of the following formula

$$\frac{a \cdot 60{,}83}{s}$$

$a$ = cinnamic aldehyde semi-oxamazone found
$s$ = quantity of oil used.

The chemical process which takes place during the conversion may be made clear by the following equation

$$\begin{array}{l} CONH-NH_2 \\ | \\ CONH_2 \end{array} + C_8H_7-CHO = \begin{array}{l} CONH-N=CH-CH=CH-C_6H_5 \\ | \\ CONH_2 \end{array} + H_2O.$$

Hanus proves the usefulness of his method by means of a series of analyses, which partly refer to pure cinnamic aldehyde, partly to Ceylon cinnamon oils and cassia oils, and further to mixtures of the latter with pure cinnamic aldehyde.

In the case of the cinnamon oils, Hanus gives at the same time the results obtained by means of the bisulphite method; in the cassia oils they agree well with the values obtained by Hanus' method, but in the Ceylon oils they were from 6 to 7% too low.

We have carefully checked the method in question in our laboratory, and on the strength of numerous analyses made by us of commercial oils and our own distillates, and also of mixtures of cinnamic aldehyde and pinene, we are convinced that this method is very useful for the estimation of cinnamic aldehyde: it yields results correct to within

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[1]) Hanus has proved by experiments that if the proportions here given are adhered to, quantitatively correct results will be obtained; when too much diluted he found the figures too low.

[2]) With regard to the production of semi-oxamazide, comp. Kerp and Unger, Berliner Berichte **30** (1897), 585 and Weddige, Journ. f. prakt. Chemie **10** (1874), 196.

We have also found the higher melting point of 223° to 224° mentioned by Hanus for semi-oxamazide, but we are unable to confirm his statement regarding the colour (white with pink tinge), as our preparation had a pure white colour.

about 1 $^0/_0$, and it therefore answers all the requirements of such a quantitative method of estimation.

In the course of our experiments we found it a very suitable plan to dissolve the oil in 10 cc. alcohol of 95 to 96 $^0/_0$ by volume, before the water is added. By these means the oil can be divided so minutely, that the aqueous solution in most cases only has a cloudy opalescence, which naturally removes the danger which threatens under ordinary circumstances, namely that the unattacked cinnamic aldehyde may be enveloped by the semi-oxamazone. Under these conditions the precipitate could also in every case be filtered off rapidly, and the results obtained were excellent, so that we can strongly recommend this slight modification.

Hanus' method will be particularly advantageous wherever it is a question of only a small quantity of cinnamon oil, or of a specially exact determination of the aldehyde-content; but for ordinary practice it may be recommended to retain the easier and more readily applied bisulphite method, the more so, as with pure cinnamic aldehyde and cassia oil the results are very satisfactory, — a fact which we were again able to confirm on the occasion of the present experiments.

In the case of the Ceylon cinnamon oils the difference in the results obtained by the two methods was rather considerable (up to 8 $^0/_0$); this is also clear from the examples mentioned in Hanus' work. This difference is very probably due to the presence of the other aldehydes contained in the Ceylon oil. When the percentages by volume obtained by the bisulphite method are converted into percentages by weight the values increase no doubt by 2 $^0/_0$, but in spite of this they still remain 4 to 5 $^0/_0$ below the values according to Hanus.

But the method indicated by Hanus has a further special value, inasmuch as it enables us to ascertain in a convenient manner the aldehyde-content of a cinnamon bark, which up to now was only possible by means of a trial-distillation, and which consequently often gave rise to difficulties.

For this determination, which he has also tested thoroughly as to its usefulness, Hanus gives the following directions: In a large Erlenmeyer flask 5 to 8 grams of finely ground cinnamon are weighed off, and 100 cc. water added. The flask is then closed by means of a rubber stopper with two holes, through which pass a thin glass tube drawn out at the lower end, which serves for admission of the steam, and which reaches almost to the bottom of the flask, and a second shorter tube, bent in the shape of a knee, which forms the connection between the flask and a Liebig's condenser. First of all the flask with the cinnamon is heated to boiling temperature, and only then a powerful stream of water vapour admitted. At this point attention should be paid that the steam admission tube does not become choked up at the bottom. At first the temperature should be raised carefully, as the mixture frequently foams strongly. The distilling is done in a retort which holds up to the mark 400 cc., and it is completed in about 2 hours. The distillate is then extracted with ether three to four times in a separating funnel. The ether extracts are collected together in an Erlenmeyer flask, and the ether driven off on a water bath of 60° to 70°. The further examination takes place in the same manner as mentioned above for cinnamon oil.

Whilst Hanus has the intention of testing his method also for the determination of vanillin and piperonal, we have made experiments to ascertain whether the method is not generally useful for aldehyde and ketone-determinations, and we have for this purpose taken in the first place citral, citronellal, menthone, and carvone. The results thereby obtained were so unsatisfactory, that for the present we have given up further experiments. The determination of ketones by Hanus' method would furthermore not again come under consideration, as their conversion with semi-oxamazide proceeds so slowly, that their application for quantitative determinations is out of the question.

For the purpose of distinguishing between cassia oil and Ceylon cinnamon oil F. Billon[1]) recommends the following reaction: If a few drops of the oil to be examined are strongly shaken with a few cc. water, the emulsion filtered, and a few drops of a 1 per cent. solution of sodium or potassium arsenite added to the filtrate, the liquid will acquire a characteristic green-yellow colour, if the oil is Ceylon cinnamon oil; cassia oil is said not to give this reaction.

When we, however, tried this reaction, we found exactly the reverse to be the case. The filtrate of the Ceylon cinnamon oil remains completely colourless, whilst the filtrate of cassia oil acquires a faint green-yellow colour. This colouration, however, has very little intensity, and we therefore do not recognise this colour-reaction as a distinguishing method between cassia oil and Ceylon cinnamon oil. If it is absolutely desired to make use of a colour-reaction as a means of distinction, the ferric chloride reaction should decidedly be preferred. This reaction is, as is well known, carried out by adding a drop of ferric chloride solution to the alcoholic solution of the oils; this produces in Ceylon cinnamon oil a green, in cassia oil a brown colour. But we think it desirable to dismiss the colour-reactions altogether, as they are not entitled to the importance which is often attached to them. Generally speaking, the odour and the specific gravity should be sufficient indications whether it is a question of cassia oil, or of Ceylon cinnamon oil.

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[1]) Pharm. Ztg. **49** (1904), 107.

Another colour-reaction for cassia oil is recommended by Pool[1]); this one has reference to the test of cassia oil for oil of cloves, by means of Jacquemin's phenol-reaction. According to this, 1 cc. of a dilute aniline solution is decomposed with so much of a solution of sodium hypochlorite, as is required to produce a violet colour in the liquid, and a drop of the cinnamon oil to be examined is then added. The mixture is agitated, diluted with water, and filtered. Pure cassia oil under these conditions is said to give a bright violet filtrate, whilst the latter has a dark green colour if oil of cloves is present.

We scarcely believe that this test has any advantage over the much simpler ferric chloride reaction, which, as is well known, is also mentioned in the German Pharmacopœia, as, in the case of a slight admixture of clove oil, differences of opinion as to the shades of colour are also certain to arise. Once more we can only point out the unreliability of colour-reactions, and for this reason are also unable to recommend the test indicated by Pool.

**Oil of Cassie flowers.** Our examination of the essential oil of cassie flowers, mentioned already in earlier Reports[2]), has meanwhile been continued. As crude material for the oil of *Acacia Farnesiana*, we made use of the Indian cassie pomade met with in commerce. 115 kilos of this pomade were three times extracted with alcohol, the alcohol carefully distilled off from the combined washed extracts, and the essential oil obtained by steam-distillation from the residue which still contained large quantities of fat. The distillation-water, which contained the bulk of the aromatic substance in solution, yielded, on extraction with ether, 315 gm. of a dark-coloured oil. For the purpose of further purification this was next treated with soda solution, when 28 gm. fatty acids (caprinic acid?), probably originating from the fat, and a very small quantity of salicylic acid were obtained. The oil once more rectified with steam was heavier than water, had a bright yellow colour, and a pleasant strong cassie odour. The yield amounted to 197 gm. = 0,171 % of the pomade. The constants were as follows:

$d_{15^\circ} = 1{,}0475$; $\alpha_D \pm 0^\circ$; $n_{D20^\circ} = 1{,}51331$; saponification number = 176.

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[1]) Pharmaceutisch Weekblad **40** (1903), 1101; according to Chem. Centralblatt **1904**, I, 404.

[2]) Report April **1899**, 58; April **1901**, 18; April **1903**, 17; October **1903**, 18. Besides our principal Patent No. 139635 of 17th July 1902, whereby we protected the use of linalool, geraniol, terpineol, ionone, irone, cuminic aldehyde, decylic aldehyde, nonylic aldehyde, and octylic aldehyde, in combination with benzyl alcohol and methyl ester of salicylic acid, for the production of artificial oil of cassie flowers, we have obtained an additional Patent No. 150170 dating from 16th May 1903, which also protects the use of anisic aldehyde, benzaldehyde, eugenol, and eugenol methyl ether, substances which we have lately detected in the oil of acacia flowers. We would here point out that we recently examined an "artificial oil of cassie flowers" met with in commerce, which contained 54 % ethyl alcohol!

180 gm. of this oil were first of all extracted repeatedly at a low temperature with one per cent. soda liquor, and the lye saturated with carbonic acid. The phenols separated off (21 gm.), consisted chiefly of methyl ester of salicylic acid, boiling point 224° to 226°; $d_{15^\circ} = 1,1770$; in addition to this, other higher and lower boiling fractions were obtained. When they were saponified with 10% aqueous potash liquor, a gas with a trimethylamine-like odour was evolved, which coloured litmus blue, and on saturating the lye with carbonic acid, a phenol separated out. This phenol had the odour of cresol; when treated with ferric chloride in alcoholic solution it acquired a brownish-green colour. As the quantity was very small, it was further examined in the following manner. The alkaline solution of the phenol, when treated with dimethyl sulphate, yielded p-cresol methyl ether with its characteristic odour, and this could be converted by oxidation with solution of permanganate into anisic acid of the melting point 180°.

The silver salt of the acid was analysed. 0,1622 gm. yielded after combustion 0,0673 gm. Ag; found 41,49% Ag; calculated for anisic acid 41,70% Ag. It is therefore most probable that the phenol which is present in the essential oil of *Acacia Farnesiana* in addition to methyl ester of salicylic acid already previously detected, is p-cresol. Eugenol, which is present in abundant quantity in the oil of *Acacia Cavenia*, could not be detected, and is in any case but a subordinate constituent of this oil.

After removal of the bulk of the phenols and of the ester of salicylic acid, by treatment with soda liquor, the oil of acacia blossoms distilled at 6 mm pressure from 38° to 140°, chiefly from 70° to 120°. In the lowest-boiling portions benzaldehyde was detected. The semicarbazide compound of the latter melted at 214°. From the fractions boiling between 70° and 80°, at 6 mm, there could be isolated, by means of phthalic acid anhydride, benzyl alcohol: 23,5 gm., boiling point 204° to 206°, at 745 mm; $d_{15^\circ} = 1,0435$; $\alpha_D \pm 0^\circ$; $n_{D20^\circ} = 1,53804$.

For further identification the benzyl phthalic ester acid was produced from this alcohol. 2 gm. of the latter with 2 gm. phthalic acid anhydride and 1 gm. benzene are heated for 2 hours on the water bath; soda solution is then added, and the mixture extracted with ether. When sulphuric acid is added to the extracted soda solution, the ester acid is precipitated in the form of a rapidly congealing oil After recrystallisation of the substance from benzene, the melting point lies at 105° to 106°. When boiled with soda liquor, the benzyl alcohol is regenerated.

Analysis:

0,1732 g of the substance yielded 0,4436 g $CO_2$ and 0,0720 g $H_2O$.

| Calculated for $C_{15}H_{12}O_4$: | found: |
|---|---|
| C 70,28 % | 69,85 % |
| H 4,686 % | 4,608 % |

In the portions not reacting with phthalic acid anhydride, a compound was present which had a characteristic menthone odour. This fraction distilled from 200° to 205°. $d_{15^\circ} = 0{,}9372$; $\alpha_D = -3^\circ 50'$. On treatment with semicarbazide in alcoholic solution, a solid semicarbazone was obtained, which, after repeated recrystallisation from alcohol, melted at 177° to 178°, and which, on being heated with dilute sulphuric acid, split off an oil with a strong menthone odour. Whether it was here a question of menthone, or of an allied ketone, could not be decided, as the quantity of pure substance obtained was insufficient for an analysis. From a fraction boiling from 90° to 105°, at 6 mm, a semicarbazide compound could be obtained, which, after recrystallisation from alcohol, melted indistinctly at 200°, and which on distillation with dilute sulphuric acid split off an oil with an odour of cuminic aldehyde and anisic aldehyde. On oxidation of this oil with dilute solution of potassium permanganate, only anisic acid of the melting point 180° was obtained.

It follows that the presence of anisic aldehyde in the essential oil of *Acacia Farnesiana* has now been proved, whilst the exact determination of cuminic aldehyde has not yet been possible, owing to the apparently exceedingly minute quantity in which it is present as a constituent of this oil.

The examination of the oil of acacia blossoms is being continued.

**Cedar Oil, inspissated for optical purposes.** With regard to this preparation, we would point out that, contrary to all other essential oils, this oil should not be kept in too cool a place, as otherwise it frequently becomes turbid. The turbidity may, however, generally be easily removed by warming the oil.

**Cinnamon Oil, Ceylon.** The prices of the fine brands of cinnamon chips fluctuated during the last half-year between 2 d. and 2 1/4 d., and those of cinnamon oil in the same proportion.

The export of cinnamon chips from Ceylon was: —

| | | |
|---|---|---|
| in | 1903 . . . . | 2 253 269 lbs. |
| against „ | 1902 . . . . | 1 763 679 „ |
| „ | 1901 . . . . | 1 516 083 „ |
| „ | 1900 . . . . | 1 863 406 „ |

In this export, Germany participated in the first place with 687 159 lbs., or more than 30 %. In view of the great increase in the production of all kinds of cinnamon, the present low prices may also be expected to continue in the future.

We have repeatedly mentioned the adulterations to which Ceylon cinnamon oil is subject. The adulterants above all coming under consideration, are oil of cinnamon leaves and cassia oil, or pure cinnamic aldehyde. The physical constants of Ceylon cinnamon oil generally alter but little through the addition of these oils, but the aldehyde-content, on the other hand, is thereby affected in a more or less marked degree.

With our own distillates we have observed that the content of cinnamic aldehyde (determined by the bisulphite method) mostly fluctuates between 70 and 75 %, and only in rare cases the limits are 65 or 77 %. But the addition of oil of cinnamon leaves greatly diminishes the content of cinnamic aldehyde, while raising the eugenol-content which in Ceylon cinnamon oil amounts to only 4 to 8 %. On the other hand, cassia oil, or cinnamic aldehyde, raise the aldehyde-content.

In valuing Ceylon cinnamon oil, this fact should be specially noted, as here of course cinnamic aldehyde is not the constituent which determines the value — as in the case of cassia oil. In Ceylon cinnamon oil just the non-aldehydic constituents are those which are valuable, as they bring about the finer aroma of this oil as compared with cassia oil.

We would once more call attention to this, because, when we recently sounded the market, we came across several Ceylon cinnamon oils (apart from an oil of cinnamon leaves which went by the name of Ceylon cinnamon oil) whose aldehyde-content lay between 80 and 85 %; this can only be explained by the fact that to the oils in question the distinctly cheaper cinnamic aldehyde had purposely been added.

As oils adulterated in such manner may yet come up to the British Pharmacopœia standard, — although this was only the case with a small proportion of the oils referred to, — it is all the more advisable to exercise caution in purchasing Ceylon cinnamon oil.

On this occassion we wish to mention that with our own unobjectionable distillates, we have repeatedly observed lower specific gravities than the British Pharmacopœia allows. Whilst the latter requires for Ceylon cinnamon oil a specific gravity of 1,025 to 1,035 (15,5°), we have had before us on several occasions oils distilled by ourselves of which the specific gravity was 1,023 (15°). In view of the high specific gravity of cinnamic aldehyde on the one hand, and eugenol on the other, these comparatively light Ceylon cinnamon oils offer a guarantee that they are pure distillates, to which neither cassia oil, nor oil of cinnamon leaves has been added. We again call attention to this fact in order to prevent possible claims as far as lies in our power.

**Citronella Oil, Ceylon.** The rise in the value of this eminently important perfume, caused by the conditions affecting the production, and predicted in our last Report, has meanwhile become an established fact. With continued insufficiency of supplies the prices advanced from 9 d. to about 1/1½ per lb., and at present they still stand at about 1/-, a quotation which may possibly remain in force for the future, it having been found that pure oils can absolutely not be supplied at lower prices.

The following statistics show that the export, and accordingly also the production, has fallen off considerably, and has not been so low for many years.

The export was: —

| | | |
|---|---|---|
| in | 1903 | 1 062 594 lbs. |
| against „ | 1902 | 1 294 750 „ |
| „ | 1901 | 1 430 168 „ |
| „ | 1900 | 1 409 050 „ |
| „ | 1899 | 1 478 756 „ |
| „ | 1898 | 1 365 917 „ |
| „ | 1897 | 1 182 867 „ |

It is made up of shipments to the following countries: —

| | |
|---|---|
| United Kingdom | 348 029 lbs. |
| America | 554 689 „ |
| Germany | 96 422 „ |
| Australia | 18 492 „ |
| China | 28 520 „ |
| France | 711 „ |
| Singapore | 5 121 „ |
| India | 10 530 „ |
| Turkey | 80 „ |
| Total | 1 062 594 lbs. |

which is about 23% below that of 1902.

Stocks of any importance exist nowhere, — on the contrary, the demand exceeds the supply. A decline in the prices under these circumstances is inconceivable, nor would it be desirable, as it could only take place at the expense of the quality.

**Citronella Oil, Java.** The distiller working exclusively for our firm has, at our urgent request, increased his production again by about

25 %, and we now hope to be in a position to meet the constantly growing demand. The prevailing difficult local conditions are unfortunately opposed to an actual production on a large scale.

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Supplementing the information contained in our last Report with regard to the character of the adulterant employed in Ceylon, we are now in a position to state that our examinations in this direction made with a very large quantity of citronella oil, have shown that the oil examined by us had been adulterated with petroleum, and not with resin-spirit.

The decisive point in this connection was for us the possibility of detecting metacymol, a substance discovered by Kelbe[1]) in resin-spirit. After repeatedly fractionating the first runnings of citronella oil, the portions boiling between 170° and 180° were finally taken for further examination. 1000 grams of the fraction were in the first place, for the purpose of removing the terpenes, treated in the cold with dilute permanganate solution, until the latter, even after a prolonged period, showed no discolouration.

The oil not attacked was driven over with steam and distilled over sodium so as to remove oxygenated portions. Thus resulted about 30 grams oil of the following constants:

$$d_{15^\circ} = 0{,}8071; \ \alpha_D = -0^\circ 4'; \ n_{D20^\circ} = 1{,}44428.$$

Apart from the fact that these constants do not agree with those given by Kelbe[2]) and Wallach[3]) for metacymol, the oil, when oxidised with permanganate solution at increased temperature, did not yield the oxypropyl benzoic acid characteristic of metacymol.

From these results we must conclude that at least the citronella oil worked up by us had been adulterated with petroleum.

During the frequent controversies regarding the extensive adulteration of Ceylon citronella oil, the value of "Schimmel's test" for judging these oils has repeatedly been discussed. Whilst this method has met with decided recognition on the part of experts, we have frequently heard complaints from the side of merchants about the difficulties with which they have thereby to contend in Ceylon, especially with regard to maintaining the correct temperature required for the observation.

We admit that with the high temperature of the air in Ceylon, it is difficult to maintain a constant temperature of 20° for many hours, and we would point out that a constant temperature for observation is not absolutely necessary, — in fact, it may fluctuate within a few degrees below 20°, which no doubt can be attained without much

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[1]) Liebig's Annalen **210** (1881), 10.

[2]) Loc. cit.

[3]) Liebig's Annalen **275** (1893), 159.

trouble by using an ordinary refrigerator; only, the temperature should not exceed 20°.

Moreover, when the test[1]) is properly carried out, it will but rarely be necessary to observe the solutions for any prolonged time, as in most cases the possible separation of oil occurs either very soon, or immediately. It might also be tried whether these objections cannot be removed by using in Ceylon a slightly weaker alcohol.

Further, Schimmel's test is also blamed for being unreliable, as pure oils are said occasionally not to pass the test, whilst other oils containing up to 15 % petroleum form a clear solution with 80 % alcohol.

The first complaint is certainly without foundation, as really pure Ceylon citronella oils will always pass Schimmel's test. With regard to the oils adulterated with petroleum, our experience is, than even a small admixture of the difficultly soluble American petroleum can be detected by the solubility test, whilst the more readily soluble Russian petroleum[2]) may remain undetected, if it is only a question of slight admixtures — up to at most 10 %. But in order to render Schimmel's test also useful in such cases, we recommend a method which, we are informed, is sometimes employed in Ceylon[3]) in a similar manner. To the oil to be examined, 5 % Russian petroleum is added, and the behaviour of the mixture towards 80 per cent. alcohol is now watched. An oil which originally was pure will under these conditions pass Schimmel's test. By these means we have in many cases detected adulteration, even when it was only slight.

Now Kelway Bamber[4]) has recently published a method, which is said to be more serviceable for judging a citronella oil than Schimmel's test, and which is said to have moreover the advantage that it permits of ascertaining at the same time the quantity of adulterant (insoluble in alcohol) which has been employed. This method is as follows: —

A mixture of exactly 2 cc. pure cocoanut oil free from acids, and 2 cc. of the citronella oil to be examined, is shaken in a suitable graduated glass tube, at 29° to 30°, for one minute, with 20 cc. alcohol of 83 % by weight ($d\frac{30^\circ}{15^\circ} = 0{,}8273$)[5]), and is then centrifuged

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[1]) Comp. in this respect our Report October **1903**, 26, note. In order to avoid all misunderstanding, we would add to what we said there, that even when less than 10 vol. alcohol are added, a separation of oil should not occur.

[2]) According to reports from Ceylon it is said that Russian petroleum now controls the market. Comp. Chemist and Druggist **62** (1903), 630.

[3]) In Ceylon the oil to be examined is mixed with 4 to 6 % petroleum, and the mixture tested for solubility in alcohol of 85 % by volume.

[4]) Proc. Chem. Soc. **19** (1903), 292.

[5]) The Imperial Commission for Standards mentions, on the strength of the formulæ calculated by Mendelejeff, for an alcohol of exactly 83 % by weight,

for $^1/_2$ to 1 minute. Whilst under these conditions, according to Bamber's statements, when pure citronella oil is used, the latter remains in solution, and only the cocoanut oil is separated again quantitatively, there would be, if the citronella oil contained an adulterant insoluble in alcohol, a corresponding increase in the volume of cocoanut oil, from which the quantity of the adulterant could be immediately ascertained. By multiplying with 50, the percentage of the adulterant is found. In order to obtain correct results, it is, according to Bamber, especially necessary to use an alcohol of the strength mentioned by him, viz. 83 % by weight. In doubtful cases he recommends to compare the oil to be examined with an authentic pure oil for its behaviour towards Bamber's test. Bamber does not mention any results of tests whatever.

With the view of forming an opinion on the value of Bamber's method, we have made a number of tests, partly with mixtures of Java citronella oil[1]) and petroleum, and partly with commercial Ceylon citronella oils. As at the same time we wished once more to verify the reliability of Schimmel's test[2]), we have also submitted all the oils to the latter, and for the purpose of greater clearness have summarised the results obtained by both methods in the following tables. When Bamber's test was employed, the alcoholic mixture was in every case centrifuged for 1 minute, corresponding to about 1500 revolutions.

The results obtained show clearly that Bamber's method renders satisfactory services for the qualitative estimation of an oil, and in a few cases also shows an adulteration where the ordinary Schimmel's test fails. With regard to the quantitative estimation of the adulterant, however, the new test is a failure. This must be attributed on the one hand to the more or less ready solubility of the adulterant in the alcohol employed, and on the other, to the fact that with the closely graduated scales slight errors in reading easily occur, which, in consequence of the small quantities of citronella oil used for the estimation, produce fairly large differences in the percentages.

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$d_{15^\circ} = 0{,}84108$; such an alcohol has $d\frac{30^\circ}{15^\circ} = 0{,}8283$. According to the tables referred to, the specific gravity $d\frac{30^\circ}{15^\circ} = 0{,}8273$ mentioned by Bamber, corresponds to an alcohol of 83,39 % by weight.

[1]) As at the present time the commercial Ceylon citronella oils are mostly untrustworthy, we have employed Java oils in the mixtures with petroleum, in order to be more certain. In consequence of the somewhat different composition of these oils, it is possible that the results may vary slightly if an authentic pure Ceylon citronella oil is used, but in our opinion the difference cannot amount to much.

[2]) In some of these cases the "raised Schimmel's test" (test of the oil after adding 5 % Russian petroleum) has been employed.

To this must be added that Bamber's test requires much more exact work than Schimmel's test, and for this reason alone it is already questionable whether in the long run it will be adopted, the more so, as the whole apparatus is also much more complicated.

On the other hand, it is probable that with Bamber's method there will just be an increase in the number of cases in which unadulterated oils are considered objectionable because they do not pass Bamber's test[1]).

Java Citronella oil No. 1.

| | Schimmel's test | Bamber's test | |
|---|---|---|---|
| | | Increase in volume of the cocoanut oil in cc. | in % |
| Pure oil . . . . . . . . . | Passes Schimmel's test even when 5% Russian petroleum is added | — | — |
| with 10% American petroleum | Does not pass Schimmel's test . . | 0,2 | 10 |
| „ 20% „ „ | Does not pass Schimmel's test . . | 0,4 | 20 |
| „ 10% Russian petroleum | Passes Schimmel's test, but passes no longer after 5% Russian petroleum is added . . . . . . | 0,15 | 7,5 |
| „ 20% „ „ | Does not pass Schimmel's test . . | 0,35 | 17,5 |

Three other Java citronella oils showed exactly the same behaviour towards Schimmel's test as the above.

For this reason, we give in the following table only their behaviour towards Bamber's test:

| | Java citronella oil No. 2 | | Java citronella oil No. 3 | | Java citronella oil No. 4 [2]) | |
|---|---|---|---|---|---|---|
| | Bamber's test | | Bamber's test | | Bamber's test | |
| | Increase in volume of the cocoanut oil in cc. | in % | Increase in volume of the cocoanut oil in cc. | in % | Increase in volume of the cocoanut oil in cc. | in % |
| Pure oil . . . . . . . . . | — | — | — | — | 0,1 | 5 |
| with 10% American petroleum | 0,2 | 10 | 0,2 | 10 | 0,3 | 15 |
| „ 20% „ „ | 0,35 | 17,5 | 0,35 | 17,5 | 0,4 | 20 |
| „ 10% Russian petroleum | 0,15 | 7,5 | 0,15 | 7,5 | 0,2 | 10 |
| „ 20% „ „ | 0,25 | 12,5 | 0,3 | 15 | 0,35 | 17,5 |

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[1]) Comp. in the table Java oil No. 4, and Ceylon oils Nos. 1 and 2.

[2]) It should be noted that Bamber's test shows adulteration in the oil to which no petroleum had been added, although it was an authentic pure oil.

## Ceylon Citronella oils.

| | Schimmel's test | Bamber's test | |
|---|---|---|---|
| | | Increase in volume of the cocoanut oil | |
| | | in cc. | in % |
| Ceylon citronella oil No. 1 . . | Passes Schimmel's test even when 5 % Russian petroleum is added | 0,15 | 7,5 |
| " " " No. 2[1] . | Passes Schimmel's test even when 5 % Russian petroleum is added | 0,2 | 10 |
| " " " No. 3 . . | Does not pass Schimmel's test . . | 0,25 | 12,5 |
| " " " No. 4 . . | Passes Schimmel's test, but no longer does so after 5 % Russian petroleum is added . . . . . | 0,35 | 17,5 |
| No. 4 with 5 % Russ. petrol. . | Does not pass Schimmel's test | 0,4 | 20 |
| No. 4 " 10 % " " | | 0,45 | 22,5 |
| No. 4 " 15 % " " | | 0,45 | 22,5 |
| No. 4 " 20 % " " [2] | | 0,5 | 25 |

These examinations have convinced us that the best way of meeting the present-day adulteration of citronella oil with petroleum, is to test the oil in the first place for its solubility in 80 % alcohol (Schimmel's test), and then to repeat the test after adding 5 % Russian petroleum. According to our present experience, the Ceylon citronella oils should in the latter case have about the same solubility as the oil not mixed with petroleum, but the opalescence should be stronger; a separation of oil should, however, not take place in this case.

We will call this method of testing, for the sake of brevity, the "raised Schimmel's test", and will put it in practice from now. We would ask all those who are interested in this question to support as far as possible our efforts to make a clean sweep of the system of adulteration practised in Ceylon.

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Parry and Bennett[3] report on a case of adulteration of citronella oil with alcohol. When this oil was distilled at atmospheric pressure, about 20 % passed over between 82° and 83°; this portion consisted (as was shown by further examination) chiefly of ethyl alcohol. This adulteration is especially remarkable, inasmuch as it cannot be detected either by Schimmel's test, or by the method recommended by Bamber, as these tests only refer to the adulterants insoluble in alcohol.

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[1] Nothing could be said against the Ceylon citronella oils Nos. 1 and 2, even after the most minute examination.

[2] With regard to the adulteration of 17,5 % determined for the original oil, the results in the mixtures should have been: 22,5; 27,5; 32,5; and 37,5 %.

[3] Chemist and Druggist **63** (1903), 1061.

We recommend that in future purchases, adulterants soluble in water (alcohol, acetone, and such like) should also be looked for, by strongly shaking the oil to be examined with an equal volume of water in a graduated tube. In the presence of adulterants soluble in water, a corresponding increase in the layer of water occurs, whilst otherwise no change in the proportions of the volume takes place.

**Clove Oil.** In order to be able to form some opinion on the enormously high quotations of Zanzibar cloves, such as have not been known for many years, and to decide in how far this is due to the failure of the harvest, and how far to speculation, we here reproduce an annual report from the German Consulate at Zanzibar:

In the course of the year 1902/03 ending on 31st August, the total quantity of cloves gathered in Zanzibar came to 112354 bales of 4 frasileh¹) each, or a total weight of 15729560 lbs. This harvest must therefore be considered as the most profuse one among those of the last few years, the latter being 1899/1900 = 8884715 lbs.; 1900/01 = 9486225 lbs.; and 1901/02 = 11510975 lbs. Of the harvest of 1902/03 (and 1901/02) the island of Zanzibar accounts for 6373500 (1384775) lbs., and Pemba for 9356060 (10126200) lbs. It follows that the island of Zanzibar shares in last year's harvest in the ratio of 1 in 1,46, whilst the proportion during the three preceding years was 1 : 3,6, 1 : 5,8, and 1 : 7,3. The cause of this growing increase in the production must be attributed to the fact that on the island of Zanzibar the Government does all in its power to overcome the lack of labour, which is here considerably greater than on the island of Pemba.

The prices obtained for cloves in Zanzibar were in the period September 1902 to May 1903, 6 to 7 rupees per frasileh; they then advanced up to 8 rupees, in view of the expected failure of the harvest, but fell again when the Indian market did not follow suit. In the last few days of September 1903, the demand from India became especially strong, and this caused the price to advance within 2 days up to 17 1/2 rupees, but it fell again to 10 3/8 rupees, only to advance once more briskly in the first few days of October, up to above 14 rupees.

The price of Zanzibar cloves is usually 4 annas²) higher than that of the Pemba cloves, because the former as a rule are better dried and treated with greater care.

The export of cloves from Zanzibar amounted in the year 1902 to 10125769 lbs. value 2957589 rupees, against 11962069 lbs. and 2465373 rupees in the previous year. Of last year's export, 4160485 lbs. value 852006 rupees went to Europe, 412300 lbs. value 88031 rupees to America, 5412143 lbs. value 1091456 rupees to Asia, and 140841 lbs. value 26096 rupees to Africa.

The export to America is shipped exclusively to New York, that to Asia almost exclusively to Bombay. The latter amounted to 4924255 lbs. value 996820 rupees, and the Bombay market consequently drew about one-half of the total exports. This had the effect, that the prices of the European market generally remained firm, in spite of the fairly large harvest of that year. In February 1903 a downward tendency in the quotations became apparent, but it came to an immediate stop when Bombay showed itself capable of taking further deliveries. The exports shipped to Bombay apparently only serve for the Indian home requirements.

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¹) Frasileh = 35 lbs.

²) 1 Rupee = 16 annas.

With regard to the principal European ports, the export of 1902 was made up as follows: to Rotterdam 2 210 420 lbs. value 472 430 rupees, London 1 295 910 lbs. value 253 490 rupees, Hamburg 425 015 lbs. value 78 172 rupees, and Marseilles 188 475 lbs. value 39 214 rupees.

The position of London towards Rotterdam has therefore again become worse. Whilst in the previous year the advantage of Rotterdam amounted to a little over half a million, the difference in 1902 has increased to nearly one million in favour of Rotterdam. The shipments to Hamburg, which up to the previous year had greatly fallen off from year to year, now again show a slight advance. The export to Marseilles is of hardly any consequence.

The exports of clove-stems last year were 2 158 942 lbs. value 106 927 rupees to Europe, and 177 252 lbs. value 9965 rupees to Asia. America has taken no share whatever of the 1902 exports. Of the quantities exported to Europe, the bulk, 1 873 874 lbs. was shipped to Hamburg, 46 200 lbs. to London, 27 300 lbs. to Marseilles, and 201 095 lbs. to Amsterdam. Rotterdam has imported nothing last year, but Amsterdam has taken its place. The principal market of clove-stems is Hamburg.

It is clear from the foregoing Report that the last harvest of cloves, which commenced in September, is considered a failure, but that authentic and unvarnished reports as to the quantity of the crop are not yet available.

It is generally believed to be chiefly due to Indian and European speculators who have jointly started the upward movement. But the artificial structure already commences to tremble, and it is most strongly recommended to exercise the greatest reserve in purchasing cloves and clove oil.

We may here mention from a statistical point of view, that when in the year 1876 a natural phenomenon of unprecedented severity destroyed the clove-plantations, the prices of cloves advanced up to 310 marks per 100 kilos, and those of clove oil up to 24 marks per kilo. It was not until six years later that the plantations had recovered, and during that crisis the quotations moved as follows: —

| | Zanzibar cloves. | Clove oil. |
|---|---|---|
| 1877: | 260 marks per 100 kilos. | 18 marks per kilo. |
| 1878: | 300 „ „ 100 „ | 18 „ „ „ |
| 1879: | 300 „ „ 100 „ | 18 „ „ „ |
| 1880: | 280 „ „ 100 „ | 18 „ „ „ |
| 1881: | 235 „ „ 100 „ | 16 „ „ „ |
| 1882: | 190 „ „ 100 „ | 13 „ „ „ |
| 1883: | 140 „ „ 100 „ | 11 „ „ „ |
| 1884: | 130 „ „ 100 „ | 8 „ „ „ |
| 1885: | 110 „ „ 100 „ | 7 „ „ „ |
| 1886: | 120 „ „ 100 „ | 7.50 „ „ „ |

In 1891 the situation again became more normal, and the fluctuations were only unimportant until the autumn of last year, when from Holland operations were conducted at high pressure to bring about an advance. The cheapest quotation for prompt in the terminal market, in August last year, was 19$^3/_4$ florins, the highest in February and April of this year, 46$^1/_2$ florins per 50 kilos.

Under these conditions it is a difficult matter for the manufacturers of clove oil always to hit the right mark in the quotations given in the price-lists, and it is necessary, in purchasing larger quantities, to fix the price of the day by an exchange of telegrams. Assisted by large stocks bought at favourable prices, we have been able to help many of our clients through the crisis, and it will always be our endeavour to maintain our leading position in this important article.

Taking into consideration the fact that eugenol also occurs in the form of esters in oil of cloves, Thoms, in a lengthy treatise on the valuation of clove oil[1]), in which he again advocates the usefulness of his method of eugenol-determination, mentions inter alia a modification of this method, which renders it possible to ascertain the total esterified eugenol in oil of cloves, which could not be done by the original method.

The modification consists of this, that the clove oil (5 gm.) serving for the eugenol-determination, is previously saponified in a beaker with 20 gm. 15 % soda-lye, by half-an-hour's heating on a water bath, and the eugenol sodium solution is separated from the sesquiterpenes before the benzoyl chloride is added. For this purpose the contents of the beaker, while still warm, are placed in a small separating funnel with a short delivery tube, and after separating the two layers of liquid the eugenol sodium solution is returned to the beaker. The residual sesquiterpenes are twice more washed each time with 5 cc. 15 % soda liquor, and the lyes combined with the eugenol sodium solution. To this is now added the necessary quantity benzoyl chloride (6 gm.) and the whole shaken, when conversion takes place with a considerable rise in temperature. The last portions of unattacked benzoyl chloride are destroyed by heating for a short time on the water bath, and the process is continued in the usual manner[2]).

Thoms also proceeds in a slightly different manner with regard to the estimation of the free eugenol contained in oil of cloves, and he gives the following directions therefor:

5 gm. oil of cloves are dissolved in 20 gm. ether, and this solution quickly extracted in a separating funnel with 20 gm. 15 % soda liquor. The eugenol sodium solution is then placed in a beaker; the ether containing the sesquiterpenes is again washed twice, each time with 5 gm. soda liquor of the same strength; the combined alkaline solutions

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[1]) Archiv der Pharmacie **241** (1903), 592.

[2]) Comp. Gildemeister and Hoffmann, "The Volatile Oils" p. 516.

are gently heated on a water bath for the purpose of driving off the dissolved ether, and the liquid is then benzoylised in the usual manner.

By these means it is possible to ascertain both the free eugenol in clove oil, and that present in the form of ester.

The modification in his method mentioned by Thoms appears advantageous in so far, as by these means the sesquiterpenes, which occasionally act in a disturbing manner, are previously removed. By this modification Thoms succeeded in obtaining satisfactory results, even with mixtures of a low eugenol-content (below 70 %), whilst under ordinary conditions, according to Thoms' own experiments, this was only possible with oils of high-percentage.

**Coriander Oil.** The situation with regard to this article is extraordinary. In Thuringia the oldest sources of supply have failed completely. The merchants there are now even obtaining supplies from Morocco, but unfortunately that quality is not suitable for distillation on account of its low oil-content. The production in that country has increased largely. The exports from Casablanca amounted in 1902: —

| | | | | | |
|---|---|---|---|---|---|
| To Germany | 453 000 | kilos, | value | 54 360 | marks |
| „ the United Kingdom | 393 000 | „ | „ | 44 620 | „ |
| „ France | 342 750 | „ | „ | 41 129 | „ |
| „ Italy | 2 000 | „ | „ | 240 | „ |
| „ Portugal | 28 474 | „ | „ | 3 555 | „ |
| „ Spain | 42 500 | „ | „ | 4 800 | „ |
| Total: | 1 261 724 | kilos, | value | 148 704 | marks. |

As compared with 1901, they show an increase of about 30 %.

Moravia and Hungary helped to supply the required coriander for the distillation of oil, and sufficient quantities could finally be obtained, although only at very high prices.

**Cypress Oil.** In the year 1892 Dr. J. M. Bravo strongly recommended in the Revista medica de Chile[1]) the use of cypress oil against whooping-cough. As the result of repeated enquiries, we were led, in 1894[2]), to manufacture and introduce into commerce the oil which up to that time could not be obtained anywhere. Although we subsequently repeatedly recommended the use of this oil in our Reports, as we constantly heard its excellent effect highly praised, it would appear that, with a few rare exceptions, it is very seldom prescribed by physicians. For this reason it was a source of great pleasure to hear that Professor Dr. Soltmann, director of the hospital for children at Leipzig, was prepared to test the value of this oil on a large scale in his excellently equipped institution.

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[1]) Abstract in the Deutsche Medizinalzeitung **13** (1892), 45.

[2]) Report October **1894**, 70, and April **1895**, 22.

The exceptionally favourable results of this trial have recently been published[1]), and we reproduce the following abstract from this interesting work[2]): —

The experiments extended over 19 cases in which children suffering from whooping cough were treated with the remedy in this manner, that an alcoholic solution of cypress oil, in the proportion of 1 part oil to 4 parts alcohol, was 4 times daily sprinkled on the coverlet, pillow and underclothing of the children.

Every individual case was studied in detail from beginning to end. Without selection, all the children, as they were admitted, both the older and younger ones, mostly in the transition from stage 1 into the paroxysmal stage, were treated in the same manner; not one was passed over or afterwards omitted. The patients were all placed in the detached ward for whooping-cough patients of the division for infectious diseases of the hospital for children, in which children who were suffering from other affections were under no circumstances admitted. In every case the number of paroxysms during 24 hours was marked daily by means of lines on the diagram; these were marked with control-numbers and specially entered, when at the same time the duration and severity of the paroxysm, the duration of the free intervals, and all other details were noted.

It would lead us too far to mention in this place the individual history of each case described in detail, and for these particulars we must refer to the original. It is a remarkable fact that whenever and wherever the use of the oil was temporarily discontinued, the symptoms of the disease increased. At the end of his work, Soltmann summarises his experience with cypress oil and says word for word: —

> "In all cases of whooping-cough, both in older and younger children, cypress oil reduces the number ot paroxysms promptly and rapidly. It diminishes their intensity, shortens their extensity, prolongs the free intervals, removes the enfeebling after-effect of the paroxysm and single attack. No injurious action on the gastro-intestinal canal, respiratory tract, nervous system, heart, or kidney has been observed; on the contrary, the complications which have arisen from these are rendered less intense, or are partly removed, and their occurence is generally prevented; it therefore shapes the whole course of the disease into a mild form. These favourable effects are specially noticeable in this, that choking and vomiting either do not occur, or rapidly disappear if they were present at the commencement of the treatment. Symptoms of suffocation disappeared rapidly in every case; the cyanotic redness in the face, the distention of the veins of the neck, the œdema of the face, became unimportant; ecchymosis and bleeding from the nose did not occur; and after a short time no complaints were heard about pains in the epigastrium and at the sides of the

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[1]) Keuchhusten und Cypressenöl, by Professor Dr. O. Soltmann, Leipzig, March 1904.

[2]) We shall be pleased to place reprints at the disposal of those who are interested in the matter.

thorax. Finally, control-tests, where the application of oil was purposely suddenly discontinued, showed almost regularly an increase in the number and intensity of the attacks. The treatment which was then again taken up was responded to by a renewed decrease of the attacks. The individual paroxysm frequently ended with one single attack, i. e. the "reprise" remained absent, or only one or two feeble night-attacks occurred. On the whole, the period of the second (paroxysmal) stage of whooping-cough appeared under this treatment to be shortened in a marked degree, although this is very difficult to judge in view of the great fluctuations of this period in individual cases. I do not feel justified in assuming that the total duration of the disease is shortened; at least, the medicament had very little or no influence on the slight and more "catarrhal" attacks of coughing of the third stage.

But the fact that the patients — including the younger ones, — had suffered very little constitutionally in the course of the disease, even with a severe commencement of the whooping-cough, was specially noticeable, as compared with previous observations, not only by their healthy appearance, but also by the fact that almost all the children could be dismissed in a good state of nutrition. During the weighing, which was continued with regularity, considerable increases in weight were observed, so much so, that the difference between the weights of the patients when admitted and when dismissed showed from $^1/_2$ to 2 lbs. even up to 4 lbs. in favour of the latter, as will be seen from the reported histories of the individual cases. Loss of weight could only be recorded in two cases which had been admitted with severe complications, and of which one died.

How the cypress oil acts, and to which constituents the favourable action is due, are questions which still remain to be solved. Further examinations respecting the constitution of the oil are necessary, and are now being carried on in the laboratory of Messrs. Schimmel & Co.

If further trials by others should confirm my favourable results (as I believe will be the case), — whereby it would be desirable to work under as nearly as possible the same conditions, — and if cypress oil should then become the common property of practical physicians against a disease which is propagated so extensively by the spread of infection-bearers capable of reproduction, and in which the mortality of the younger generation is so considerable, but where long years of suffering are still more frequently the consequences, — then my modest contribution would not have been without value, and its purpose would have been accomplished."

The examination referred to above has meanwhile been carried out by us, and we are able to report on it as follows. Up to now, only d-pinene and cypress camphor had been detected in cypress oil. On further examination we found in it, in addition to these, some other interesting bodies. The oil worked up had the following constants: $d_{15^\circ} = 0{,}8922$; $\alpha_D = + 16^\circ 5'$; $n_{D20^\circ} = 1{,}47416$. Saponification number 25,3. Saponification number after acetylisation 50,5. These values correspond to a content of 8,8 % of esters $C_{10}H_{17}OCOCH_3$, and 7 % of alcohols $C_{10}H_{18}O$. The oil did not make a clear solution with 10 parts 90 % alcohol. The examination commenced with a distillation of 2 kilos oil in vacuo.

Furfurol. The first drops passed over at 44° (10 mm pressure), and with a solution of aniline hydrochlorate in aniline gave the purple colouration which is characteristic of furfurol.

d-Pinene. In order to confirm our previously reported[1]) detection of d-pinene, we have once more identified this terpene in portions which had all the properties of pinene. The constants were: $d_{15^\circ} = 0{,}8587$; $\alpha_D = + 28^\circ 4'$. The nitroso chloride formed melted at 102° to 103°, its benzylamine derivative at 122° to 123°.

d-Camphene. This hydrocarbon could be detected, by means of the isoborneol-reaction, in all fractions distilling between 160° and 170°, representing the bulk of the oil. From this it may be concluded that camphene must be reckoned among the principal constituents of the oil. A fraction boiling at 161° to 162° ($d_{15^\circ} = 0{,}8606$, $\alpha_D = + 28^\circ 50'$) was fairly rich in camphene. The crude isoborneol formed from the isobornyl acetate on saponification, possessed a peculiar, powerful, musty odour, which was possibly due to a slight admixture of isofenchyl alcohol. This renders it not improbable that cypress oil also contains fenchene, which on treatment with glacial acetic acid and sulphuric acid (analogous to camphene) yields isofenchyl alcohol. The last-named body could not be isolated as such. The isoborneol purified several times from petroleum ether, and sublimed, melted at 206° to 207°. It is of course well-known that considerable quantities of this compound are required in order to bring the melting point by repeated recrystallisation from petroleum ether to 212°. In this case we were satisfied with the melting point mentioned above.

Reactions for limonene, dipentene, and phellandrene, made by us with the portions of the oil boiling between 170° and 180°, gave negative results.

d-Sylvestrene. This terpene had hitherto only been discovered in a few essential oils; it appears to be present in cypress oil in fairly large quantities. We detected the hydrocarbon, by means of its dihydrochloride, in fractions which after rectification over sodium had the following physical properties:

| | | | |
|---|---|---|---|
| Boiling point | 172° to 175° | 175° to 179° | 179° to 181°. |
| $d_{15^\circ} =$ | 0,8592 | 0,8558 | 0,8567 |
| $\alpha_D =$ | $+ 22^\circ 21'$ | $+ 20^\circ 35'$ | $+ 20^\circ 16'$ |

The melting point of the dihydrochloride purified from alcohol lay at 72°. The sylvestrene regenerated from this compound by heating with sodium acetate and glacial acetic acid, boiled chiefly at 180° to 184°. (Owing to scarceness of material the constants could not be determined). The terpene had a pleasant and very characteristic odour. Dissolved in acetic acid anhydride, it showed a wonderful blue colouration when a drop of concentrated sulphuric acid was added. It was difficult to obtain the tetrabromide from the pure sylvestrene, as oily products occurred on brominating. But these congealed partly after prolonged

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[1]) Report October **1894**, 71.

standing in winter cold. The bromide recrystallised from acetic ether, formed flat, colourless prisms of the melting point 134° to 135°.

Cymene. This body is present in cypress oil only in small quantity. It was isolated from a portion boiling from 174° to 180°. The terpenes, of which a large admixture was present, were decomposed by oxidation with one per cent. chameleon-solution at ordinary temperature. The cymene, which was thereby not attacked, was abstracted from the oxidation-liquid by steam distillation. It distilled at 175° to 177°, but still showed a dextrorotation of 3°; $d_{15^\circ} = 0{,}8590$. Oxidation with 5 % permanganate solution yielded p-oxyisopropyl benzoic acid of the melting point 155° to 156°. Boiling with concentrated hydrochloric acid effected its conversion into propenyl benzoic acid of the melting point 160° to 161°.

Ketone. The fraction boiling at 80° to 90° (3 to 4 mm pressure) contains a ketone with a peculiar odour, reminding both of menthone and of thujone. We isolated the ketone from this fraction in the form of its semicarbazone, melting distinctly at 177° to 178°. It does not appear to be a mixture of two bodies. When mixed with synthetic menthone semicarbazone, the melting point falls to 163° to 164°. The quantity of the substance was not sufficient for further identification. We hope later-on to be able to report on a second ketone which is chiefly present in the portions of the above-mentioned boiling point.

Sabinol (?). We believe to have detected this alcohol, which had up to now only been found by E. Fromm[1]) in savin oil, in a fraction of cypress oil distilling between 70° and 85° (3 to 4 mm pressure). We are as yet unable to decide whether the alcohol as such, or in the form of its ester, occurs as a constituent of cypress oil, as the oil which we had under examination for its detection had been saponified with alcoholic potash. Unfortunately sabinol does not form a phenyl urethane, which would provide a more certain and readier means of identification than the present conversion into $\alpha$-tanacetogene dicarbonic acid. The alcohol isolated by us was characterised by its high specific gravity, which amounted to 0,9433. The optical rotation was $+ 14° 8'$. It distilled in vacuo between 70° and 74°, at ordinary pressure at 208° to 212° (i. e. almost corresponding to sabinol). We endeavoured to prove its identity with sabinol by the oxidation into $\alpha$-tanacetogene dicarbonic acid. We also obtained a mixture of an acid which did not yet melt at 250°, with one melting between 130° to 140°. On the strength of these results, we feel justified in stating that the presence of sabinol in cypress oil is probable.

Terpene alcohol. On treating an oil boiling at 90° to 95°, in a solution of benzene, at the temperature of the wather bath, with

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[1]) Berliner Berichte **31** (1898), 2025.

phthalic acid anhydride, we obtained a few drops of an alcohol which had a very pleasant odour like roses. With the small quantity at disposal, a phenyl urethane could not be obtained. On further examination it may possibly be found to be a terpene alcohol (geraniol, citronellol).

Esters. The saponification number of the original oil already shows that the oil contains small quantities of esters. Especially the fractions boiling above 95° (3 to 4 mm pressure) were fairly rich in esters. We determined the saponification number of an oil of the melting point 96° to 98° (4 mm pressure) obtained by repeated fractionating, at 191,0, corresponding to an ester-content of 66,85% $C_{10}H_{17}OCOCH_3$. Saponification with alcoholic potash yielded d-terpineol of the melting point 35°. Specific gravity of the compound purified from alcohol: 0,938; optical rotation: at 22° + 18° 16′ (50 mm). The terpinyl phenyl urethane melted at 112°. Of acids, we isolated from the individual ester-fractions, acetic acid and valeric acid. Nothing definite can as yet be said with regard to the proportion of these two acids in the detected alcohols, as, for the purpose of more convenient working up, we combined and fractionated small quantities of the individual acids. But it is very probable, judging at least from the pungent odour of the acid, that terpineol is present in cypress oil as acetic acid ester. The principal fraction of the mixture of acids boiling at 115° to 140°, could be recognised by its odour as acetic acid. This was also proved by the analysis of the silver salt, which, however, no doubt contained an admixture of small quantities of silver valerianate:

0,2374 g of the substance yielded 0,1501 g Ag
0,2016 g „ „ „ „ 0,1273 g „

| | Found: | Calculated for $C_2H_3AgO_2$: |
|---|---|---|
| Ag | 1. 63,23 % | 64,67 % |
| | 2. 63,19 % | |

The second acid, distilling between 140° and 210°, could be identified by the odour and the analysis of the recrystallised silver salt, as valeric acid:

0,2408 g of the substance yielded 0,1237 g Ag

| | Found: | Calculated for $C_5H_{11}AgO_2$: |
|---|---|---|
| Ag | 51,37 % | 51,67 % |

A third acid, boiling at 210° at 260°, was obtained in the form of long, silky needles melting at 129°.

No free terpineol was found in cypress oil. We are at present still occupied with the portions of the oil passing over above 114° (3 to 4 mm pressure), in which the cypress camphor must be looked for. It follows from the above examination, that cypress oil contains about 65% terpenes, of which the bulk consists of camphene and sylvestrene. Cymene is represented by 1 to 2%, alcohols by about 8%, esters, especially of terpineol, by about 8%. Ketones are only present in fractions of 1%, and about 15% constitutes cypress camphor.

## Essential Oils, Sicilian and Calabrian.

Mr. Eduardo Jacob, German Consul at Messina, has this year, with his usual courtesy, again kindly supplied us with the following report, for which we beg to express to him, also in this place, our most sincere thanks.

The report shows that the export of essential oils of last year has fallen behind that of the previous year by 220557 kilos or 3229599 lire, i. e. by about 20% (see tables on pages 43 and 44). This is readily explained by the abnormally high export figures of 1902, and further by the fact that the summer, both in the Old World and in the New, has been very cold and rainy, and therefore very unfavourable for the consumption of lemon oil. At the same time, it should be noted that the demand from abroad, in spite of the heavy export of 1086497 kilos in the year 1902, during the year under review accounts for no less than 864940 kilos, i. e. the largest quantity exported during any of the last 10 years — with the exception of the year 1902.

A more convincing proof of the constantly increasing world-consumption of Sicilian essential oils can scarcely be produced; and the same is confirmed by the comparative figures of the last five years, and of the five years immediately preceding. Whereas during the period 1894 to 1898 an average annual export of 626876 kilos or 8540731 lire has taken place, the figures for the period 1899 to 1903 have grown to an average of 870162 kilos or 12234757 lire, and the exports during the months December, January and February of the present year again show an increase as compared with those of the same months of the previous season, as will be seen from the following summary: —

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1902 | December | 73440 | kilos | 1903 | December | 83356 | kilos |
| 1903 | January | 95975 | „ | 1904 | January | 105877 | „ |
| 1903 | February | 97646 | „ | 1904 | February | 98897 | „ |

By far the largest share of the increase in the exports naturally falls to the article lemon oil.

The physico-chemical constants of the various citrus oils during this season have shown no variations worth mentioning; oil of bitter orange alone has from first to last shown an exceptionally low rotatory power. The majority of the oils has not exceeded the rotation of 89°, and parcels with a higher rotatory power are quite exceptional.

## Export of Essential Oils.

| | in 1902 | | in 1903 | |
|---|---|---|---|---|
| | Kilos | Lire | Kilos | Lire |
| | **a) from Messina** | | | |
| to North German Ports . . | 21 773 | 304 822 | 23 740 | 332 360 |
| ,, Austria-Hungary . . . . | 75 280 | 1 053 920 | 79 111 | 1 107 554 |
| ,, Belgium . . . . . . . . | 2 225 | 31 150 | 2 844 | 39 816 |
| ,, Denmark . . . . . . . | 3 085 | 43 190 | 2 317 | 32 438 |
| ,, France . . . . . . . . | 43 609 | 610 526 | 40 272 | 563 808 |
| ,, Greece . . . . . . . . | 704 | 9 856 | 464 | 6 496 |
| ,, The United Kingdom . . | 235 108 | 3 291 512 | 198 782 | 2 782 948 |
| ,, Holland . . . . . . . | 8 345 | 116 830 | 9 937 | 139 118 |
| ,, Russia . . . . . . . . | 10 631 | 148 834 | 9 808 | 137 312 |
| ,, Scandinavia . . . . . | 7 308 | 102 312 | 7 844 | 109 816 |
| ,, Spain & Portugal . . . | 1 721 | 24 094 | 4 324 | 60 536 |
| ,, Turkey . . . . . . . . | 1 726 | 24 164 | 1 672 | 23 408 |
| ,, The United States . . . | 436 566 | 6 111 924 | 294 368 | 4 121 152 |
| ,, South America . . . . | — | — | 585 | 8 190 |
| ,, Australia . . . . . . . | 39 749 | 556 486 | 40 923 | 572 922 |
| ,, Egypt . . . . . . . . | 1 672 | 23 408 | 1 238 | 17 332 |
| ,, India . . . . . . . . | 1 330 | 18 620 | 3 992 | 55 888 |
| ,, Malta . . . . . . . . | — | — | 495 | 6 930 |
| ,, Other countries incl. Italy . | 12 487 | 174 818 | 17 266 | 241 724 |
| Total | 903 319 | 12 646 466 | 740 152 | 10 362 268 |
| | **b) from Reggio** | | | |
| to North German Ports . . | 3 804 | 53 256 | 1 527 | 21 475 |
| ,, Austria-Hungary . . . . | 31 062 | 434 868 | 24 808 | 347 310 |
| ,, France . . . . . . . . | 32 459 | 454 426 | 17 164 | 240 300 |
| ,, The United Kingdom . . | 24 032 | 336 448 | 20 953 | 293 342 |
| ,, Holland . . . . . . . . | 1 745 | 24 430 | 2 591 | 37 274 |
| ,, The United States . . . | 31 388 | 439 432 | 20 010 | 280 140 |
| ,, Other countries . . . . | 835 | 11 690 | 1 975 | 27 650 |
| Total | 125 325 | 1 754 550 | 89 028 | 1 247 491 |
| | **c) from Catania** | | | |
| to North German Ports . . | — | — | 20 | 200 |
| ,, Austria . . . . . . . . | 2 761 | 37 394 | 2 083 | 20 830 |
| ,, The United Kingdom . . | 1 715 | 24 010 | 445 | 4 450 |
| ,, Other countries . . . . | 52 | 728 | 28 | 280 |
| Total | 4 438 | 62 132 | 2 576 | 25 760 |
| | **d) from Palermo** | | | |
| to North German Ports . . | 20 | 280 | 43 | 430 |
| ,, Austria . . . . . . . . | 7 433 | 104 062 | 6 081 | 60 810 |
| ,, France . . . . . . . . | 2 970 | 41 580 | 3 057 | 30 570 |
| ,, The United Kingdom . . | 31 535 | 441 490 | 16 350 | 163 500 |
| ,, The United States . . . | 9 049 | 126 686 | 4 920 | 49 200 |
| ,, Other countries . . . . | 1 408 | 19 712 | 2 733 | 27 330 |
| Total | 52 415 | 733 810 | 33 184 | 331 840 |

Total Exports:

| | in 1902 | | in 1903 | |
|---|---|---|---|---|
| | Kilos | Lire | Kilos | Lire |
| From Messina . . . . . | 903 319 | 12 646 466 | 740 152 | 10 362 268 |
| „ Reggio . . . . . . | 125 325 | 1 754 550 | 89028 | 1 247 491 |
| „ Catania . . . . . . | 4 438 | 62 132 | 2 576 | 25 760 |
| „ Palermo . . . . . | 52415 | 733 810 | 33 184 | 331 840 |
| Grand Total | 1 085 497 | 15 196 958 | 864 940 | 11 967 359 |
| i. e. in 1903 . . . . . . | 220557 | 3 229 599 | less than in 1902. | |

Table of Exports during the last ten years:

| | Kilos | Lire | | Kilos | Lire |
|---|---|---|---|---|---|
| 1903 | 864 940 | 11 967 359 | 1898 | 667 293 | 9 015 083 |
| 1902 | 1 085 497 | 15 196 958 | 1897 | 732 092 | 9 719 133 |
| 1901 | 820 982 | 12 314 730 | 1896 | 514 067 | 7 579 424 |
| 1900 | 842 246 | 10 972 295 | 1895 | 554 191 | 8 081 870 |
| 1899 | 797 145 | 10 722 445 | 1894 | 666 740 | 8 308 148 |
| | 4 350 810 | 61 173 787 | | 3 134 383 | 42 703 658 |

| | |
|---|---|
| Average figures:<br>870 162 kilos<br>12 234 757 lire | Average figures:<br>626 876 kilos<br>8 540 731 lire |

With regard to the individual kinds of essences, we have to state, in continuation of our Report of october 1903, that the situation of the **Bergamot Oil** market has not developed during the last few months of 1903 in the manner which had been expected.

In view of the anticipations of a rich new harvest, and of the attitude of expectation assumed by buyers abroad in consequence of the original high prices, the article had in September fallen from 19 to 15 marks. Whilst the general expectation was that the prices would continue to decline down to the time of the new harvest, and very low prices for new oil were also discounted, there came in October, in a most surprising manner, a brisk demand from abroad, which not only forced up the prices of old oil by several marks, but also completely absorbed the not unimportant stocks, and left the market absolutely denuded of oil.

If by these purchases the requirements of the foreign markets had been covered for some months to come, it might just have been possible that the new oil, on being placed upon the market, would have found no buyers, and that new stocks had accumulated, which in face of the good harvest and the rich oil-content of the fruit would undoubtedly have depressed the prices. But this expectation also was not realised; with the high prices ruling during the summer, the foreign requirements had not been covered until the very last moment, so that the stocks of old oil were no longer sufficient, and the first new oil, in spite of its low ester-content, at once found purchasers at high prices. It is only due to the cool-headed behaviour of the exporters in this town, and to the patience of the large firms abroad, that during December of last year and January 1904 a sharp rise in the prices of the article was averted. But in spite of this, it has not been possible to avoid considerable losses to most exporters in the settlement of the liabilities, — especially to those who had made contracts for export at low prices on speculation. Only in the course of February stocks have again accumulated; this has exerted a pressure on the market and on the quotations, and has depressed the prices to a level which is proportionate to the rich result of the present season's manufacture.

Bergamot oil with higher degrees of ester was this year about four weeks late and the lack of this oil has rendered the return to normal prices much more difficult.

The prospects regarding the further development of this article will chiefly be influenced by the hope which may be entertained for the coming harvest, but, in a secondary degree, also by the more or less large demand from abroad during the next few months. The winter has been mild, and the atmospheric conditions have been favourable rather than injurious to the trees. Although after the last large harvesst it would not be wise to reckon on an equally large one for the coming season, there yet appear to be signs that the development of the blossoms will be middling, and that for the present a bad harvest need not be feared.

A return to higher prices does not seem probable, so long as purchases from abroad are conducted quietly and sensibly; on the other hand, cheaper prices than at present can hardly be expected, as to all appearances the foreign buyers are not yet abundantly provided with bergamot oil.

**Lemon Oil.** Since the price of this article has dropped to such an extent, it becomes more and more difficult to make even an approximate forecast of the probable fluctuations of the quotations in the course of one season, as the very fact of the low value of the oil imparts a considerable importance even to small fluctuations of 0,25 to 0,50 mark.

It may be said that during the last two years the quotations in one season have shown no greater difference in price than 0,50 mark per kilo, and it can be readily understood that with an article of such universal consumption, which is moreover only a by-product, such fluctuations cannot be calculated beforehand.

The present harvest appears on the whole to turn out somewhat smaller than that of the previous year, but an estimate of the harvest has lately become more difficult than before, as during the last decade large areas which were previously devoted only to agriculture, have since then been converted into luxuriant fruit-tracts, and the lemon tree has frequently been cultivated successfully even in districts situated some 1000 or 1200 feet above sea-level. These new plantations yield a quantity of fruit increasing from year to year which equalises the loss due to the dying trees, and which can be estimated correctly only with great difficulty.

But taking all in all, the present harvest does not appear to come quite up to the last one, and as at the end of last season the stocks of old oil left over were considerably lower than those of the same period last year, the assumption seemed justified that the article in the course of the season would rather fetch higher than lower prices.

In spite of the financial weakness of the manufacturers, who for three years had experienced nothing but failures and losses, the article has maintained its position until the warlike events in the Far East began to exert a strong depression on the world's money markets, which found here an immediate and powerful response, inasmuch as the trade in lemons in cases declined from day, and, as regards Russia, even ceased almost entirely.

In consequence of the large drop in the prices of the lemons, a quantity of fruit has become available for the manufacture of oil which had not been reckoned upon before. This has also had a weakening effect, during the last ten days of February, on the quotations of lemon oil, which have declined by about 5 %.

This movement has been supported by continued spot sales of a large export firm, which by all accounts is said to be engaged at low prices for large quantities for shipment abroad, and which, while endeavouring to force the market down still further by the spot sales, at the same time depresses the disposition towards this article abroad by offers at absurdly low prices.

At the same time, a further downward movement seems hardly possible, for the prices have now reached a level at which the manufacture can scarcely pay.

For this reason the future of the article is not unfavourable, unless indeed the political situation in Europe should also become complicated.

Stocks of any importance are at present not in existence, as the manufacturers have not been sufficiently strong financially to hold back part of their production, and as the heavy shipments abroad have not afforded an opportunity to the export trade to accumulate stocks. True, the manufacture is at this moment still in full swing; but if the export of lemon oil should continue at the same brisk rate during the next few months, there is no prospect during this season of an accumulation of such large stocks as was the case last year, — a factor which may be of importance in view of the annual increase of the world's consumption.

## The citral-determination of lemon oil.

The question regarding the citral-content of lemon oil, to which we have already referred in our last Report (page 34), has led to some further publications with which we will deal briefly in the following pages.

Bertè[1]), who had stated already before Gulli and Stavenhagen that lemon oil contains about 6,5 % citral, again takes this matter up, and strongly advocates the use of the estimation-method published by him in conjunction with Soldaini, a process which we have already discussed in previous Reports, and of which we have there also given a detailed description[2]).

Parry[3]), against this, maintains his previous statements that lemon oil contains at most 3 % citral, and points out that otherwise the citral-content of terpeneless oils would be decidedly higher.

Kremers and Brandel[4]) also discuss this subject. Their work is of special interest, inasmuch as it supplies a very noticeable contribution to the history of all methods for citral-determination recommended up to the present. We have dealt with the individual processes already in our Reports, in some cases in great detail, with the exception of the one which has been published quite recently by Sadtler, and to which we return further down. We can therefore refer in this connection to our previous publications and also to Kremers and Brandel's work. But the authors also mention their own experiments on this subject; they have carried out citral-determinations partly by the bisulphite method, and partly by the method recommended by Sadtler, in which in the one case a 5 % solution of citral in limonene was used, and in the other a natural lemon oil.

The bisulphite method recommended by Kremers and Brandel is as follows:

5 cc oil are placed in a cassia flask and 25 cc sodium bisulphite solution (30 %) added, and the mixture maintained on the water-bath at a temperature of 60° for half an hour, with frequent shaking. It is then left to cool, after wich distilled water is gradually added up to the mark, the mixture being each time shaken. The content of percentage by volume is then determined in the usual manner.

The results thereby obtained by Kremers and Brandel agree well in some respects, but the limits thus obtained differ by 3 to 4 %;

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[1]) Chemist and Druggist **63** (1903), 752.

[2]) Report April **1897,** 18; **1900,** 22.

[3]) Chemist and Druggist **63** (1903), 820.

[4]) Pharm. Review **22** (1904), 15, 72.

in view of the low citral-content of lemon oil this difference is very marked and renders the practical utility of the process very doubtful. In the lemon oil examined, a citral-content of 4 to 4,5% was determined.

Determinations recently again made by us by Berté's and also by Kremers' method with mixtures of known citral-content led to no better result than our previous experiments; for this reason we are still sceptical about such a process for the estimation of citral in lemon oil. We are all the more doubtful about the reliability of the method, as, in view of the low citral-content of lemon oils, added to the small quantity of only 5 cc oil employed, the possibility of errors appears altogether too great.

Now Sadtler has recently recommended a method of estimating the aldehyde[1]), which is based upon the fact observed by Tiemann, that when citral is shaken with a neutral solution of sodium sulphite, citral dihydrosulphonic acid is formed with simultaneous splitting off of sodium hydrate:

$$C_9H_{15}CHO + 2Na_2SO_3 + 2H_2O = C_9H_{17}(SO_3Na)_2CHO + 2NaOH.$$

By titrating with semi-normal hydrochloric acid the quantity of liberated sodium hydroxide is determined, and from this the citral-content calculated. The process is carried out as follows:

5 to 10 gm. lemon oil in an Erlenmeyer flask, after neutralising the free acid with semi-normal potash liquor, are mixed with 5 times the quantity of a 20% solution of sodium sulphite which has previously been neutralised, at the temperature of the water-bath, with semi-normal hydrochloric acid, whereby rosolic acid is used as indicator. The mixture is heated in the boiling water-bath, with frequent shaking, and the sodium hydroxide formed during the reaction is from time neutralised with semi-normal hydrochloric acid. The reaction is completed as soon as the solution remains neutral, which is the case in about half an hour. From the quantity of hydrochloric acid used up, the quantity of liberated sodium hydroxide is ascertained, and from this the citral-content. If $a$ represents the number of cc semi-normal acid consumed, and $s$ the quantity of oil employed, in grams, the percentage of citral is calculated by means of the following formula:

$$\frac{3{,}8 \cdot a}{s}.$$

Sadtler mentions in his work only four analyses by way of evidence; Kremers and Brandel have made a whole number of determinations in putting this method to the test. In every case the result obtained was most satisfactory; in 16 determinations the extreme difference was only once as high as 0,8%, but generally the difference observed did not exceed 0,3%.

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[1]) Americ. Journ. Pharm. **76** (1904), 84.

In lemon oil Sadtler determined by this method a citral-content of 5,25 %, whilst Kremers and Brandel only found 4,2 % on the average. But in this connection it should be noted that in both cases the determinations were made with only one lemon oil each.

The method is said to be applicable not only for fatty but also for aromatic aldehydes. When putting it to the test, we, however, encountered various difficulties, — in the first place with regard to the final reaction, the clearness of which leaves something to be desired. In neutralising with semi-normal acid the soda liquor split off, the original red colouration caused by rosolic acid very gradually changes into a pink of increasing brightness, and it is difficult to decide which shade has to be considered as decisive for the completion of the reaction. But the titration must not be continued up to the stage when the solution has become colourless, as in such case results are obtained which are too high by several per cent.

We have also observed that the titration must not in any case be carried on at an elevated temperature, as, in consequence of the strong dissociation of the sodium sulphite which then takes place, the solution always acquires a very vivid red colour, which has nothing to do with the actual reaction. For this reason the solution heated on the water-bath was each time cooled by us previous to the neutralisation of the sodium hydroxide split off. Even after the reaction has long been completed, the liquid, for the reason stated, again acquires a vivid red colour when it is heated.

In spite of the negative results obtained up to the present, we do not as yet wish to pronounce a definite opinion on Sadtler's method of citral-determination; on the contrary, we will make this dependent upon further detailed tests. We will return to this matter in our next Report.

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The *Revue des Cultures coloniales*[1]) contains a short study respecting the working up of lemons for the essential oil, juice, citric acid, citrate and peel, as it is carried on in Sicily and Calabria. In view of the great importance of this industry for the above-named districts, the cultivation of lemons is warmly recommended for the French Possessions in Indo-China, and calculations are presented which are intended to demonstrate how this might become a flourishing industry for Cochin China. If the value of 1 kilo lemon oil is taken as 10 francs, a hectare (about 2 ½ acres) covered with 300 trees of which each yields 75 kilos fruit per year, would produce 2250 kilos fruit, representing a value of 2025 francs. We would point out in this connection, that the author must have been badly informed with regard to the low level of the

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[1]) Revue des Cultures coloniales **14** (1904), 54.

prices which are at present paid for lemon oil and the other products. For this reason, it is necessary to caution against the opening up of new districts of production for the above-mentioned articles.

**Mandarin Oil.** The harvest of mandarins this year can only be called feeble, and if, in spite of this, the season commenced with low prices for this article, this must be attributed to the fact that the development of the fruit had been impeded by the long-continued drought of the summer, and the fruit thus remained small and unsuitable for export in cases. For this reason the fruit had to be used up for the manufacture of oil. The small harvest has, however, already made itself felt, and during the last few weeks mandarin oil has fetched higher prices, which will probably improve still further in the course of the next few months.

E. Charabot and G. Laloue[1]) have supplied a fresh contribution to the study of the production and distribution of organic substances in the plant[2]) during its period of development, a study which was commenced with the geranium plant (*Pelargonium odoratissimum*). The present examination deals with the formation of the essential oil, and especially of methyl ester of methyl anthranilic acid, in the leaves and stalks of the mandarin tree. It was found that the formation of the essential oil in the leaves takes place most strongly while they are young, and that the leaves are richer in oil than the stalks. At a later stage the content of terpene-compounds present in addition to the methyl anthranilic acid ester becomes lower in the leaves, but the terpene-content increases in the stalks.

It appears, as a matter of fact, that during the vegetation the constituents soluble in water (methyl anthranilic acid ester) become richer in the leaves, but that the opposite takes place in the stalks.

**Orange Oil, sweet.** The quantity of this oil produced during the present season is probably about equal to last year's production. In Sicily, where the conditions were favourable, more oil has been obtained than in the previous year, but Calabria shows a falling-off as compared with the last harvest.

The prices of new oil commenced at 11,75 marks, but soon afterwards a slow rise in the value took place, which in the last weeks of December degenerated into an advance by leaps and bounds, by which the article was driven up to 14,50 marks. If these high prices have not led to an important increase in the production, this must be due in the first place to the low content of oil of this season's fruit, and

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[1]) Compt. rend. **137** (1903), 996. Bull. Soc. chim. III. **31** (1904), 195.

[2]) Compt. rend. **136** (1903), 1467. Report October **1903**, 40.

secondly to the greater facility with which the damaged fruit, by means of the reduced railway rates, could be placed on the Upper-Italian and even on the Swiss and German markets.

At the same time, the high prices have brought about a certain increase in the production and a reactionary movement downwards, which, however, has come to an end at the present quotation, and which in all probability will soon again make place for higher prices.

The stocks of this oil at disposal amount at most to 7000 kilos, and the Sicilian market must be considered as practically exhausted.

**Orange Oil, bitter.** This oil has only been produced in very small quantities, as the fruit gave an exceptionally low yield. For this reason the prices have advanced right from the commencement to the unusual level of 15 marks. In the course of the summer the quotations of this article will probably advance still further.

**Eucalyptus Oil.** There has lately been on the market an excellent selection of oils rich in eucalyptol, among which the Australian product ranked first. The production in Portugal has also increased considerably, but Algeria is no longer able to compete. For example, of a contract for 10000 kilos which we had made with a French distiller, only a small part could be executed.

In commerce, eucalyptol has gained the upper hand, and its cheap price may possibly lead to a gradual displacement of the ordinary oil. The fact that it has been possible to create with little expenditure such a perfect product, may truly be called a triumph of technical science. When comparing the quotations, the constants of the pure body should be taken into consideration. Our eucalyptol has a melting point of $-1^\circ$, and is optically inactive.

In the last runnings of a distillation of the oil of *Eucalyptus globulus,* we observed crystals which were freed from the adhering oil by pressing them on a tile, and by recrystallisation from 70 per cent. alcohol were obtained in the form of brilliant, almost odourless needles of the melting point 88,5°. The boiling point was determined at 283° (755 mm), and the specific rotatory power $[\alpha]_D - 35^\circ 29'$ ascertained in 12 per cent. chloroform solution.

Analysis:

0,0946 gm. of the substance yielded 0,2808 gm. $CO_2$ and 0,1032 gm. $H_2O$.

| | Found: | Calculated for $C_{15}H_{25}OH$: |
|---|---|---|
| C: | 80,95 % | 80,99 % |
| H: | 12,12 % | 11,81 % |

In view of these results the compound must be considered as a sesquiterpene alcohol.

For further identification an attempt was made to acetylise the alcohol by means of acetic acid anhydride, but the reaction-product only showed a content of 5 % ester, which was not submitted to further examination. The bulk of the alcohol had passed over into a hydrocarbon, with loss of water. 90 per cent. formic acid is most suitable for splitting off water. 100 gm. sesquiterpene alcohol each were heated to boiling point with three times the quantity formic acid, well shaken up, and after cooling mixed with water. The layer of oil removed from the liquid was freed from resinous impurities by steam-distillation, and then fractionated at atmospheric pressure. It was then found that we had before us a mixture of dextrorotatory and lævorotatory hydrocarbons. By very frequently repeated fractional distillation, partly in vacuo, partly at ordinary pressure, it was possible to separate two isomeric sesquiterpenes, which, after treatment with aqueous alkali, and distillation over metallic sodium, showed the following physical constants:

### I. l-Sesquiterpene.

Boiling point 102° to 103° (6 mm); 247° to 248° (748 mm); $\alpha_D = -55^\circ 48'$.

$n_{D20^\circ} = 1{,}49287$; $d_{15^\circ} = 0{,}8956$. MR = 65,96 (calculated for $C_{15}H_{24} = 66{,}15$).

Elementary analysis gave the following results:

0,0934 gm. of the substance yielded 0,3014 gm. $CO_2$ and 0,1000 gm. $H_2O$.

| | Found: | Calculated for $C_{15}H_{24}$: |
|---|---|---|
| C: | 88,0 % | 88,13 % |
| H: | 11,89 % | 11,86 % |

### II. d-Sesquiterpene.

Boiling point: 265,5° to 266° (750 mm); $\alpha_D = +58^\circ 40'$; $n_{D20^\circ} = 1{,}50602$; $d_{15^\circ} = 0{,}9236$.

On combustion 0,0712 gm. of the substance yielded 0,2300 gm. $CO_2$ and 0,0758 gm. $H_2O$.

| | Found: | Calculated for $C_{15}H_{24}$: |
|---|---|---|
| C: | 88,10 % | 88,13 % |
| H: | 11,8 % | 11,86 % |

With the use of other agents splitting off water, such as sulphuric acid and phosphorus pentoxide, both hydrocarbons were again obtained, though in varying proportions.

The above-described sesquiterpene alcohol, and also the two sesquiterpenes derived from it, do not correspond in their physical constants with any of the hitherto-known isomers. The further identification of the two new sesquiterpenes by means of a crystalline derivative, unfortunately did not succeed.

By hydratation of the terpenes of the oil of *Eucalyptus globulus*, Bouchardat and Tardy¹) had obtained terpineol, isoborneol, and fenchyl alcohol. We have made the same experiments with a terpene-fraction of the same oil (boiling point 154° to 159°; $\alpha_D = + 37°$), and have been able to confirm on the whole the observations made by Bouchardat and Tardy, — but up to the present we have not succeeded in obtaining fenchyl alcohol by heating a terpene-fraction of the boiling point 155° with benzoic acid to 150°. The high rotatory power of the individual terpene-fractions ($\alpha_D = 37°$ to 39°) is probably not a characteristic feature of the pinene, but on the contrary due to an admixture of camphene, which latter could also be readily detected in the fractions boiling about 155°.

In the portions boiling about 130°, Bouchardat and Oliviero²) have detected amyl alcohol, without, however, deciding whether it was a question of normal or of isoamyl alcohol. By the purification process usual for primary alcohols, we obtained, by means of calcium chloride, amyl alcohol of the constant boiling point 131°, which formed with carbanil a urethane of the melting point 52° to 53°. As the urethane of the technical amyl alcohol possesses the same melting point, and as a mixture of the two did not lower the melting point, it is here clearly a case of isoamyl alcohol. When the portions boiling about 140°, which showed the saponification number 38, were freed from terpenes by oxidation with permanganate in the cold, the remaining oil possessed distinctly the characteristic odour of amyl acetate; unfortunately the quantity available was too small for a chemical demonstration of the presence of the latter.

It is of course well known, from the numerous observations which have now been made for a long time chiefly in the Roman Campagna, (also in Algeria and the United States), that the eucalypts possess in a high degree the property of drying up marshy districts, and that they therefore indirectly provide active means for the reclamation of the land, and for combating malaria. From this property of the tree it had been assumed that in a corresponding degree the leaves would

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¹) Compt. rend. **120** (1895), 1417.

²) Bull. Soc. chim. III. **9** (1893), 429.

show a comparatively high exhalation. Recent experiments by Griffon[1]) have proved the error of this assumption; according to these, the exhalation of the eucalyptus leaves, as compared with that of our indigenous trees, especially the willow, birch, and ash, is twice to three times less powerful. For this reason the draining action of the eucalyptus tree, which has even given rise to the name "fever tree", must doubtless be attributed chiefly to the property of producing in a very short time an abundant foliage.

**Fennel Oil.** The distillation of this oil has been carried on by us in the present season on a large scale and with the most satisfactory result, as the export of fennel was dependent upon both Galicia and Roumania and these two countries competed with each other. At the same time the price of fennel oil came higher, and had to be raised several times.

The indigenous fennel from the Lützen and Weissenfels districts was this season again of no importance for the oil-distillation.

**Geranium Oil.** In Algeria the exceptionally abundant rainfall has had a beneficial effect on the geranium-cultivations, and the growers show an accommodating disposition. The distillate from the first crop is usually ready for shipment in May to June, that of the second crop at the end of August. Very fine qualities are expected this year.

In Réunion the cultivation of geraniums has again increased considerably, and the distillation now appears to be carried on during the greater part of the year, for the shipments do not come to an end. The steamer "Djemnah" which recently arrived at Marseilles, brought no less than 83 cases, or about 2000 kilos.

These facts do not agree very well with the animating reports which have now been issued from Marseilles, and according to which a rise in the quotations was to be expected. In the middle of April a cyclone has wasted the island to such an extent that the production of oil has since been interrupted.

With regard to the East Indian geranium or so-called palmarosa oil, the conditions mentioned in our last Report still prevail. The producing districts have been extended so largely, that it is very difficult to arrive at a proper estimate of the market, and it is an extremely difficult matter whether to advise buying at the present low prices, or not. In our opinion we are face to face with a large overproduction.

Ordinary gingergrass oil is exactly in the same position. Never before has this oil been on the market in such fine quality as at present, a fact to which we desire to call special attention.

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[1]) Compt. rend. **138** (1904), 157.

Shipments at Bombay of East Indian Geranium oils from Jan. 1st to Dec. 31st 1903.

| | |
|---|---|
| to The United Kingdom | 13016 lbs. |
| „ France | 56091 „ |
| „ Germany | 25901 „ |
| „ The United States | 8000 „ |
| „ Turkey | 250 „ |
| „ Egypt | 22337 „ |
| Total | 125595 lbs. |

We have added to the knowledge of Réunion geranium oil by an examination of the constituents boiling lower than citronellol and geraniol. For this purpose we used the first runnings of 30 kilos geranium oil, which had been collected in five fractions of 1 kilo each. By far the largest part consisted of menthone (which had already been found by Flatau and Labbé[1]), and of linalool, whose presence had been suspected by those authors but which they had been unable to prove with certainty. The alcohol could not be separated from the menthone by fractional distillation, but it was accomplished very easily and rapidly by oximating the menthone, and subsequently separating it by steam distillation. The bulk of the oxime then remained in the distillation-residue; it solidified after some time in crystalline form, and after suitable purification melted at 58° to 59°. The alcohol distilled of boiled at 68° to 70° (5 mm) and at 198° to 200° (760 mm), and had the following physical constants: $d_{15°} = 0{,}872$; $n_{D20°} = 1{,}4619$; $\alpha_D = -1° 40'$. With carbanil we obtained the linalyl phenyl urethane of the melting point 65° to 66° first produced by Walbaum and Hüthig, and we finally identified the linalool also by oxidation into citral (melting point of the citrylidene-$\beta$-naphtho cinchoninic acid 197° to 200°).

The lower boiling portions, amounting only to about 30 gm., were carefully fractionated. The fraction of the boiling point 100° to 140° had the unmistakable cough-inducing odour of amyl alcohol. The phenyl urethane melted at 41° to 43°; for this reason it cannot have been the ordinary isoamyl alcohol whose phenyl urethane melts at 52° to 53°. The quantity available was not sufficient for a more detailed examination. The next fraction, which boiled at 155° to 162°, had the following physical constants: $d_{15°} = 0{,}854$; $\alpha_D = -19° 11'$. By means of amyl nitrite and hydrochloric acid, the pinene nitrosochloride melting at 102° was obtained, which was identified as such by its benzylamine compound of the melting point 122° to 123°.

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[1] Bull. Soc. chim. III. **19** (1898), 788.

The portions boiling slightly higher (60° to 70° at 6 mm pressure) gave a feeble phellandrene-reaction. The quantity of phellandrene nitrite obtained was too small for the necessary purification by recrystallisation from acetic ether. It consequently melted already at 114° to 115°, after recrystallisation from a mixture of acetic ether and alcohol. But to all appearances it is here a question of the nitrite of the melting point 120° to 121°.

By the foregoing examination, amyl alcohol, pinene, phellandrene, and linalool have been detected in addition to the already previously known constituents of geranium oil (geraniol, citronellol, menthone, tiglinic acid, fatty acids, and a paraffin of the melting point 63°).

In a short treatise on "Rose geranium oil and its substitutes", Lyman F. Kebler[1] calls attention to the difficulties connected occasionally with the valuation on the more expensive geranium oils, when they are adulterated with the cheaper East Indian oils. Kebler mentions for example the results of the examinations of a series of geranium, palmarosa, and gingergrass oils, from which it appears that the oils had partly been greatly adulterated. The nature of the adulterants used though, does not appear at first glance from the data given.

In the course of last year we have repeatedly observed that palmarosa oil is sometimes added to geranium oils, and we quite agree with Kebler's opinion as to the difficulties of detecting such adulteration.

Gingergrass Oil is considered an inferior kind of palmarosa oil, and up to the present it was found in commerce nearly always adulterated. A thorough chemical examination of this oil, whose mother-plant is as little known as the actual place where it is produced, has not been made. In literature we only find a short communication by E. Gildemeister and K. Stephan[2] on a genuine gingergrass oil, whose constants were as follows: $d_{15^\circ} = 0{,}897$; $\alpha_D = -2^\circ 8'$; the oil was soluble in 70 % alcohol. They found that the oil — contrary to palmarosa oil — gave a feeble phellandrene-reaction with sodium nitrite and glacial acetic acid. We have lately received several consignments of this oil which made the impression of being genuine; at least, adulterations such as used to be frequently met with, could not be detected.

The oil had the following constants: $d_{15^\circ} = 0{,}9380$; $\alpha_D = +22^\circ 40'$; saponification number 24; saponification number after acetylisation 166. One part dissolved in 2,3 parts 70 % alcohol; when more alcohol

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[1] Adulterated Drugs and Chemicals. U. S. Department of Agriculture, Washington 1904.

[2] Archiv der Pharm. **234** (1896), 326.

was added, the solution became slightly cloudy. The oil gave no phellandrene-reaction. At 5 to 6 mm pressure it distilled over from 50° to 100°. The ester number and the saponification number after acetylisation show that the oil contains abundant quantities of an alcoholic constituent, but on the other hand, but little ester. In order to obtain the alcoholic constituent, the oil was first saponified and then distilled in vacuo. At 4 to 5 mm pressure it passed over between 48° to 103°. In the portions boiling up to 80°, phellandrene could be detected. Its boiling point, at 4 mm pressure, lay at 44° to 45°; at 754 mm pressure, at 175° to 176°; $d_{15^\circ} = 0{,}8565$; $\alpha_D = + 44^\circ 40'$.

Treatment with sodium nitrite and glacial acetic acid yielded a very small quantity of phellandrene nitrite melting at 120°.

The bulk of the saponified oil distilled at 10 mm pressure about 106°, had the specific gravity 0,950 at 15°, and consisted of a mixture of geraniol and an as yet unknown alcohol with a peculiar odour reminding of linalool. Attempts to produce this alcohol absolutely free from geraniol have not yet succeeded, as the boiling points of these two bodies lie close together. When acetylised with acetic acid anhydride, the new alcohol forms an acetate of a characteristic spearmint odour. This acetate shows the following constants: boiling point 90° to 91°, at 4 mm; $d_{15^\circ} = 0{,}9725$; $\alpha_D = - 4^\circ 30'$; $n_{D20^\circ} = 1{,}47615$; ester number 282. Ester-content 98,70 %, calculated for $C_{10}H_{17}O \cdot CO \cdot CH_3$, or 97,71 % calculated for $C_{10}H_{15}O \cdot CO \cdot CH_3$. By saponification the unknown alcohol was again obtained from this acetate. The constants were as follows: boiling point 92° to 93° at 5 mm; $d_{15^\circ} = 0{,}9503$; $\alpha_D = + 8^\circ 40'$; $n_{D20^\circ} = 1{,}49735$. After distilling once more, the specific gravity had been raised to $d_{15^\circ} = 0{,}9520$, whilst the boiling point had altered but little. According to the analysis, the alcohol appears to have the composition $C_{10}H_{16}O$.

Analysis:

0,2262 gm. yielded 0,6484 gm. $CO_2$ and 0,2126 gm. $H_2O$.

| | Calculated for $C_{10}H_{16}O$: | Found: |
|---|---|---|
| C | 78,84 % | 78,18 % |
| H | 10,64 % | 10,44 % |

The oxidation-products of the alcohol have not yet been examined. With phenyl isocyanate, a liquid phenyl urethane was obtained.

In order to separate the whole of the alcoholic constituents of the gingergrass oil from the non-alcoholic constituents, the following process was adopted:

400 gm. of the portion of the saponified oil boiling between 98° and 112° at 9 mm pressure, were mixed with 200 gm. benzene and 200 gm. pyridine, and 350 gm. benzoyl chloride slowly added

whilst the mixture was stirred. The benzoic acid esters of the alcohols thus formed, were, after adding soda, distilled off with steam, in order to remove those parts which had not entered into reaction. At 4 mm pressure the benzoic acid esters distilled between 160° and 165°, and on saponification they formed a mixture of alcohols of the boiling point 95° to 100° (at 4 mm pressure) and a specific gravity of 0,9212, at 15°. This mixture could be decomposed into geraniol and the unknown alcohol, both by treatment with calcium chloride, and with phthalic acid anhydride.

The geraniol thus obtained distilled at 229° to 230°, at atmospheric pressure, and was further identified by conversion into its diphenyl urethane of the melting point 82°, and by oxidation into citral (melting point of the $\beta$-citryl naphthocinchoninic acid 197°). The alcohol separated from the geraniol, which did not react with calcium chloride, and reacted only incompletely with phthalic acid anhydride, approximately corresponded in its constants with the one obtained by saponification of the acetic ester: boiling point 94° to 95°, at 5 mm; $d_{15^\circ} = 0{,}951$; $\alpha_D = +13^\circ 46'$; $n_{D 20^\circ} = 1{,}49582$. The optical rotation alone had increased considerably. In a dry ethereal solution the alcohol absorbed 2 atoms bromine, calculated for the formula $C_{10}H_{16}O$. The bromide was a colourless, viscid oil. With diphenylcarbamine chloride and pyridine no crystallising product was obtained.

The acids obtained on saponification of the ginger-grass oil were purified by conversion into the calcium salts. The mixture of acids separated from this, distilled from 220° to 300°, and solidified after some time. The crystals collected were obtained after recrystallisation from petroleum ether, in the form of fine leaflets of the melting point 106° to 107°, and formed a silver salt soluble with great difficulty in alcohol and water, whose silver-content was found as 38,90 %.

Analysis: 0,3912 gm. contained 0,1520 gm. Ag = 38,90 %.

P. Jeancard and C. Satie¹) publish the results obtained by comparative studies made during the last three years on the effect of the weather-conditions on the constitution of the essential oil of the geranium plant *(Pelargonium odoratissimum)*. According to these, cold nights reduce the alcohol-content, without equalising this reduction by a more abundant formation of ester, as is the case with neroli and petitgrain oils. This is equivalent to a decrease in the quantity of oil present in the leaves. From this it also follows, that the content of the terpene alcohols geraniol and citronellol varies; with regard to the specific gravity, the geraniol-content decreases, whilst the content of citronellol increases. The physical constants are only subject to slight

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¹) Bull. Soc. chim. III. **31** (1904), 43.

fluctuations. The specific gravity varies between 0,8968 and 0,8990, the optical rotation between — 8,50°, and — 9,44°. Solubility, viscosity and acid number show only very small differences. The saponification numbers in the different years fluctuated between 46,9 and 56,7. These correspond to a content of esterified alcohol of from 12,3 to 14,8 %. The lowest saponification number after acetylation was 217 (corresponding to a content of 71,28 % of total alcohols); — the highest was 228,2 (corresponding to a content of 75,6 %). The citronellol-content fluctuates between 37,09 and 40,0 %.

**Oil of Geum urbanum.** According to examinations by Bourquelot and Herrisey[1]), the essential oil of *Geum urbanum* contains eugenol; this body, however, does not occur in the plant as such, but is only formed by the action of a ferment on a glucoside, when the cut-up fresh plant is macerated for twelve hours and then distilled. From an alcoholic extract of the root, an odourless aqueous solution can be obtained. If to this a ferment is added, the odour of clove oil is immediately formed. Emulsin, though, does not produce the odour even after two days, nor does yeast from beer destroy the glucoside.

**Oil of Guaiac-wood.** The scarcity of this oil has thrown a striking light on the important part which it plays in the perfumery industry. Meantime sufficient consignments of wood from South America came in and we are now again able to meet any demand.

**Hop Oil.** Based upon the present prices of hop, the pure distillate would come to about 450 marks, a price at which it will not be easy to find purchasers. It is to be hoped that the new harvest will make it possible to provide a cheap equivalent.

**Jasmine "Schimmel & Co."** Although the number of jasmine oils which are now met with in commerce has grown considerably in the course of time, they all (as far as we have tested them) differ so considerably in point of quality from our original product, which was the first placed on the market, that they cannot be looked upon as products competing with our oil.

For this reason we are unable to enter into a competition in prices, and in future, as before, we will follow our own way in the composition, as well as in the quotation.

**Oil of Laurel leaves.** The essential oil of laurel leaves has been submitted to an examination by Br. Molle[2]). From the oil diluted with ether, he separated, by extraction with 2 % soda solution, free acids volatile with water vapour, which were identified, by conversion into their silver salts, as acetic acid, isovalerianic acid, and

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[1]) Journ. pharm. chim. VI. **18** (1903), 369.

[2]) On the composition of the essential oil of laurel and the knowledge of its principal constituent, cineol. Inaugural Thesis, Basle.

isobutyric acid. Eugenol, already detected by us in laurel oil on a previous occasion[1]), was also found by Molle in the oil examined by him, and that in quantities of 1,7 % as free eugenol, and 0,4 % as esterified eugenol. The author was unable to detect the presence of aldehydes and ketones in the subject of his examination. By saponifying the oil from which the free acids and phenols had been removed with alcoholic potash liquor, the acids originally present in the form of esters were converted into their potassium salts, and from these were produced compounds of the acids capable of analysis. Acetic acid was detected with certainty; in addition to this, valerianic and caproic acids are probably present in the form of their esters, in an approximate mixture-proportion of 40 % valerianic and 60 % caproic acid. In addition to these acids, he also isolated 0,07 % of a monobasic solid acid $C_{10}H_{14}O_2$ whose melting point lay at 146° to 147°. This acid was strongly attacked by potassium permanganate; of bromine it absorbed two atoms. This last acid is probably not present in the original oil, but is only formed when the oil is treated with alcoholic potash liquor. Presumably a genetic relationship may exist between this acid and camphene. Pinene, which Wallach[2]) had already discovered in laurel oil, could only be detected by Molle when he used oil for the reaction, which had not yet been treated with alkali. On fractional distillation of the oil freed from acids and phenols, cineol was found in the portions passing over from 170° to 180°, which represent about 50 % of the oil. This had also been established previously by Wallach. Molle was unable to detect methyl chavicol whose presence was suspected in the portions boiling above 180°. The fraction passing over from 212° to 230° contained geraniol, which was identified as such by oxidation into citral and conversion into citryl-β-naphthocinchoninic acid. From the same fraction, terpinene $C_{10}H_{16}$ could be obtained by splitting off water, and terpin hydrate by treatment with dilute sulphuric acid. In the high-boiling portions of laurel oil there may possibly be present, in addition to sesquiterpenes, also sesquiterpene alcohols, but no characteristic derivatives of such could be obtained.

Experiments made on the occasion of this examination with regard to the reduction of cineol, showed that for this purpose only hydriodic acid was useful. Molle obtained the best results by one hour's heating to 220° to 225°, in a sealed tube, with metallic mercury as the iodine-binding agent, when a hydrocarbon $C_{10}H_{18}$, named "cineolene", and a polymeric hydrocarbon $(C_{10}H_{16})_n$ were formed. Cineolene boils at 165° to 170°, is optically inactive, and has the specific gravity 0,8240 at 18°; $n_D = 1,45993$. This body does not absorb bromine; if it is attempted

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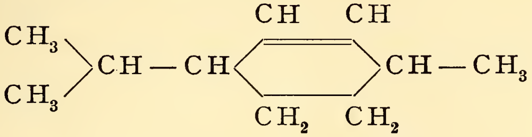
[1]) Report April **1899**, 31.

[2]) Liebig's Annalen **252** (1889), 95.

to attach the latter, hydrobromic acid is split off. When sulphuric acid is allowed to act on cineolene, α-2-cymene sulphoacid is formed, which was identified by its barium salt. Molle believes that the following formula may be given to cineolene:



**Lavender Oil.** The purchases during the last season were a source of great difficulty, as there were more buyers than sellers. It is also due to this fact that the producers were able to carry through their exaggerated demands for the first parcels, for the total result of the crop did not justify the high prices. At the present time the bulk of the production of finest oils is lying in the cellars of middlemen, and only lately some fine parcels passed from the producers into our possession, which enables us to reduce somewhat our prices. On the other hand, some large parcels of medium qualities with 25 % ester and a strong suspicion of spike oil are on the market, which may be sold below the value if an opportunity arises.

In continuation of our previously[1]) published work on French lavender oil, we wish to mention that the acid obtained by saponification from the portions boiling at 155° to 172°, has been found to be butyric acid[2]).

Analysis of the silver salt: 0,2464 gm. of the substance left behind 0,1355 gm. Ag.

Found: Calculated for $C_4H_7AgO_2$:
Ag 54,99 %. 55,38 %.

The alcohol contained in the neutral saponification-products had the distinct odour of isoamyl alcohol, but, unfortunately, could not be identified further.

Umney[3]) calls attention to the fact that some English lavender oils met with in commerce do not answer the requirements of the British Pharmacopœia of 1898. He believes that the cause of this must be found in the method of manufacture, as for example in Mitcham it is usual to collect the lavender distillates in two portions, whilst experience has shown that the last portions of the distillate do not possess such a pleasant odour as the first. For this reason, many

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[1]) Report April **1903**, 45; Report October **1903**, 43.
[2]) Journ. f. prakt. Chemie **45** (1892), 593.
[3]) Chemist and Druggist **63** (1903), 825.

English oils are not normal distillates, but only fractions, whose specific gravity in many cases is below 0,885.

Observations made during the last three years with oils produced at Mitcham by submitting 1 1/2 tons freshly cut lavender with 1200 gallons water to distillation, led to the result that the first portion of distillate, which was separated after three hours' distillation, differs slightly from the portions subsequently passing over. The freshly distilled first portion seldom possesses the specific gravity required by the British Pharmacopœia, and has a lower ester-content than the second distillate, which, in spite of its somewhat higher ester-content, has a less agreeable odour than the portions passing over first. But the specific gravity of the latter, after keeping them for two to three years, had increased from 0,881 to 0,885 or 0,886. Contrary to these oils, an oil destilled from fresh lavender from another district, which had been collected without separating, during an observation-period of five years constantly answered the requirements of the British Pharmacopœia. It appears to Umney that the nature of the soil and the situation of the producing districts have a distinct influence upon the characters of lavender oil, as oil distilled in precisely the same manner in the Warlingham district had a higher specific gravity than oil from Mitcham lavender. In conclusion, Umney considers the minimum specific gravity limit of 0,883, conjointly with the other characters, as sufficient to ensure practically an unsophisticated oil.

**Linaloe Oil.** Up to the present, demand and supply have approximately been equal. The trade is now chiefly in the hands of a few firms in Mexico and Puebla, who are said to have difficulties in obtaining supplies, as the oil is distilled by Indians with whom intercourse is said to be difficult. The present state of the market is firm, with an upward tendency.

We estimate the annual production at about 20000 kilos. From 1901 to 1902 the exports from Mexico were 14000 kilos, value 37046 silver dollars.

**Oil of Monodora myristica.** The seed of *Monodora myristica* Dunal, which is highly valued by the aborigines of the West Coast of Africa as a spice and medicine, contains in addition to fat an essential oil, on which Thoms[1]) reports more in detail. On distillation with steam under pressure, the yield of oil amounts to about 7 %. The oil has a yellow colour, shows a greenish-yellow fluorescence, has a very pleasant odour, and the specific gravity 0,896 at 20°. The specific rotation amounts to — 64,96°. The oil, from which the free acids and the phenols (present in very small quantity) had been

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[1]) Berichte der deutsch. pharm. Ges. **14** (1904), 24.

removed, was fractionated in vacuo. The terpene fraction had the specific gravity 0,842 at 20°, and consisted chiefly of limonene; boiling point 74° to 76° at 16 mm, $\alpha_D = -105{,}68°$, and $[\alpha]_D = -125{,}5°$, melting point of the nitrosochloride 103° to 105°. In the third fraction, which represents 20% of the oil, and which boils at 110° to 116° (at 16 mm), a body $C_{10}H_{16}O$ could be detected, which is probably identic with myristicol.

We ourselves distilled the oil of *Monodora myristica* Dunal about a year ago, when a yield of 5,37% was obtained. The constants of the oil were $d_{15°} = 0{,}859$; $\alpha_D = -117°\,40'$; acid number = 1,36; ester number = 3,4; ester number after acetylation 27,11. Soluble in about 4 volumes and more 90% alcohol.

It consisted chiefly of phellandrene. The melting point of the nitrite recrystallised from acetic ether, was found at 114° to 115°.

**Mustard Oil, artificial.** Our participation in the competition in this article has reduced the value considerably. The cost at which we can produce it enables us to supply it to our clients on the most advantageous terms.

The method for the quantitative estimation of mustard oil given in the German Pharmacopœia, has been tested by R. Firbas[1]), who found that the decomposition of the thiosinamine silver compound is not fully accomplished within 24 hours in the cold. By applying heat, he obtained values which were higher in proportion to the period during which the substance had been heated, but he leaves it an open question whether the increase in the values may not be partly due to the constituents of mustard oil (such as carbon disulphide) which become decomposable only at a higher temperature and by a prolonged application of heat.

According to examinations made by Schlicht[2]), the methods hitherto employed for the estimation of mustard oil in mustard seed, which have also been adopted by the German Pharmacopœia IV. Ed., are not sufficiently exact, as for the development of the total mustard oil, a digestion or maceration of two hours is not sufficient, and on distillation a small quantity of mustard oil adheres to the condenser, which consequently is lost for the estimation. Schlicht therefore recommends the following method: The powdered seed (25 gm.) is first of all digested with water for four hours at the temperature of the room; the mixture is then heated to boiling point, and maintained at

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[1]) Apotheker-Zeitung **19** (1904), 53. Ztschr. allgem. österr. Apoth.-Ver. **58** (1904), 222.

[2]) Pharm. Ztg. **48** (1903), 184.

that temperature for 15 minutes. When the liquid has cooled down completely, myrosin solution is added, and is left to act for 16 hours without heating. Instead of the above method, the powdered seed can also be digested for 16 hours at the temperature of the room with 300 cc. water, to which 0,5 gm. tartaric acid has been added. In both cases the generating flask is connected direct with the suitably-arranged receiver, and after digestion, as much as possible is distilled off from the generating flask, without reducing the temperature at all. The mustard oil distilled over is either oxidised with alkaline permanganate solution, and the sulphuric acid thus formed determined, — or the oil is examined according to the German Pharmacopœia IV. Ed.

**Neroli Oil.** Jeancard and Satie[1]) have set themselves the task of studying the influence of the weather-conditions on the yield and constitution of oil of orange blossoms. The observations extend over the first five months of each of the years 1901, 1902 and 1903. It is seen from the daily determinations of the relative degree of moisture during the day and during the night, the temperature, the air-pressure, the cloudiness of the sky, etc., and the simultaneous examination of the oil distillates, in what manner the weather affects the formation of essential oil. The examination of the oils collected during this time deals with the determination of the different constants, the specific gravity, optical rotation, solubility, viscosity, the determination of the acid number, saponification number and content of free alcohols (linalool). The last-named determination cannot be carried out with exactitude by the acetylation method, as we have already previously shown in the case of lavender oil[2]).

The mean yields of oil from the orange blossoms were

| | |
|---|---|
| in the year 1901 . . . . . . . . . . | 1,140 % |
| „ „ „ 1902 . . . . . . . . . . | 0,95 „ |
| „ „ „ 1903 . . . . . . . . . . | 0,96 „ |

For further details we must refer to the original work.

**Neroli "Schimmel & Co."** In view of the approaching distillation of orange-blossoms, it may be recommended to those who have not yet made a trial, not to send their orders to France without first submitting our product to a serious test. It is here no longer a question of a preconceived opinion, but of a fact acknowledged by a large number of experts of the highest standing, that our neroli surpasses the natural distillate in quality and richness.

The difference in strength is estimated rather too low at 10 %.

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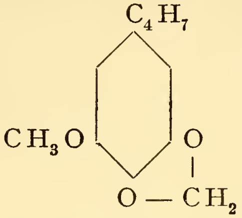
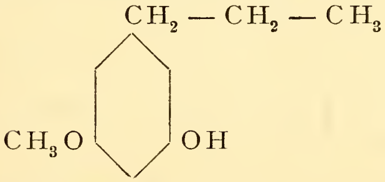
[1]) Bull. Soc. chim. III. **29** (1903), 992.
[2]) Report April **1893**, 37.

**Nutmeg Oil.** As a constituent of this oil, Semmler[1]) has isolated long ago myristicin. At that time he gave to it the formula of a (l)-butenyl-(3, 4)-methylenedioxy-(5)-methoxybenzene:



A further examination of this body by Thoms[2]), however, showed that instead of the butenyl-group, an allyl-group must be accepted[3]).

The myristicin examined had the following constants: boiling point 149,5° at 15 mm; $d_{19^\circ} = 1{,}1425$. By the action of alcoholic potash the allyl compound could be changed into the propenyl compound, isomyristicin, which, contrary to myristicin, is solid, and melts at 44° to 45°. In addition there was formed, by splitting up the methylene linking, a very small quantity of a phenol. Myristicin and isomyristicin also differ in a marked degree in their behaviour towards bromine. The first-named forms an oily product when submitted to the action of two atoms bromine, the last-named a crystalline product of the melting point 109°, which is identical with the one obtained by Semmler. If to the myristicin or isomyristicin dissolved in glacial acetic acid, and cooled in ice, bromine is added up to the formation of a permanent yellow colour, there are formed in both cases disubstituted dibromides. The dibromomyristicin dibromide melts at 130° and the dibromisomyristicin dibromide at 156°. By reducing myristicin with sodium in alcoholic solution, dihydromyristicin (boiling point 149° to 150° at 17 mm) is obtained. In this case, analogous to isosafrol and isoapiol, the methylenedioxy-group is split up, and there is formed a (1)-propyl-(5)-methoxy-(3)-phenol (boiling point 160° to 161° at 17 mm; $d_{20^\circ} = 1{,}0598$).



That the oxygen atom situated in para-position towards the propyl-group is actually eliminated, is proved by the fact that the methyl ether of the phenol (boiling point 136° to 137° at 16 mm; $d_{19^\circ} = 1{,}0194$) differs from the dihydromethyl eugenol which ought to have been formed if the oxygen atom situated in the meta-position had been

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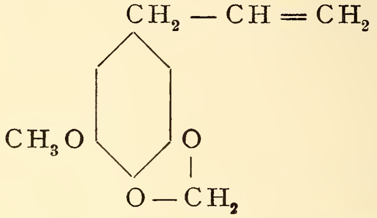
[1]) Report October **1890**, 41.

[2]) Berliner Berichte **36** (1903), 3446.

[3]) Semmler has also expressed himself verbally in this sense to the author.

eliminated. By oxidising isomyristicin with potassium permanganate according to Semmler[1]), Thoms also obtained myristicin aldehyde (m. p. 131°) and myristicinic acid (m. p. 210°). With regard to the facts hitherto known about the products split off from myristicin, Thoms proposes for this body the following formula:



**Orris Oil.** Our Italian buyers report as follows on the present state of the market of Florentine orris-roots: —

| | |
|---|---|
| According to our previous communications, the available quantity of Florentine roots at the end of August 1903 amounted to . . . . | 560 tons |
| Added to this the last results of the harvest of 1903 about . . . | 750 „ |
| gives a total of | 1310 tons |
| Shipments from the beginning of September 1903 to the end of February 1904 . . . . . . . . . . . . . . . . . . . . | 630 „ |
| Leaves at present at disposal about . . . . . . . . . . . . | 680 tons |

The yield of the harvest in 1903 shows therefore a deficiency, as compared with 1902, of about 250 tons. Moreover, the quality shows a great falling-off, as chiefly only medium qualities have been produced, in consequence of which picked orris-root can practically only be supplied by drawing on the old roots, and for this reason the latter fetches a higher price than the roots of the new crop. There can be no doubt that the decline both in quantity and in quality is due to the ruinous selling prices which do not nearly cover the cost of production, a state of affairs which leads to a general neglect of the cultivation. At the present time the yield from cereals is worth about five times that from orris-root to the peasant; the orris-root cultivation pays neither for interest nor wages, and a continued decline in the production must therefore be expected. As a matter of fact, the last new plantations are on a much more modest scale than previously. During the twelve months from September 1902 to August 1903, the total shipments amounted to about 840 tons, that is to say, somewhat less than the average annual export of 900 tons recorded by us; but the twelve months from September 1903 to August 1904, judging from the shipments made to this date, will probably again make up the difference.

At the time of the harvest, from September to November, the following prices were paid: —

35 to 37 marks per 100 kilos cif. Hamburg for assorted roots
31 to 32 marks per 100 kilos cif. Hamburg for pickings.

To-day, in consequence of the important purchases which have meanwhile been made, the market quotations are 38 and 33 marks. Will these prices be maintained, or will the article improve further? This is a question which many people put to themselves, but who can read the future? It will be readily understood that this will depend chiefly on the result of the next harvest, on which, however, an opinion cannot as yet be very well given. The decrease

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[1]) Berliner Berichte **24** (1891), 3818.

in the quantities newly planted out, will only influence the harvest-results in two to three years' time, as of course orris-root may be gathered after two years, and must be gathered in three years. For this reason, the quantities planted out in 1901 and 1902 come under consideration for the next crop, and these were on a sufficient scale not to give rise to any scarcity. It should be noted, in this connection, that of the former, i. e. the roots planted out in 1901, only a small quantity was gathered during last autumn. Finally, it will have to be taken into consideration that buyers abroad (as is apparent from the shipments made) have covered themselves freely, and can therefore afford to consider fresh purchases with equanimity. At the same time, the opinions of competent persons all agree that a serious drop in the prices is not to be expected in future, also in view of the fact that purchasers for further large parcels came on the market already when the price went slightly back. The scheme for the production of orris oil proposed by Mr. Pegna has not been developed further after the death of that gentleman.

It follows from the foregoing report, the clearness of which leaves nothing to be desired, that orris oil in the near future can be produced under the same favourable conditions as hitherto.

Both the concrete and the liquid oil are manufactured by us as specialities on a large scale, in rooms which, in conformity with the delicate character of the oil, are separated from the rest of the factory. The qualities enjoy the highest reputation. The liquid, tenfold concentrated orris oil, which we were the first to introduce into commerce, is universally recognised as one of the most beautiful products of this branch. It is a source of satisfaction to us that we were the originators of this article.

**Parsley Oil.** When producing apiol from French oil of parsley seed, we came across an oil which contained small quantities apiol only in the last runnings, whilst the principal fractions could not be made to solidify. Professor Thoms has at our request examined this oil more in detail, and reports on it as follows¹):

The oil ($d = 1{,}017$; $[\alpha]_{D20^\circ} = -5{,}7^\circ$) was mixed with ether, and was freed from acids, phenols and aldehydes, or ketones, by shaking with 5 % solution of sodium carbonate, 2 % potash liquor, and sodium bisulphite solution. As acid, palmitic acid (0,0804 %) could be identified; the phenols (0,0516 %) and the residue of the bisulphite solution could not be separated as the quantity was too small. The oil treated in this manner was fractionated.

In the individual fractions the following bodies were detected: pinene as nitrosochloride, and myristicin as dibrom-myristicindibromide (melting point 130°). The myristicin found here proved to be identic with the myristicin obtained from oil of nutmeg²). It also yielded isomyristicin. From the last fractions of the oil of parsley seed, apiol

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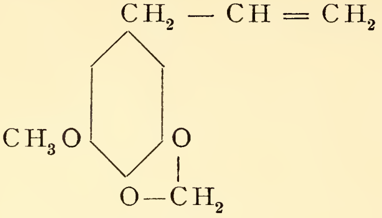
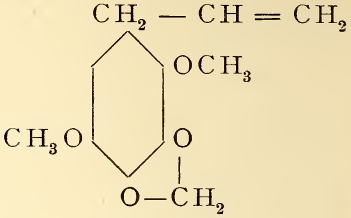
¹) Berliner Berichte **36** (1903), 3451.

²) The present Report, p. 65.

could be obtained by freezing. The latter differs from myristicin by the fact that it contains an additional methoxyl-group:



Myristicin



Apiol

and is the principal constituent of German oil of parsley seed. As the inability of the French parsley of adding another methoxyl-group cannot be explained by a difference in the anatomical construction of the fruit, the author desires to determine by cultivation-tests, whether perhaps external causes contribute towards this occurrence.

**Patchouli Oil.** There has been a fair demand for our production at advancing prices, which could not be prevented, as a higher figure than in the autumn of last year had to be paid for good quality leaves in India. We were able to ensure regular supplies by liberally allowing fair prices.

Up to the present little was known of the chemical composition of patchouli oil; moreover, the data found in literature refer only to cadinene and patchouli alcohol, i. e. two constituents which are of no importance for the extraordinarily characteristic and powerful patchouli odour. For this reason we have occupied ourselves rather thoroughly with the examination of the oil, and have endeavoured to clear up its chemical constitution. Unfortunately, the work, undertaken at great expenditure of material, has up to now had but little result. We will here communicate the results obtained.

We worked up a patchouli oil of our own distillation, which had the following constants: $d_{15^\circ} = 0{,}9769$; $\alpha_D = -55^\circ 45'$; acid number 2,2; saponification number 4,2; saponification number after acetylation 15,4. The colour was dark brown. 1 volume and more of 90 per cent. alcohol made a clear solution with the oil. A test for compounds containing methoxyl, made with the original oil according to Zeisel's method, showed no reaction. The oil, of which 3 kilos were fractionated in vacuo with column, distilled between 118° (17 mm pressure) and 151° (7 to 8 mm pressure).

We wish to state already in this place, that about 97 °/₀ of the patchouli oil consists of bodies which are almost valueless for the odour. Of this, about 40 to 45 °/₀ belongs to the portions distilling between 260° and 280°, which consist chiefly of one or more sesquiterpenes. The remainder is probably represented by patchouli alcohol.

The first fraction, boiling from 228° to 240°, amounted to about 5 grams, and had an extremely disagreeable odour, which, however, did not remind of patchouli. In view of the small quantity available, nothing could be decided as to the character of the unpleasantly smelling body.

We were equally unsuccessful in our endeavours to identify a body in the portions passing over between 240° and 260°. We therefore continued our examination with larger quantities of material. On the strength of preliminary trials in which we extracted patchouli oil with alcohol of varying percentage, we extracted 22 kilos oil with 70 per cent. alcohol, and thereby obtained an enrichment (though only slight) of the more readily soluble, smelling constituents.

The alcohol was removed from the oil dissolved in vacuo. The latter did not differ in any marked degree in the physical constants from the original oil, but we were now able to detect some bodies. The quantity of oil, amounting to 7,2 kilos, was fractionated in vacuo.

Benzaldehyde. Traces of this body were present in the lowest-boiling portions (54° to 70° and 70° to 95°, at 4 mm pressure). It was detected by the semicarbazone of the melting point 214°, from which dilute sulphuric acid during boiling liberated the characteristically smelling aldehyde. The melting point of the above-mentioned derivative was not lowered by adding the semicarbazone from the synthetic aldehyde.

Eugenol. By repeated treatment with dilute soda liquor, we abstracted from the oils passing over between 70° and 108° and 108° to 125° (4 mm pressure), a phenol which after distillation in vacuo was recognised already by its odour as eugenol. The bulk (8 gm.) boiled at 109° to 110°, at 5 mm pressure, and 253° to 256° at ordinary pressure; $d_{15^\circ} = 1{,}0705$. The benzoyl compound obtained according to Schotten-Baumann melted at 69° to 70°. The phenol in alcoholic solution showed with ferric chloride the well-known eugenol colouration. Traces of a slightly lower boiling phenol appeared to be mixed with the eugenol.

Cinnamic aldehyde. On shaking the above fractions with bisulphite liquor, traces of a bisulphite compound separated off. The aldehyde regenerated from the latter had a distinct odour like cinnamic aldehyde. Its semicarbazone was characterised by difficult solubility in alcohol, and, like the synthetic semicarbazone, melted at 208°. The mixture of the two had the same melting point.

Terpenic Alcohol. From the portions distilling under diminished pressure at 54° to 95°, we isolated, by heating the oil in benzene solution with phthalic acid anhydride for about one hour on the water bath, a few drops of an alcohol which had a very pleasant rose-like odour. An attempt to produce a solid derivative of it — in this case a diphenyl urethane, — failed. Possibly it is here a question of a higher alcohol of the aliphatic series.

Ketone. The same fractions contain a ketone with a caraway-like odour, but this also in such small quantity, that we must content ourselves with mentioning the melting point of its semicarbazone. The derivative, crystallising from alcohol in glittering compact prisms, melts at 134° to 135°. Another body of the melting point 246° to 247°, which is also present, but in larger quantity, and only crystallises from water, may possibly in the course of further examination prove to be the hydrazodicarbonamide $NH_2CONH \cdot NH \cdot CONH_2$ of Thiele¹), which compound H. Rupe and W. Schlochoff²) have recently also found in producing the semicarbazide-semicarbazone. The values obtained by us on preliminary analysis do not quite agree with those required for it, but this may possibly be explained by an admixture of a second ketone semicarbazone; for, if the substance is heated with sulphuric acid, a peculiar orris-like odour is evolved.

Base. For the purpose of obtaining this body, which is remarkable on account of its stupefying odour, and which was found in all the lower, and also in the sesquiterpene fractions of patchouli oil in a smaller or greater degree, we treated the portions boiling at 250° to 270° several times with 20 % sulphuric acid. The base was liberated from the acid solution by means of soda and driven off with steam. It has a lower specific gravity than water, and is readily volatile with water vapour. The water oil appears to contain it in more abundant quantities than the normal oil. From a portion of 6 to 7 kilos of the first-named oil we abstracted about 10 gm. base. On purification of the latter though, it was found that the bulk of it had a higher specific gravity than water and had a less powerful odour than the first. Distillation in vacuo led to the following two fractions:

80° to 130° and 135° to 140° (3 to 4 mm pressure).

The first portion, amounting to 2 gm., yielded in absolute ethereal solution with dry hydrochloric acid a strongly hygroscopic, partly somewhat greasy hydrochloride melting indistinctly at 105° to 115°. Its aqueous solution yielded with platinum chloride a well-crystallising platinum salt. Melting point 208°, after recrystallising 3 times from water. The salt dissolves with great difficulty in alcohol and ether. Platinum-determination and elementary analysis:

0,2281 gm. of the substance yielded 0,3003 gm. $CO_2$ and 0,0833 gm. $H_2O$.
0,1585 „ „ „ „ „ 0,0427 „ Pt.

Found: C = 35,90 %
H = 4,06 „
Pt = 26,04 „

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¹) Liebig's Annalen **270** (1892), 44.

²) Berliner Berichte **36** (1903), 4377.

Nitrogen determination:

0,2239 gm. of the substance yielded 10,3 cc N at 14,5° and 754 mm

Found: N = 5,36 %.

The foregoing figures are, however, given with reserve. The base (8 gm.) boiling at 135° to 140° (3 to 4 mm pressure) had the specific gravity 1,0148, the optical rotation $\alpha_D = -9^\circ 5'$, the index of refraction, at 20°, 1,54282. Its platinum double salt could not yet be obtained sufficiently pure for analysis, but may possibly melt lower than the one mentioned first. In alcohol it dissolves fairly easily. Further tests are being made with both bases.

Sesquiterpenes. We have repeatedly endeavoured, but always without success, to detect in the fractions boiling between 264° and 278°, the cadinene found by Wallach in patchouli oil, by means of its dihydrochloride. Even the experiments made during continued winter-cold remained without result. Nor could a crystalline nitrite, nitroso chloride, or nitrosate be isolated. The specific gravity of the sesquiterpenes distilled over sodium fluctuated between 0,9217 and 0,9379, the rotatory power between — 27° 37′ and — 40° 37′.

Patchouli alcohol. This body, which probably represents the bulk of the oil, is present in the portions boiling above 140° (8 mm pressure). After repeated recrystallisation from petroleum ether, it forms a colourless compound melting at 56°, which in the pure state may possibly be odourless. The specific rotation, calculated from a 23,94 % chloroform solution, was — 97° 42′. In spite of a recrystallisation repeated 6 times, we were unable to remove a faint musty odour, which of course is so characteristic of patchouli oil. The hydrocarbon patchoulene, which is formed from the alcohol already at ordinary temperature by the action of strong formic acid or other agent abstracting water, is a colourless liquid of a cedar-like odour, which has the boiling point 255° to 256°. The specific gravity of the body distilled over sodium was (contrary to Wallach's[1]) statement) 0,9334, the optical rotation — 36° 52′. We were unable to produce solid derivatives of patchoulene, such as the alcohol, a nitrosite, nitrosochloride, or nitrosate. On oxidation with 1 % permanganate solution an oily product was formed, which was not examined further. The question whether the sesquiterpene, which is readily formed from patchouli alcohol, is present in patchouli oil, can only be settled by further examinations.

**Peppermint Oil, American.** As predicted in our Report of October last, the attempts made by a clique of speculators to drive the prices up, have failed completely. The quotations have remained

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[1]) Liebig's Annalen **279** (1894), 394.

practically without change during this period, and only recently the market has to some extent responded to the influences created by a diminishing stock.

At the present prices, the majority of the holders who have remained outside the ring of speculators, realise good profits, and if the value of the article remains at the present level, an era of great prosperity is in store for the American peppermint oil industry, for even with medium crops the cultivation and distillation of peppermint in America is then still remunerative.

It is too early to pronounce at present a fair opinion on the prospects of the new harvest. For months the trade in American oil has now been very languid, with unimportant sales.

The "Twentieth Annual Report of the Bureau of Labor" of the State of Michigan gives, on page 447, some interesting information on the peppermint oil production in that State during the years 1900 to 1902: —

| | 1900 | 1901 | 1902 |
|---|---|---|---|
| Acres of land under cultivation | 2112 | 2782 | 6410 |
| Quantity of oil obtained, lbs. | 47628 | 63718 | 82420 |
| Yield of oil per acre, lbs. | 22,5 | 23,9 | 12,8 |

In these three years therefore 11,305 acres were cultivated, from which all in all 193,767 lbs. oil were obtained, or on the average 17,1 lbs. from one acre. 299 farmers took part in the cultivation.

**Peppermint Oil, Japanese.** The prospects of a good harvest, mentioned in our last Report, have been realised, for still in October last we heard that the crop was estimated, as a matter of fact, at 200000 catties, or about 120000 kilos. The rise brought about towards the end of September was artificial, and consequently but of short duration; in November, crystals could already be bought again at 15/- per lb. In December, the prices showed again a slight movement, but on the whole the fluctuations did not exceed about 3/- per lb. for crystals and 1/- for separated oil, which, in view of the impulsive nature of the Japanese, cannot be called an actual rise, for such like slight movements occur almost every month.

The Russo-Japanese war has also failed up to now to bring about the great advance which had been expected from many quarters; this is no doubt chiefly due to the fact that the ports of Yokohama and Kobe, from which the peppermint oil trade is carried on, have so far not been touched by the warlike events. Shipments to Europe have hitherto been made punctually and regularly.

The market was further influenced in a marked degree by the dullness in America for home-made peppermint oil, and by the bad experience in that country from the admixture of Japanese to American oil. There is no doubt that the American merchants have done themselves an enormous amount of harm by this manipulation, and have brought the American oil into ill repute in Europe.

According to official data, the total shipments from Japan during the year 1903 to the different ports, were as follows: —

### I. Liquid separated oil.

| | | | | |
|---|---|---|---|---|
| To | London . . . | 12735 | catties | |
| „ | Hamburg . . . | 9900 | „ | |
| „ | Hong Kong . . | 4546 | „ | |
| „ | New York . . | 1790 | „ | |
| „ | Bombay . . . | 1375 | „ | |
| „ | Havre . . . . | 675 | „ | 31021 catties |

### II. Peppermint crystals.

| | | | | |
|---|---|---|---|---|
| To | Hamburg . . . | 17235 | catties | |
| „ | London . . . | 14895 | „ | |
| „ | Hong Kong . . | 5862 | „ | |
| „ | New York . . | 3825 | „ | |
| „ | Bombay . . . | 2359 | „ | |
| „ | San Francisco . | 900 | „ | |
| „ | Java . . . . | 630 | „ | |
| „ | Seattle . . . . | 450 | „ | |
| „ | Australia . . . | 135 | „ | |
| „ | Shanghai . . . | 94 | „ | |
| „ | Calcutta . . . | 25 | „ | 46410 „ |
| | Total (oil and crystals) | | | 77341 catties |
| | | | | = 103340 lbs. |

If the result of the last harvest is taken as already mentioned, it is probable that at the close of the year 1903, at least an equal quantity was still in Japanese hands.

Since the beginning of 1904 the trade in this article has been exceptionally brisk; it may be taken for granted that at the present time the stocks in Japan are much reduced, and they may now scarcely amount to 50000 catties, a figure which must lead to a favourable opinion on the situation.

The exaggerated prices of American oil have in many cases assisted the introduction of the Japanese oil.

**Peppermint Oil, Mitcham.** The available stocks of pure original distillates are estimated very low, and are mostly held back for the home demand. There is an absolute absence of offers of this oil: "so-called" Mitcham oil, on the other hand, can, as always, be bought at any price, and as long as it is not possible to differentiate chemically between the various types of peppermint oil, the article will always be obtainable at all prices.

Experiments made by E. Charabot and A. Hébert[1]) with the peppermint plant, have proved that the green parts of the plant experience an enrichment of essential oil in consequence of a systematic and complete removal of the inflorescences. It also follows from the above that the formation of the terpene compounds takes place in the chlorophyl-bearing organs from which they then advance towards the inflorescences. How important a part is played by the green parts of the plant in the formation of the odoriferous constituents of the oil, is proved by the fact that the plants grown in the shade show a smaller content of essential oil, than those which are exposed to direct sunlight.

**Petitgrain Oil, Paraguay.** The situation in the distilling districts is said to be so precarious that new contracts are only accepted with all possible reserve. Since the trust of manufacturers has been dissolved, the individual distillers appear to use their utmost endeavours to spoil the trade for each other. At the present low value, this industry cannot be particulary remunerative.

In a similar manner as with oil of orange blossoms (see there), Jeancard and Satie have studied the influence of the weather on the formation and composition of petitgrain oil[2]). The determination of the meteorological conditions in the neighbourhood of Cannes comprises the periods from January 1st to July 10th of the years 1901 to 1903. By determining the constants of the petitgrain oils obtained during that time, it was here also possible to detect an influence of the weather-conditions on the composition of the oil.

Umney and Bennett[3]) report on the examination of a South American orange oil, which had most probably been distilled from the leaves and blossoms of the bitter orange, and had been imported from Buenos Ayres. The properties of this oil as mentioned are: $d_{15^\circ} = 0,887$; $\alpha_D = +2^\circ$; ester, calculated for linalyl acetate = 36,5%; free alcohol, calculated for geraniol = 38,4%; total alcohol = 67,1%; soluble in 2 volumes 70% alcohol. According to these, the oil greatly resembled petitgrain oil, but it had a better odour and a higher percentage-content of alcoholic constituents, whilst, on the other hand, the ester-content

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[1]) Compt. rend. **138** (1904), 380.

[2]) Bull. soc. chim. III. **29** (1903), 1089.

[3]) Pharm. Journal **72** (1904), 217.

was lower than that of normal Paraguay petitgrain oil. It is specially worthy of note that the oil contained only traces of methyl ester of anthranilic acid. When the oil was fractionated in vacuo, the individual fractions showed a constantly increasing specific gravity, and, on the whole, an increasing dextrorotation. In the first fraction, rich in terpene, the authors were able to detect l-pinene and dipentene, whilst the last consisted chiefly of geranyl acetate. From intermediate fractions linalool and geraniol were obtained in the pure state, — the latter in larger quantity than the former, — two other intermediate fractions had a strong odour like terpineol, but it was not found possible to obtain this body in the solid state.

**Pimento Oil.** Up to the present, eugenol and a not further identified sesquiterpene had been detected in oil of pimenta[1]). An examination made by us has enriched our knownledge of this oil with a few constituents of which we give the following details.

We worked up 1 kilo of the first runnings of a distillation, which had the following constants: $d_{15^\circ} = 0{,}9715$; $\alpha_D = -11^\circ 30'$ (100 mm). On shaking the oil with 3% soda liquor, acid constituents were abstracted from it, and the oil not combined with soda liquor (about 500 gm.) was fractionated in vacuo.

Cineol. The lowest boiling portions (boiling point 40° to 50° at 5 mm pressure) had a pronounced cineol-like odour. After destroying any terpenes and other readily oxidisable substances which might be present, by treatment with 3% permanganate solution, the remaining oil was driven off with steam and distilled at ordinary pressure. Between 170° and 180° about 2 gm. passed over, which were oxidised with permanganate (according to Wallach and Gildemeister's method[2]) into cineolic acid of the melting point 202° to 203°. A further proof of the presence of cineol was supplied by its additional combination with iodol of the melting point 112°.

l-Phellandrene. The slightly higher boiling portions (50° to 60° at 5 mm pressure) had the specific gravity 0,8619 at 15°, and the rotatory power $-36^\circ 36'$ (100 mm). With nitrous acid they formed after a short time a dense flocculent precipitate, which in the crude state melted at about 100°, and after having been twice recrystallised from acetic ether at 119° to 120°; by these means it was identified as phellandrene nitrite. The nitrite melting at 102° to 104° was not observed in this examination. As the nitrite showed the specific rotatory power in 10% chloroform solution $[\alpha]_D = +95^\circ$, the phellandrene itself is lævorotatory.

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[1]) Bonastre, Journ. de Pharm. **13** (1827), 466. — Oeser, Liebig's Annalen **131** (1864), 277.

[2]) Liebig's Annalen **246** (1888), 268.

Caryophyllene. The fraction boiling at 120° to 125°, at a pressure of 6 mm, which according to previous examinations consists of a sesquiterpene, was first of all tested for caryophyllene, whose presence was considered probable in view of the similarity between pimento oil and oil of cloves. By attaching water by means of sulphuric acid and glacial acetic acid, according to Bertram-Walbaum's method, a good yield was obtained of the caryophyllene alcohol melting at 97°, which was identified by its phenyl urethane melting at 136° to 137°. The melting point of the caryophyllene nitrosate recrystallised from benzene was found at 159°, that of the nitrol piperidide at 146° to 147°. As the corresponding compounds from clove oil caryophyllene showed the same melting points, it appears that the data given in literature (melting point 148° to 149°, and 141° to 143°) are a little too low. The examination hereof has not yet been concluded.

Eugenol methyl ether. The high specific gravity ($d_{15^\circ} = 0{,}941$) of the fraction boiling at 120° to 125° (6 mm) pointed to the presence of an oxygenated compound, in addition to caryophyllene. A methoxyl-determination after Zeisel had a positive result, and by oxidation of a fraction boiling at 248° to 260° with potassium permanganate, veratric acid melting at 179° to 180° was obtained, which proved the presence of eugenol methyl ether. Attempts to produce tribrommethyl eugenol failed, probably owing to the formation of brominated products of caryophyllene.

Eugenol. The oil liberated from the alkaline liquors by means of sulphuric acid passed over almost entirely at 120° to 125° on distillation at 5 mm pressure, and boiled at ordinary pressure at 249° to 251. By the formation of the benzoyl compound of the melting point 69° to 70°, and also by the physical constants ($d_{15^\circ} = 1{,}0717$; $n_{D20^\circ} = 1{,}54062$) it was identified sufficiently as eugenol.

Palmitic Acid. The distillation-residue of the constituents soluble in alkali solidified after a short time in the form of crystals. Petroleum ether dissolved almost only the crystals, whilst the resinous impurities remained behind undissolved. After recrystallisation from aqueous alcohol, fine small needles were obtained, which were identified by their melting point of 60°, and by analysis of the silver salt, as palmitic acid.

0,1644 gm. of silver salt yielded 0,0462 gm. Ag.

| Calculated for $C_{16}H_{31}O_2Ag$: | Found: |
|---|---|
| Ag 27,0 % | 28,1 %. |

The further examination dealt with a few quantitative estimations of a normal pimenta oil distilled by ourselves, which had the following constants: $d_{15^\circ} = 1{,}044$; $\alpha_D = -4^\circ 30'$; acid number and saponification number very low, and impossible to determine correctly in consequence of a strong brown colouration. The eugenol-content was ascertained according to Umney-Schimmel & Co. and Verley and Bölsing; by the first method 78 % eugenol were found, by the second 72,8 and 72,9 % respectively. A methoxyl-determination by Zeisel's method, of the oil from which the phenols had been removed, gave the following result:

1,527 gm. of the substance yielded 1,9613 gm. AgI. From this was calculated a content of 43,6 % methyl eugenol in the oil free from phenol.

By this examination the following have been detected as constituents of pimenta oil:

1. cineol
2. phellandrene
3. caryophyllene
4. methyl eugenol
5. eugenol
6. palmitic acid.

The presence of small quantities terpene alcohols is probable, but up to the present it was not found possible to prove this chemically.

**Pine-needle Oils.** The fine Swiss distillate from the cones of *Abies pectinata,* also called *Ol. templini,* could at last again be obtained in abundant quantities, whilst the oil from the needles of *Abies pectinata* — the commercial pine-needle oil — like the genuine oil from *Pinus montana,* could only be supplied under very difficult conditions and in insufficient quantities. The distillation carried on high in the Tyrolese and Styrian Alps is absolutely dependent upon the weather, and interruptions lasting from one to two months are in winter the order of the day.

The fine Siberian pine-needle oil, an absolutely pure distillate with a fine, powerful and yet characteristic odour, comes more and more to the front. Its price is exceptionally low. Our sales of this oil last year reached an unusual height. It can be supplied in any quantity.

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The fact that certain aldehydes of the aliphatic series have an important bearing on the odour of some essential oils, has recently found further confirmation by our discovery of laurinic aldehyde in the oil of *Abies pectinata*, — a body which in the diluted state has a pleasant odour like pine needles, and whose occurrence in nature had up to the present not yet been observed. We isolated it by shaking the fractions of 3 kilos oil (800 to 900 gm.) which boiled above 82° (5 mm pressure), for a considerable time, in an extracting-apparatus, with bisulphite liquor; the bisulphite compound separated off in a slimy condition, was then purified with alcohol and ether, and from this absolutely dry compound the aldehyde was liberated by means of soda-solution. It was fairly volatile with water vapour. The quantity amounted to only 9 gm., i. e. 0,3 % of the oil. The specific gravity of the principal fraction which passed over at 5 mm pressure between 108° and 120°, was 0,8388. When the temperature was much reduced, the oil congealed into a white radiated crystalline mass, which at ordinary temperature again liquefied. This shows that the fraction did not consist of pure aldehyde, as the latter is solid at ordinary temperature. As a matter of fact we succeeded by means of soda-solution, in abstracting from the oil an acid of the melting point 43°, which we recognised as laurinic acid, for a mixture of this acid and laurinic acid also melted at 43°, — a proof of the identity of both bodies. The acid would therefore have been formed by oxidation of the aldehyde in the air. With synthetically produced laurinic aldehyde we could also observe that the oxidation into laurinic acid in the air occurs fairly rapidly.

The aldehyde from which the acid had been removed yielded a semicarbazone of the melting point 101,5° to 102,5°. The synthetic aldehyde produced for comparison from laurinic alcohol (obtained by reduction and saponification of the ethyl ester of laurinic acid by L. Bouveault and G. Blanc's[1]) process), yielded the same derivative of the same melting point and the same properties. The mixture of the two semicarbazones melted at 101° to 102°. As a further proof, we obtained on oxidation of the aldehyde freed from acid, with moist silver oxide, laurinic acid of the melting point 43°. Combustion of the acid and of the silver salt, and silver-determination and analysis of the semi-carbazone, all confirmed that the new aldehyde was laurinic aldehyde.

### Analysis of laurinic acid.

9,1708 gm. of the substance yielded 0,1853 gm. $H_2O$ and 0,4490 gm. $CO_2$.

| | Found: | Calculated for $C_{12}H_{24}O_2$: |
|---|---|---|
| C: | 71,69 % | 72,00 % |
| H: | 12,05 % | 12,00 % |

### Analysis of the silver salt.

0,1466 gm. of the substance yielded 0,0977 gm. $H_2O$ and 0,2516 gm. $CO_2$.
0,2244 „ „ „ „ „ 0,0786 „ Ag.

| | Found: | Calculated for $C_{12}H_{23}AgO_2$: |
|---|---|---|
| C: | 46,79 % | 46,91 % |
| H: | 7,41 % | 7,49 % |
| Ag: | 35,03 % | 35,18 % |

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[1]) Compt. rend. **136** (1903), 1676, and **137** (1903), 60.

Combustion of the semicarbazone.

0,1725 gm. of the substance yielded 0,1733 gm. $H_2O$ and 0,4105 gm. $CO_2$.

| | Found: | Calculated for $C_{13}H_{27}N_3O$: |
|---|---|---|
| C: | 64,90 % | 64,73 % |
| H: | 11,16 % | 11,20 % |

In addition to laurinic aldehyde, a second aldehyde appears also to be present in the oil of *Abies pectinata*, which we would designate as decylic aldehyde. At least, we obtained as the first runnings of the above-mentioned principal fraction, about 1,8 gm. of an aldehyde of the boiling point 94° to 108° (5 mm pressure) which had a distinct odour of orange oil. Its semicarbazone melted at 93° to 95°. We endeavoured without success by fractional crystallisation to obtain the body sufficiently pure for analysis, but we could ascertain from the combustions that the derivative consisted chiefly of the semicarbazone of laurinic aldehyde.

**Rose Oil.** Since our last Report, business in this important article has been so slow, that on the whole the prices since the harvest have scarcely advanced by as much as the normal rate of interest. The enormous yield of the harvest has frustrated the contemplated manipulation of the prices by a few speculators, although the lifeless condition of the market is also in part attributed to the uncertain political situation in the Balkans.

The normal state of affairs in the rose oil trade has, according to our experience, become worse rather than improved, for we have not in any previous year encountered the same difficulties as this year in finding faultless qualities.

The following figures of the exports of 1903 show a considerable increase, as compared with the export of 1902; about half of this is due to speculative enterprise, which cannot cause surprise in view of the low quotations.

Rose oil exports of Bulgaria in 1903.

| | | | |
|---|---|---|---|
| To | Austria-Hungary | 64,— | kilos |
| ,, | The United Kingdom | 1054,— | ,, |
| ,, | Belgium | 4,— | ,, |
| ,, | Germany | 1027,— | ,, |
| ,, | Greece | —,400 | ,, |
| ,, | Italy | 26,— | ,, |
| ,, | Russia | 250,— | ,, |
| ,, | The United States | 1456,— | ,, |
| ,, | Constantinople | 393,082 | ,, |
| ,, | France | 1870,— | ,, |
| ,, | Holland | 2,— | ,, |
| ,, | Switzerland | 11,— | ,, |
| ,, | Other countries | 53,— | ,, |
| | Total | 6210,482 | kilos |

as against 3676 kilos in 1902
3028 „ „ 1901
5346 „ „ 1900
3534 „ „ 1899
3430 „ „ 1898

For the future course of the prices the weather-conditions during the next two months will be decisive. The distillation usually commences in the beginning of May.

**Rose Oil, artificial “Schimmel & Co.”** (German Patent No. 126736). The use of our original product is constantly growing. This proves conclusively that the introduction of this article of sterling value has filled a real want. We hereby recommend it most warmly.

**Rosemary Oil.** For the Dalmatian product new competitors have come in the field, which has had the effect of rendering the previously very independent producers a little more amenable. A pure quality, answering the most stringent requirements, was available in sufficient quantity. For this reason it makes an all the more disagreeable impression that there is still hawked about unblushingly a so-called rosemary oil for denaturating purposes, which is nothing but a fraction of oil of camphor, and which is sold at half the price of rosemary oil. The law only permits rosemary oil and not camphor oil, even though the latter may have approximately the same constants. To call such an oil rosemary oil is by itself already an act to which the term “dishonest competition” applies. But under no circumstances should it be designated as rosemary oil before the authorities, at the expense of those who only supply pure rosemary oil. We are about to call the attention of the highest Customs Authorities of the prevailing abuses, and will not rest until the matter has been thoroughly cleared up.

French oil of rosemary of unobjectionable quality can only be obtained with difficulty. The best parcels can always be had immediately after the harvest. The tendency of the prices is upward.

In a short note on rosemary oil, Pancoast and Graham¹) also publish the results of an examination of a series of Italian and French oils of rosemary, without, however, further expressing an opinion on the quality of the oils. Of 15 samples examined, 6 oils were greatly adulterated, as is proved by the constants found by Pancoast and Graham, which differ considerably from those of normal distillates. Turpentine and camphor oils appear to have been used in these adulterations. This shows once more how the American market is often flooded with inferior products, and how necessary it is to exercise caution in the purchases.

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¹) Amer. Journ. Pharm. **75** (1903), 453.

**Oil of Wild Rosemary** (*Ledum palustre*). Lomidse1) distilled from the young shoots of the flowering marsh wild rosemary, in a yield of about 1 %, a viscid oil from which in course of time crystals were deposited. Complete separation of the crystals from the oil was not possible with 90 % alcohol, better by distillation in vacuo at 20 mm and 80° (?). The liquid portion boiled from 282° to 286°, and contained a ketone of the formula $C_{15}H_{24}O$. The crystals remaining in the retort had the melting point 106°, and boiled in an atmosphere of carbonic acid at 281°. Their composition was that of an alcohol $C_{15}H_{25}OH$. This body, which may possibly be identic with the already known ledum camphor, oxidised readily, but did not contain double linkings, as was proved by its behaviour towards bromine.

**Sandalwood Oil, East Indian.** The first consignments of wood from the Indian December auctions reached us early in March, and show again the reliable assortment which is usual with the Government classification. The prices, according to our average calculation, have changed but little, so that there is at present no immediate necessity of raising our quotations of sandalwood oil. In so far as our sales enable us to draw a final conclusion, the consumption appears to be still on the increase.

With regard to the spike-disease broken out among the sandalwood-trees, no further official information has appeared since the date of our last Report. We must therefore conclude that up to the present no remedy has been found with which this disease can be effectually combated. It is equally impossible to form an opinion as to whether, and in how far, the value of the wood will be affected by this incident which has so suddenly made its appearance. We hope to be able to give some authentic information on the subject in our Autumn Report.

The distillation of sandalwood oil which was formerly carried on with quite primitive installations in India, was first taken up by us, and that in June of the year 1871. The selling price at that time was 48 marks per kilo. On account of the great difficulties met with at that time in obtaining the wood, the prices of the oil advanced in the year 1872 to 84 marks per kilo, and with that figure reached their highest level, as far as we can remember.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| In the years | 1875 | to | 1878 | the | price | was | about | 64 | marks |
| | 1879 | „ | 1882 | „ | „ | „ | „ | 50 | „ |
| | 1883 | „ | 1886 | „ | „ | „ | „ | 48 | „ |
| | 1887 | „ | 1891 | „ | „ | „ | „ | 40 | „ |
| | 1892 | „ | 1896 | „ | „ | „ | „ | 32 | „ |
| | 1897 | „ | 1898 | „ | „ | „ | „ | 25 | „ |

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1) Farmaz. J. **42** (1903), 1037; by Chem. Ztg. Repert. **27** (1903), 284.

after which competition gradually forced it down to 22 marks. With this quotation, the extreme limit appears to have been reached. The laborious work of pulverising the tough wood, and the difficult distillation, do not meet with an adequate reward at this figure, and the hope that the prices may improve is therefore legitimate.

Whether this hope, though, will be realised is a question which under the present circumstances can scarcely be answered in the affirmative.

Parry and Bennett[1]) supply a contribution to the knowledge of East Indian sandalwood oil. On the one hand, they determined the physical constants of acetylised oils, and found as the limits of value of six samples:

$$d_{15^\circ} = 0{,}986 \text{ to } 0{,}9885$$
$$\alpha_D = -13^\circ 50' \text{ to } -14^\circ 30'$$
$$n_{D20^\circ} = 1{,}4894 \text{ to } 1{,}4916.$$

On the other hand, they distilled four sandal oils under reduced pressure, in fractions of 10 % each, and examined the individual fractions for their physical constants.

They then found that the specific gravities and rotations of the successive fractions differ from each other in this manner, that at first towards the middle a decrease takes place, and then the values again increase. The specific gravities go down to 0,964, and show as highest value 0,984, whilst the rotations fluctuate between — 14° and — 22°.

These statements do not agree with the observations made previously by Potvliet[2]) on the same subject. This author, on the contrary, found a gradual increase of the values, viz. from 0,920 to 0,986 and from —10° to —25°48′ respectively. As it was in both cases a question of authentic samples, it is all the more surprising that the results show such variations.

In a report[3]) published in the early part of this year, J. D. Riedel recommends once more Conrady's colour-reaction[4]) as a test for the purity of sandalwood oil. We have repeatedly expressed an opinion on the unreliability of such unscientific methods of testing, and we wish to state here again explicitly that Conrady's reaction is useless for the valuation of sandalwood oil, a fact of which we have now again convinced ourselves by a whole series of tests.

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[1]) Chemist and Druggist **64** (1904), 202.

[2]) "Sandalwood and sandalwood oil." Pamphlet issued by the "Oranje" Company Amsterdam; May **1901**.

[3]) According to Pharm. Ztg. **49** (1904), 26.

[4]) Pharm. Centralhalle **38** (1897), 297; Report October **1897**, 57.

**Spearmint Oil.** It is still difficult to obtain sufficient quantities of the pure American distillate, and it is only possible to buy small parcels here and there. This state of affairs will no doubt continue until the autumn.

St. Joseph County, in the State Michigan, supplied in 1902 341 lbs. spearmint oil[1]) which had been produced by four farmers. The area cultivated with the plant amounted to 17 acres. Accordingly, the yield from 1 acre was 20 lbs. oil.

**Spike Oil.** Fine qualities of guaranteed purity are already becoming very scarce, a fact which points to a dearth of this oil before the new harvest. For current contracts we are holding back proportionate quantities.

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Parry and Bennett[2]) report on an adulterated oil of spike which during the last few months has been placed on the English market. Although the oil answered the usual requirements with regard to specific gravity, rotatory power, and solubility, a closer examination revealed an admixture of one or more foreign bodies, such as oils of turpentine and rosemary, and safrol. The autors have found that pure spike oil can be mixed with 25 % of certain cheap adulterants, without causing a striking alteration in the specific gravity, the angle of rotation, and the usually accepted solubility. Parry and Bennett give the ordinary upper limit of the angle of rotation as + 4° and designate oils with a rotatory power above + 5° as very suspicious. The same authors recommend the use of 65 % alcohol for the determination of solubility, instead of 70 %. Pure spike oils dissolve at 15° C in 6 volumes 65 % alcohol, whilst admixtures of 5 to 10 % of most adulterants prevent this solubility. In order to guard against adulterated oils which might pass this test, fractional distillation is absolutely necessary.

**Spoonwort Oil.** In the further course of their studies on dextrorotatory sec. butylamine and on alkylised d-butyl-ureas and thio-ureas, Gadamer[3]) and his pupil Urban[4]) have arrived at the result that, as a matter of fact, as Gadamer had already suspected, a rather far-reaching racemisation occurs when sec. butyl mustard oil is heated with hydrochloric acid. According to Gadamer, the previously observed differences in the melting points of the gold salts of butylamine produced by different methods, are due to the ability of butylamine of forming abnormally composed gold salts. The splitting up of

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[1]) Twentieth Annual Report of the Bureau of Labor of the State of Michigan p. 447.

[2]) Chemist and Druggist **63** (1903), 1011.

[3]) Archiv der Pharm. **242** (1904), 48.

[4]) Archiv der Pharm. **242** (1904), 51.

synthetic sec. butylamine in which the authors did not succeed, but which they most probably only overlooked, owing to the use of a not very sensitive polarisation apparatus, has meanwhile been accomplished by Thomé by means of tartaric acid. The butylamine produced by him differs somewhat from the d-sec. butylamine obtained by Gadamer from spoonwort oil; whereas the latter gave $[\alpha]_D = +6{,}42^\circ$, Thomé found $+7{,}44^\circ$. As d-sec. butyl mustard oil by its constitution and reaction-capacity, is suitable for a more detailed study of the dependency of the rotatory power of optically active bodies on their atomistic structure, the most diverse thio-ureas, and from the latter the corresponding ureas, were produced from it, and the specific rotatory power of these bodies determined, when no law was observed, which in the case of optically active bodies might be applicable without exception.

Urban[1]) has further made experiments to prepare spoonwort oil and alcohol from the seed of *Cochlearia officinalis.* After the percentage of d-butyl mustard oil in the spoonwort seed had been ascertained by the method indicated by Gadamer[2]), to be 0,485 to 0,492 %, 4,5 kilos seed were crushed and freed from fatty oil by pressing. Unfortunately, the seed was left in this condition for about 4 weeks before it was further worked up; in the meantime, the content of essential oil had diminished to 0,25 %. The practical yield remained still far behind this percentage.

The identity of the essential oil obtained from the seed of *Cochlearia officinalis* with that obtained from the herb, was proved by conversion of the oil into butyl thio-urea (melting point 137°).

The production of spoonwort alcohol from the seed instead of from the herb would be in so far advantageous, as the seed, at the same price as the dried herb, gives a higher yield of oil, and keeps decidedly better. The Pharmacopœia requires a spoonwort alcohol with a content of mustard oil of 0,06 to 0,07 %, which can only be reached if the crude material contains 0,3 to 0,35 % mustard oil. Urban obtained a distillate answering the requirements of the German Pharmacopœia by distilling off 1,5 kilo from a mixture of 200 gm. powdered spoonwort seed freed from fatty oil, 50 grams ground white mustard, 3000 gm. water, and 1125 gm. alcohol (90 %).

**Star-anise Oil.** In this article, which had been neglected for years, business has suddenly become brisk, in consequence of which the prices were driven up, within the space of two months, from the lowest level of 4/3 to 5/3. Reports from China do not mention the cause of this advance of about 20 %, but it may be taken for granted

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[1]) Archiv der Pharm. **241** (1903), 691.

[2]) Archiv der Pharm. **237** (1899), 372.

that the same factors operate here, as in the case of the Tonquin product, for the two star-anise districts are in immediate proximity.

In conformity with what we indicated in our October Report, the yield of the distillation in Tonquin has fallen enormously below that of other years, and even allowing for the usual exaggeration may scarcely amount to one half of an average crop. In December it was reported from there that the first estimate of 200 cases was found to have been too low, as much oil was kept hidden in the villages by Chinese merchants and mandarins. The inhabitants have become suspicious, in a manner beyond comprehension, of the "Secret Societies" which work on the population and against which the French Authorities are powerless.

According to reports from the same source, a large Chinese firm at Nan-ning-foo on the Canton river has purchased 246 cases Tonquin oil of excellent quality, which are intended to be mixed with oil from Pak-se solidifying at only + 12° and which has been refused at Hong Kong; by these means a quantity of from 500 to 600 cases can be brought to a solidifying point of + 14°.

In view of the present situation, higher prices will have to be reckoned on in the near future. It is said that some 500 cases are held in London in one hand, and will not be sold at the present quotations. In Hamburg fairly large speculative stocks are also in existence.

**Tansy Oil.** The cultivation of the plant and distillation of the oil were carried on in the year 1902 in St. Joseph County, in the State of Michigan, by 2 growers[1]). The area under cultivation amounted to 52 acres from which 341 lbs. oil of tansy were obtained. The yield per acre amounts therefore to 13 lbs. oil.

**Turpentine Oil.** For the purpose of determining mineral oil which may possibly be present in oil of turpentine, by Burton's method, — viz., treatment of the oil with one and a half times the volume fuming nitric acid at reduced temperature, — H. Herzfeld[2]) has constructed a small apparatus by means of which the determination can conveniently be accomplished, and which makes it also possible to read off directly the quantity of the mineral oils not attacked by the nitric acid. For details we would refer to the literature mentioned below.

In a further publication[3]) Herzfeld proposes the use of concentrated sulphuric acid instead of fuming nitric acid; he proceeds as follows:

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[1]) Twentieth Annual Report of the Bureau of Labor of the State of Michigan, p. 447.

[2]) Zeitschrift f. öff. Chemie **8** (1902), 446, according to Chem. Centralblatt **1903**, I, 258.

[3]) Zeitschrift f. öff. Chemie **9** (1903), 454, according to Chem. Centralblatt **1904**, I. 548.

in the first place he allows 10 cc of the turpentine oil to be examined, to drop slowly and at slightly reduced temperature into 40 cc concentrated sulphuric acid. After 10 to 12 hours 8 to 9 % of the turpentine oil used separate off. Now the lower dark-brown layer is allowed to drain off, and the remaining oil is once more shaken with 3 to 4 cc fuming sulphuric acid. After standing for several hours, a further 1 to 2 % of the oil separate off, whilst if mineral oil is present the volume is proportionately larger.

M. Vèzes[1]) has published a work dealing with the examination of French oil of turpentine. He considers it useful in the examination to distinguish between normal adulterants such as resin oil and colophonium, which may enter into the turpentine oil during the manufacture, and abnormal adulterants, such as petroleum, benzine, etc., which are only subsequently added to the oil. The method tested by Vèzes resembles that recommended by Zune[2]) for testing for resin oil.

250 cc turpentine oil are divided by fractional distillation into five portions of 50 cc each, of which four are distillates, whilst the distillation-residue represents the fifth. Having regard to the fact that the boiling points of the adulterants differ from that of turpentine oil (152° to 160°), the middle fraction 3 can be regarded as pure oil, whilst the adulterants must be found in the extreme fractions. For this reason Vèzes determines under the identical physical conditions the indices of refraction $n$, $n_3$ and $n_5$ of the fractions 1, 3, and 5, and judges the purity of the oil from the differences of the values found, of which he designates $n_3 - n_1$ as $\delta$, and $n_5 - n_3$ as $\Delta$. By a systematic study of $\delta$ and $\Delta$ in mixtures of rectified turpentine oil with the adulterants possible in practice, he arrives at the conclusion that, when normal adulterants are exclusively employed, $\delta$ remains fairly constant (as in the case of rectified oil $0{,}0000 < \delta < 0{,}0010$), whilst $\Delta$ increases with the percentage X of the admixture. The experiments showed $\Delta = 0{,}0032 + 0{,}0037\,X$. From this formula the entire quantity of normal adulterants can be calculated; by determining the acid number A the percentage of colophonium is found from the equation $C = \frac{A}{1{,}7}$, so that from the difference $X - C$ the percentage of resin oil is ascertained. The addition of abnormal adulterants possible in practice is made specially conspicuous by a lowering of the boiling point, and by the considerable alteration in the differences $\delta$ and $\Delta$. Vèzes requires for a good commercial oil:

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[1]) Bull. soc. chim. III. **29** (1903), 896.

[2]) Compt. rend. **114** (1892), 490. — Gildemeister and Hoffmann, "The Volatile Oils" p. 237.

The distillation should not commence below 150°,
$\delta$ should be between 0,0000 and 0,0010,
$A < 1{,}0$,
$\Delta < 0{,}0125$ (corresponding to 2,5 % normal adulterants).

Herzfeld[1]) has also found the observation of the refraction of turpentine oil very useful for testing the oil. According to him, turpentine oil in a Zeiss' butter-refractometer, at 15°, generally shows 68° to 72°, rarely up to 75°. The refractions of the individual fractions of pure turpentine oil differ but little from each other and from the original oil, whilst even slight admixtures produce changes in this behaviour. A specific gravity below 0,865 characterises the oil always as suspicious. As even greatly adulterated turpentine oils generally still answer the requirements prescribed by the customs authorities for oil of turpentine as a denaturating agent of brandy, Herzfeld considers that those requirements should be altered.

A. Tschirch[2]) and G. Schmidt communicate the results of their examinations of the resin balsam from *Pinus laricio* Poiret (Austrian turpentine).

The turpentine obtained in the well-known manner from the black fir, represents a viscid non-transparent mass, whose specific gravity was ascertained at 1,875. By extracting the ethereal solution of the balsam with 1 % solution of ammonium carbonate, and subsequent usual treatment of the aqueous liquid, the above-named authors obtained a white amorphous acid, laricopinonic acid, in a yield of 25 %. By subsequent extraction of the ethereal solution with 1 % solution of sodium carbonate, an acid, laricopinonic acid, was isolated, which after recrystallisation formed colourless crystals and melted at 97°; the yield was 34 %. A 1 % potash-solution did not absorb anything further from the resin-solution thus treated; for this reason, the latter was freed from ether by distillation, and the residue distilled with steam, when (35 %) essential oil distilled over, whilst (2 %) resin, laricopino-resin, remained behind. On dry distillation of the resin balsam, 30 % colourless essential oil passed over up to about 100°. The essential oil driven over during steam-distillation represented a colourless, mobile liquid of the specific gravity 0,872, which had a pleasant turpentine odour. The taste is aromatic, slightly burning. The oil is soluble in ether, alcohol, methyl alcohol, benzene, carbon disulphide, acetic ether, and petroleum ether. It boils between 154° and 164°; the bulk passes over from 155° to 160°.

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[1]) Abstr. Chem. Centralblatt. **1904** I, 548.

[2]) Archiv der Pharm. **241** (1903), 570.

**Wintergreen Oil, natural.** The American market continues firm. Our New York branch, which has secured large parcels by contract at favourable prices, invoiced us the last consignments without advance in price, but holds out the certain prospect of a rise.

Artificial methyl salicylate has been depressed to the lowest limits, proportionate to the value of salicylic acid, but this has not promoted its use in any way whatever.

We have in our Reports repeatedly[1]) called attention to the observation, made from various sides, as to the wide distribution of salicylic acid in the vegetable Kingdom, and inter alia also pointed to the presence of this ester in the common pansy, *Viola tricolor*[2]). Induced by a botanical study on this plant by H. Krämer, in which it was stated that the fresh sprouting buds of *Viola tricolor*, when rubbed between the fingers, emitted the odour of wintergreen oil, we distilled at the time a fairly large quantity of the fresh flowering plant, when we obtained an essential oil which had a strong odour like wintergreen oil, and which consisted almost entirely of methyl salicylate, as was proved by the examination.

The same observations have now again been made by A. Desmoulière[3]), who appears to have no knowledge of our previous examinations, as he does not take our priority in this respect into consideration.

According to Desmoulière's further examinations, methyl salicylate is not present as such in the pansy, but, as the case of *Betula lenta* and other plants, occurs in the form of glucoside, which in the presence of water, under the influence of a ferment, is split up into methyl ester of salicylic acid and grape-sugar.

Desmoulière has succeeded in separating from *Viola tricolor* a glucoside which both on heating with dilute sulphuric acid, and by the action of the ferment contained in the plant, split off methyl salicylate. This glucoside, which is undoubtedly identic with gaultherin, could only be obtained in amorphous form, whilst the ferment (betulase or gaultherase) was not isolated at all.

From the fact that the odour of wintergreen oil only occurs when the herb is rubbed, Desmoulière concludes that the glucoside and the ferment are contained in different cells of the plant, and solely for this reason were unable to act already previously on each other. It is probable that in the other *Violaceæ* the same conditions prevail, but Desmoulière has as yet confirmed this only for the cultivated pansy.

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[1]) Report April **1898**, 55; October **1898**, 51; April **1899**, 51; October **1899**, 58.

[2]) Report October **1899**, 58.

[3]) Journ. Pharm. Chim. VI. **19** (1904), 121.

**Wormwood Oil.** The American distillate, which we had not carried in stock for a long time on account of the exaggerated prices, can now again be offered by us advantageously. French and Algerian oils are at present abundant, and can be supplied at very favourable prices.

The "Report of the Bureau of Labor" of the State of Michigan for 1902, gives interesting details on the cultivation of wormwood and the distillation of the oil in St. Joseph County. 17 farmers occupied themselves with the cultivation; from 90 acres of land they distilled 873 lbs. oil, that is to say 9,7 lbs. oil per acre.

**Ylang Ylang oil "Sartorius".** The exceptional demand for extra-fine oils, at the head of which our brand is found, has continued also during the last few weeks, and we were particularly fortunate in being able to fully meet this demand. Our sales in the year 1903 have again increased. They amounted in all to

63 cases of 4 kilos 200 gm. = 264 kilos 600 gm.
against 49 „ „ 4 „ 200 „ = 205 „ 800 „ in the year 1902.

This increase of about 60 kilos is undoubtedly the best proof of the popularity enjoyed by the brand "Sartorius". With regard to quality, it occupies without contradiction the first place.

Flacourt1) makes some interesting communications respecting the cultivation of ylang ylang trees in Réunion, which are based on practical experience, and therefore contain much useful instruction for those who are interested in the subject. Both *Unona latifolia* and *Unona odorata* which have now for a long time been grown as trees for avenues, are suitable for the cultivation. But an absolute necessity therefor are a tropical tranquil climate, and a porous soil containing a certain amount of moisture.

In order to grow the trees from seed, the latter, taken from the ripe fleshy berries, must be freed carefully by repeated washing from all traces of pulp, and immediately after the last washing be placed in the seed-bed which may be laid out in a rich, well-manured soil. The germ-plants make their appearance after 40 to 60 days and after 1 to $1^1/_2$ months are planted out in nurseries which must be situated n a shady place.

This planting out in nurseries is in Réunion generally preceded by a process which consists of this, that the young germ-plants are placed singly in vessels of beaker-form, so-called "tentes", which can be readily constructed from the leaves of *Pandanus utilis*. The plants transposed in one or other manner, require about 2 months to attain a height of 25 to 30 cm and to develop sufficiently.

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1) Revue des cultures coloniales **13** (1903), 366; **14** (1904), 16.

At this stage the plants are best suited to the process of transferring to the plantations. During the next two years the latter must be tended with care, and yield yet nothing.

From the third year onwards the trees begin to flower, and the crop can already be estimated at 150 to 200 francs per hectare ($2^1/_2$ acres). It is, however, necessary to see that the trees do not grow to a greater height than 2,5 to 3 m. This is done by cutting off the tops, which at the same time causes a powerful development of the lateral branches and an abundant formation of blossoms, so that the yield becomes very remunerative.

The flowering period of the ylang ylang trees commences in Réunion from January to February, but a regular formation of blossoms giving the best yield can only be reckoned upon from May to August. Those blossoms which are freshest when submitted to distillation yield oils of better quality. 50 to 64 kilos of freshly gathered blossoms produce 1 kilo oil, i. e. 1,56 to 2 %. The yield from one hectare of plantation laid out according to Flacourt is annually from 3 to 4 kilos oil, giving a net profit from 1116 to 1616 francs.

**Ylang Ylang "Schimmel & Co."** (German pat. No. 142 858). The demand for this excellent product was extremely brisk. This proves that the quality of our product meets with unanimous approval, and equals that of the best commercial brands. It is only intended to compete with the latter; where the requirements are not so high, a good rectified cananga oil will generally suffice.

We once more beg to call attention to our product, being convinced that trials made with it will give complete satisfaction.

## Italian Pharmacopœia.

To the new Editions of the Pharmacopœias which we have hitherto discussed in these pages, in so far as regards essential oils or their constituents, we now add the new (second) edition of the Italian Pharmacopœia, published last year. Here also we find the tests prescribed, etc., remodelled to a considerable extent, so that the advance, as compared with the previous edition, is unmistakable. Among the substances newly added is eucalyptol, whilst oil of bitter oranges and rose oil have been struck off the list of official oils.

Although the information given in the new Italian Pharmacopœia is, on the whole, correct, it requires in some places correction or amplification; for this reason we reproduce in the following pages the requirements given for the individual oils and preparations, in order to be able to discuss any details in as clear a manner as possible.

The alcohols mentioned in the Italian Pharmacopœia are, besides absolute alcohol, a strong alcohol of 90 % by volume, and a weaker one of 60 % by volume.

**Anise Oil** *(Essenza di anice).* Colourless or yellowish; $d_{15^\circ} = 0{,}98$ to 0,99[1]); congealing point + 14° [2]); soluble in every proportion in alcohol[3]); the solution of a few drops oil in alcohol must give a yellow and not a violet colouration with ferric chloride (test for phenol).

[1]) As occasionally a separation of anethol already occurs spontaneously at 15°, it is advisable to carry out the determination of the specific gravity of anise oil at 20°; in this case the limits of value are also those given above.

[2]) With good anise oils the congealing point lies between + 17° and + 19°; it is cooled below solidifying point to about 13°, and solidification is then brought about by inoculation with a crystal of anethol.

[3]) This is not correct; anise oil only dissolves in 1 to 3 volumes 90 % alcohol.

**Cajeput Oil** *(Essenza di cajeput).* Colourless, occasionally greenish owing to traces of copper; $d_{15^\circ} = 0{,}915$ to 0,930; soluble in alcohol in every proportion; if 1 cc oil is shaken with 10 cc dilute hydrochloric acid, the aqueous solution separated from the oil must give no brown-red colouration with potassium ferrocyanide (test for copper).

**Chamomile Oil** *(Essenza di camomilla comune).* Blue[1]); on exposure to air it becomes brown, also when in contact with alcoholic soda solution; $d_{15^\circ} = 0{,}93$ to 0,945[2]); soluble in 8 parts alcohol; when cooled to 0°, it should become viscous, but without congealing[3]).

[1]) The dark-blue colour of the oil changes under the influence of air and light gradually into green to brown.

[2]) More correct is: $d_{15^\circ} = 0{,}925$ to 0,940.

[3]) In consequence of its high paraffin-content, the oil only forms cloudy mixtures with 90 % alcohol, and at 0° congeals into a fairly solid mass.

**Cinnamon Oil**[1]) *(Essenza di cannella).* Colourless or bright-yellow, in course of time yellow to brown[2]); $d_{15^\circ} = 1{,}055$ to 1,065[3]); faint acid reaction; soluble in alcohol in every proportion; 4 drops cooled down to 0°, should form a crystalline mass[4]) when shaken with 4 drops fuming nitric acid; the solution of 4 drops cinnamon oil in 10 cc alcohol should acquire a red-brown colouration when 1 drop ferric chloride is added, and not green or blue (test for clove oil).

[1]) Whilst the former Pharmacopœia required Ceylon cinnamon oil, the altered specific gravity shows that cassia oil is now official; this appears to us of little advantage, as Ceylon cinnamon oil has an incomparably finer aroma than cassia oil.

[2]) The statements as to colour require correction; cassia oil is from the first dark-yellow or brown; neither of the two cinnamon oils is colourless.

[3]) More correct would be 1,055 to 1,070.

[4]) This test gives no indication of the purity of the oil. Comp. Gildemeister and Hoffmann, "The Volatile Oils", p. 384.

**Citron Oil**[1]) *(Essenza di cedro).* Greenish-yellow; the oil obtained by distillation is colourless[2]); $d_{15^\circ} = 0{,}857$ to 0,860; very slightly soluble in water, soluble in about 10 parts alcohol³), in every proportion in absolute alcohol.

[1] It is clear from the specific gravity required for the oil that the lemon oil expressed from the peel of *Citrus limonum* Risso (Essenza di limone) is meant, as the various citron oils, — which for the rest are not a commercial article at all, — are partly heavier, partly lighter than the oil mentioned above. Compare our Reports of October **1895**, 18; April **1902**, 30; April **1903**, 34.

[2] Lemon oil has a bright yellow colour; distillation of the oil is quite irrational, as such oils deteriorate very rapidly and acquire a disagreeable pungent odour.

[3] The solution in 90 % alcohol is not always perfectly clear, owing to the presence of slimy and vegetable wax-like constituents.

**Clove Oil** *(Essenza di garofani).* Yellowish, gradually changing to brown on exposure to the air; $d_{15^\circ} = 1{,}060$ to $1{,}070$ [1]; soluble in alcohol in every proportion; 4 drops oil should make a solid crystalline mass with 4 drops concentrated alcoholic potash solution. Identity-reaction and test for phenol in the usual manner.

[1] The specific gravity shows that only oils with a particularly high eugenol-content are allowed.

**Eucalyptol.** Colourless; $d_{15^\circ} = 0{,}930$ [1]; boiling point 176° to 177° [2]; almost insoluble in water, soluble in absolute alcohol, ether, chloroform and fatty oils; when cooled in a mixture of ice and common salt, eucalyptol should solidify into a crystalline mass [3] consisting of long needles melting at — 1°. If in a test tube moistened on the inside with eucalyptol, a little bromine vapour is introduced, brick-red needle-shaped crystals should be formed. With an equal volume carbon disulphide eucalyptol should form a clear solution (test for water).

[1] The specific gravity of pure eucalyptol free from water, lies between 0,928 and 0,930.

[2] The Italian Pharmacopœia unfortunately does not indicate the height of the barometer to which the boiling points relate; for this reason we would point out specially that all statements relating to the boiling point, if nothing is said to the contrary, refer to the normal height of the barometer (760 mm). Further, it should be noted that with such determinations the whole of the mercury thread which comes under consideration must be enveloped by the vapour of the liquid, which is accomplished by using normal thermometers with shortened scale. Otherwise the corrections necessary have to be made so as not to arrive at incorrect results.

[3] The solidification must sometimes be started by the introduction of a crystal of solid eucalyptol.

**Oil of Juniper berries** *(Essenza di ginepro).* Colourless or faintly greenish-yellow, becomes viscid under the influence of air and light, and then acquires a more yellow colour; $d_{15^\circ} = 0{,}865$ to $0{,}885$ [1]; soluble in nine parts alcohol [2], in one part carbon disulphide [3].

[1] The oils of juniper berries are also frequently lighter; we have had in our hands good distillates down to 0,860.

[2] Generally, quite freshly distilled oils only answer these requirements.

[3] A possible cloudiness is due to the slight content of water which is almost always present in the oil.

**Lavender Oil** *(Essenza di lavanda)*. Colourless or pale-yellow[1]); $d_{15^\circ} = 0,885$ to $0,895$; soluble in alcohol in every proportion.

[1]) Only rectified lavender oils are colourless, which, however, are inferior. Comp. Report October **1894**, 30.

**Menthol.** Colourless. Melting point 42° to 43°, boiling point 212°; almost insoluble in water, very readily soluble in alcohol and ether; menthol should dissolve without colouration in a mixture of 1 cc acetic acid, with 3 drops concentrated sulphuric acid and 1 drop nitric acid. When evaporated on a wather bath, 0,1 gm. menthol should leave no weighable residue.

**Mustard Oil** *(Essenza di senape)*. Colourless, gradually yellowish with reddish tinge; the artificial oil has the specific gravity 1,020[1]), the natural oil 1,018 to 1,025; boiling point 148°[2]); readily soluble in alcohol, ether, and carbon disulphide, very sparingly in water (1 : 1000); when a few drops of oil are boiled with alcoholic potash solution, and subsequently diluted with water, a violet coloration occurs when sodium nitroprusside is added; the solution of 0,5 cc oil in 2 to 3 cc alcohol must not be coloured red or violet by a drop of ferric chloride solution (test for phenol).

[1]) For the artificial oil, also certain limits of value should be fixed, as here also slight fluctuations cannot be avoided. The specific gravity of allyl isosulphocyanate lies between 1,020 and 1,025.

[2]) The statement with regard to the boiling point does not agree with the facts. A good mustard oil is required to boil chiefly between 147° and 152°, and the first as well as the last portion should have a specific gravity not appreciably differing from that of mustard oil itself.

With regard to the other points specially to be observed in the determination of the boiling temperature, compare eucalyptol, note 2, page 92.

**Orange-blossom Oil** *(Essenza di fiori d'arancio amaro)*. Colourless[1]), under the influence of air and light yellow to reddish; $d_{15^\circ} = 0,872$ to $0,890$[2]); soluble in 1 to 2 parts alcohol, when more solvent is added opalescence[3]); when the oil is shaken with a concentrated solution of sodium bisulphite, it should acquire a red colour[4]); the blue fluorescence of the oil becomes more pronounced when alcohol is added.

[1]) Freshly distilled neroli oil also is not colourless, but yellowish.

[2]) The specific gravity fluctuates between 0,870 and 0,880.

[3]) The statements respecting the solubility relate to alcohol of 80 % by volume, as neroli oil makes a clear solution with 90 % alcohol in every proportion; a slight opalescence in consequence of separation of paraffin occurs also in this case after some time.

[4]) This test is of no value for judging the oil.

**Peppermint Oil** *(Essenza di menta)*. Colourless, straw-coloured, or greenish; on exposure to air the colour becomes gradually yellow and the oil viscid; $d_{15^\circ} = 0,890$ to $0,920$; soluble in an equal part of alcohol; the oil solidifies between — 8° and — 20°, with separation of menthol; if a few drops of oil are heated on a watch-glass with 0,2 gm. pulverised iodine, no violent reaction should occur.

According to these statements, English as well as American oil is allowed.

**Rosemary Oil** *(Essenza di rosmarino).* Colourless or yellowish-green; $d_{15^\circ} = 0,90$ to 0,92; soluble in alcohol[1]) in every proportion.

[1]) An initial cloudiness must be attributed to the content of water always present in the oil.

**Thymol.** Melting point 50° to 51°; boiling point 228° to 230°; sparingly soluble in water (about 1 : 1200); soluble in less than 1 part alcohol, very readily in ether, glacial acetic acid, and fatty oils. When a thymol crystal is ground with a little solid potash and a few drops chloroform, a violet colouration should occur; the aqueous solution must be neutral, and should not acquire a violet colour when ferric chloride is added (test for phenol); 0,05 gm. thymol should evaporate completely on the water bath.

**Turpentine Oil** *(Essenza di trementina).* Colourless; boils at about 160°; $d_{15^\circ} = 0,865$ to 0,875; scarcely soluble in water, soluble in 8 to 10 parts alcohol, in every proportion in absolute alcohol, ether, chloroform, carbon disulphide, essential and fatty oils; on exposure to the air the oil resinifies; neutral reaction; when kept in a bottle only partly full, the oil acquires a yellow colour and an acid reaction; the oil must volatilise completely.

For many purposes the crude oil may be employed, which is colourless or faintly yellow, and which on evaporation leaves about 2 % residue.

An old ozonised oil which colours potassium iodide starchpaste blue should also be kept in stock.

## Novelties.

In the last six months a whole series of new or rare essential oils has again been submitted to examination in our laboratory, and the most interesting of these are mentioned below.

From Japan we received once more a

**Yomugi Oil.** It agrees well with the sample referred to in our last Report (p. 78): $d_{15^\circ} = 0,9126$; $\alpha_D = -18^\circ 50'$; acid number $= 1,32$; ester number $= 16,19$. The solution in 90 % alcohol, which is at first clear, becomes cloudy when more solvent is added.

With regard to the species of plant from which the oil is obtained, opinions differ. Whilst according to J. J. Rein[1]) yomogi is the Japanese

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[1]) J. J. Rein, Japan, from travels and studies. Leipzig 1886, II, 160.

word for *Artemisia vulgaris*, information which has lately reached us states that the oil is the distillate from the "kiku", i. e. chrysanthemum *(Chrysanthemum [Pyrethrum] indicum* L. and *Ch. sinense* Sabin.). The first opinion is in so far very probably correct, as the distillates are fairly similar to those obtained from our indigenous mugwort, whilst they show much less resemblance to a kiku oil¹) examined by us years ago.

From the same source is derived a

**Kuro-moji Oil.** This pale-yellow, almost colourless oil had the following constants: $d_{15^\circ} = 0{,}8947$; $\alpha_D = -14^\circ\ 29'$; ester number $= 29{,}87$; soluble in 0,9 volume and more 80 % alcohol. The oil contained cineol, which was identified by the iodol compound. The coriander-like odour of the oil renders it likely that it also contains linalool. On the whole, the composition of the oil appears to differ from those of oils examined previously ²). The decidedly finer aroma of the present oil already points to this; and this finer aroma will no doubt secure for the oil a lasting place in the perfumery industry.

Under the name of

**May Oil** we received a distillate originating from Porto Rico, of *Calyptranthes paniculata* Ruiz et Pav. belonging to the Myrtaceæ. The oil, which resembles lemongrass oil, had the specific gravity (15°) 0,9509, and an optical rotation of $-1^\circ\ 52'$. It dissolves very readily in 80 % alcohol, but in 70 % alcohol the solubility is incomplete. The oil contained 62,5 % citral.

The following distillates originate from Florida:

**Oil from Mentha citrata Ehrh.,** a plant which in Florida is popularly known as "bergamot mint". The oil, obtained in a yield of about 0,2 % from young, not flowering, but fresh plants (without roots), had a pale-yellow colour and a pleasant odour reminding even more of lavender oil than of bergamot oil. $d_{15^\circ} = 0{,}8826$; $\alpha_D = -5^\circ\ 35'$; ester number $= 31{,}28 = 10{,}95$ % linalyl acetate; soluble in 2 and more volumes 70 % alcohol.

From the same plant a distillate is obtained from the frozen leaves, in about the same yield, which differed in its properties from the above-mentioned oil. $d_{15^\circ} = 0{,}8895$; $\alpha_D = -1^\circ\ 41'$; ester number $= 111{,}28 = 38{,}95$ % ester (calculated for linalyl acetate); soluble in 2 and more volumes 70 % alcohol.

In consequence of the higher ester-content, the odour of linalyl acetate was here even more pronounced than in the previous oil. We must leave it an open question, to what cause the very considerable differences in the constants of the two distillates must be attributed.

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¹) Comp. Gildemeister and Hoffmann, "The Volatile Oils" p. 682.

²) Comp. Gildemeister and Hoffmann, "The Volatile Oils" p. 404.

**Oil from Hyptis spicata (Poit.) Briq.** *(Mesosphaerum spicatum).* The plant belonging to the family of the labiatæ, and which, like the two following, grows in Florida in great abundance, yielded a very small quantity (about 0,005 $^0/_0$) of a bright-yellow oil with a faint mint-like odour: $d_{15^\circ} = 0,915$; $\alpha_D = -27^\circ 25'$; acid number = 2,17; ester number = 4,35; insoluble in 10 volumes 80 $^0/_0$ alcohol; further determinations of solubility could not be made owing to lack of material.

Judging from the odour, it is probable that the oil contains small quantities of menthone or pulegone.

**Oil from Ambrosia artemisiæfolia L.**[1] The young not flowering plants yielded about 0,15 $^0/_0$ of a green oil with a pleasant aromatic odour, which had the specific gravity 0,876 at 15°; $\alpha_D = -1^\circ$; ester number = 7,94. The oil makes a clear solution with an equal volume 90 $^0/_0$ alcohol, which becomes cloudy when more solvent is added.

**Oil from Eupatorium capillifolium,** dog fennel oil[2]). The pale-yellow distillate obtained from the flowering herb in a yield of about 0,1 $^0/_0$, agrees well in its constants with a previously examined oil[3]), $d_{15^\circ} = 0,926$; $\alpha_D = +18^\circ 38'$; ester number = 7,11; makes a cloudy solution with 3,5 and more volumes 90 $^0/_0$ alcohol. High phellandrene content.

A number of South Australian eucalyptus and cajeput oils can also be mentioned.

All the eucalyptus oils[4]) had a high cineol-content, were free from phellandrene, and dissolved in 1 to 1,5 and more volumes 80 $^0/_0$ alcohol.

**Oil from Eucalyptus microcorys F. v. Müll.** $d_{15^\circ} = 0,9038$; $\alpha_D = +12^\circ 29'$.

**Oil from Eucalyptus punctata D. C.** $d_{15^\circ} = 0,9060$; $\alpha_D = +4^\circ 10'$; small quantities of cuminic aldehyde could be detected.

**Oil from Eucalyptus resinifera Smith.** $d_{15^\circ} = 0,9123$; $\alpha_D = +6^\circ 1'$. The oil differs considerably in its constants from one which we examined years ago, and we must therefore assume that the latter, whose origin was not quite certain, was the distillate from another species of eucalyptus.

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[1]) See also Gildemeister and Hoffmann, "The Volatile Oils" p. 672.

[2]) According to the U. S. Dept. of Agriculture, the name of the plant from which dog fennel oil is obtained, is not, as had hitherto been accepted, *Eupatorium foeniculaceum* Willd., but *Eupatorium capillifolium* (Lamarck) Small.

[3]) Gildemeister and Hoffmann, "The Volatile Oils" p. 667.

[4]) With regard to the eucalyptus oil mentioned here, comp. also Gildemeister and Hoffmann, "The Volatile Oils" p. 533, 534, 532.

With regard to the mother-plants of the South Australian cajeput oils, we are unfortunately unable to give any information. We regret this all the more, as the oils differ from those known up to the present. The properties may follow here:

**Cajeput oil, blanc.** $d_{15^\circ} = 0{,}8908$; $\alpha_D = + 8^\circ 8'$; soluble in 0,5 and more volumes 90 % alcohol. The colourless oil has a pepper-like odour, and probably contains cymol.

**Cajeput oil, vert.** $d_{15^\circ} = 0{,}8727$; $\alpha_D = + 32^\circ 40'$; soluble in 5 and more volumes 90 % alcohol. The oil which was coloured blue by copper, reminds by its odour of amyl alcohol and cineol; the latter could be detected in the oil by means of the iodol-reaction.

**Cajeput oil, larges feuilles.** $d_{15^\circ} = 0{,}8854$; $\alpha_D = + 9^\circ 7'$; soluble in 2,5 and more volumes 70 % alcohol. The oil has a pale-green colour, and is characterised by a very pleasant odour, resembling coriander; it is therefore probable that the oil contains linalool.

**Essence de Bruyère.** This oil, also originating from Australia, has a pleasant aromatic odour, a pale greenish-blue colour (traces of copper), and a specific gravity of 0,8587 at 15°; $\alpha_D = + 2^\circ 44'$; soluble in 4,5 and more volumes 90 % alcohol. We have not been able to learn anything with regard to the plant from which the oil is obtained.

**Oil from Erythroxylon monogynum.** The oil distilled from the wood of *Erythroxylon monogynum* Roxb. in a yield of 2,56 %, represents a sticky crystalline mass with a pleasant odour reminding of oil of guaiac wood. The specific gravity is less than 1; melting point = 42° to 45°; acid number = 6,77; ester number = 1,56; ester number after acetylation = 131. Soluble in 1 volume 90 % alcohol with slight cloudiness, which disappears when more alcohol is added.

For the purpose of examining the crystallising body, the last runnings of the oil were first of all submitted to distillation in vacuo, and the portion passing over between 212° and 216° (8 mm) was frozen out from the smallest possible quantity of petroleum ether. After subsequently recrystallising twice from petroleum ether, a compound of the melting point 117° to 118°, crystallising in brilliant needles, was obtained. analyses of which gave results corresponding to the formula $C_{20}H_{32}O$:

I. 0,1064 gm. of the substance yielded 0,3246 gm. $CO_2$ and 0,1070 gm. $H_2O$
II. 0,1206 „ „ „ „ „ 0,3672 „ $CO_2$ „ 0,1206 „ $H_2O$

| | Found: | | Calculated for $C_{20}H_{32}O$: |
|---|---|---|---|
| | I. | II. | |
| C | 83,2 | 83,04 % | 83,24 % |
| H | 11,18 | 11,11 % | 11,21 % |

The molecular weight was determined after lowering the freezing point in benzene solution. In consequence of the cryoscopic behaviour of the present compound the data obtained, which rose on increasing concentration from 247 to 307, were not constant. The compound $C_{20}H_{32}O$ requires the molecular weight 288. The specific rotatory power was determined in 13% chloroform solution at + 32° 28′.

In order to demonstrate the alcoholic character, 4 gm. were boiled with 6 cc acetic acid anhydride in the presence of sodium acetate. After destroying the excess of acetic acid anhydride by heating with water, the acetate crystallised out on cooling, and after recrystallisation from alcohol this acetate melted at 72° to 73°.

Analysis:

0,1711 gm. of the substance yielded 0,4986 gm. $CO_2$ and 0,1552 gm. $H_2O$

| | Found: | Calculated for $C_{22}H_{34}O_2$: |
|---|---|---|
| C | 79,48% | 80,00% |
| H | 10,08% | 10,30% |

## Notes on recent scientific work concerning terpenes and terpene derivatives.

The work in connection with the elucidation of the constitution of camphor, which numerous investigators have now been carrying on for many years, has at last reached a certain degree of finality by the synthesis of camphoric acid accomplished by Komppa[1]). Komppa selected as his crude material methyl ester of diketoapocamphoric acid, which he had already previously produced by condensation of oxalic ester with methyl ester of ββ-dimethyl glutaric acid, and methylated the ester in the usual manner, thereby obtaining diketocamphoric acid ester soluble in soda. On treatment with sodium amalgam this ester yielded a dioxy ester, from whose acid an unsaturated camphoric acid was obtained by boiling with hydriodic acid. By attaching hydrobromic acid, and subsequently reducing with zinc dust and glacial acetic acid, there was finally obtained an oily acid, which by treatment with acetyl chloride could be split up into a non-anhydrised camphoric acid (which for the moment has not been further examined), and an inactive camphoric acid anhydride. The latter showed the same melting point 217° to 219° as the anhydride produced from the natural acid, and yielded on hydratation an acid of the melting point 200° to 202°, viz., the same melting point as the inactive camphoric acid of Chautard. The synthetic products proved to be identic with the corresponding derivatives of natural camphor.

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[1]) Berl. Ber. **36** (1903), 4332 (preliminary communication).

The importance of this synthesis lies in the fact that of the many camphor formulæ proposed in the course of time, the one drawn up by Bredt in 1893, whose correctness was borne out by many important facts, now appears to be finally established. As, according to Haller, camphoric acid can be converted into camphor, the complete synthesis of camphor has now been rendered possible by Komppa's work.

In 1899, J. Klimont¹) made an attempt to draw up aromatophorous groups for the artificial and natural perfumes, and to discover the relationship between the chemical constitution and the odorous action. A. Bolis²) has inquired into the same subject. He expresses in the first place the opinion, that after the development which the chemistry of artificial perfumes has experienced during the last few years, a displacement of the natural products by those produced synthetically will follow, as has already been largely the case in the chemistry of colouring matters. The views laid down by the author on certain laws prevailing within the group of odorous substances, have in part already been expressed by Klimont. On the whole it must be said that the examples quoted are not by any means sufficient to deduce therefrom a definite relationship between the odour-intensity and the behaviour on boiling or the entrance of certain groups. The assumption that in nature only the aliphatic compounds of the iso-series occur, and never those of the normal-series, is incorrect; for, in addition to citral, citronellal, geraniol, bodies of the normal aliphatic series have often been discovered as intensive odorous matters in essential oils, — e. g., the normal octylic, nonylic, and decylic aldehydes, the normal octyl and nonyl alcohols, and also the normal amyl, heptyl, and nonyl methylketones.

It is well known that by esterification of the alcohols and ether-formation of the phenols, important perfumes are formed, frequently of greater value than the individual components; but we must point out that this rule is also not without exceptions. With regard to the example quoted by the author, that salicylic aldehyde, which already possesses a good odour, has a much lower odour-intensity than its methyl ether, anisic aldehyde, it should be said that anisic aldehyde is not the ether of salicylic aldehyde, but of p-oxybenzaldehyde. A distinct relationship is further found in homologous series, where the similarity of odour is striking, especially between the members which stand closer to each other.

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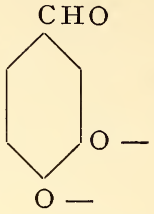
¹) J. Klimont, The synthetic and isolated aromatics. Vienna 1899.

²) A. Bolis, On the odour of organic compounds. Chemiker-Zeitung **28** (1904), 61.

It is also remarkable that in certain substances which possess the same odour, identical grouping in the molecule sometimes occurs, for example



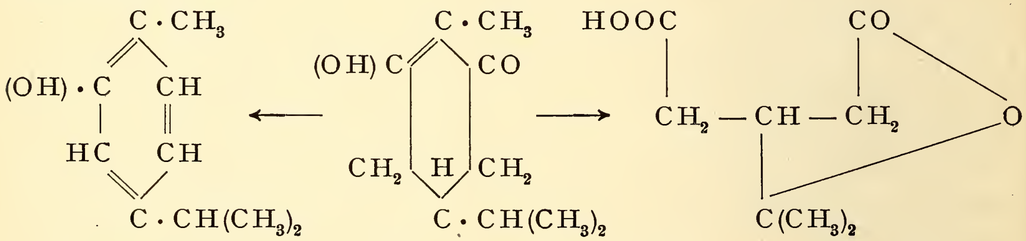
in the vanillin and heliotropin groups, and the grouping

$$C_6H_5CH = CH—$$

in the cinnamic compounds.

L. Balbiano and V. Paolini[1]) supplement their statements[2]) with regard to the reaction of mercuric acetate on terpenes and compounds which carry a $C_3H_5$-group in the molecule.

The ketone alcohol $C_{10}H_{16}O_2$ formed from l-pinene is converted almost completely into carvacrol $C_{10}H_{14}O$ by dilute sulphuric acid. From this follows, in agreement with the formation of terpenylic acid by oxidation, for the body $C_{10}H_{16}O_2$ the constitution of a $\Delta^6$-6-oxy-menthene-2-one:



Carvacrol Terpenylic acid

d-pinene yields with mercuric acetate the same oxidation-product, which proves that the oxidation simultaneously takes place in both asymmetric carbon atoms of the pinene-formula drawn up by Wagner and v. Baeyer.

The mercury compound formed on treatment of camphene with mercuric acetate has been found to be a mercuric addition-product of the formula $C_{10}H_{16}O(HgC_2H_3O_2)_2$, which, as we already mentioned in our April Report 1903, can be converted into camphene by hydrogen sulphide. The same conversion takes place on reduction with sodium amalgam, or with zinc and soda liquor. The formation of an addition-product therefore confirms Wagner's assumption that the camphene molecule contains an ethylene-linking.

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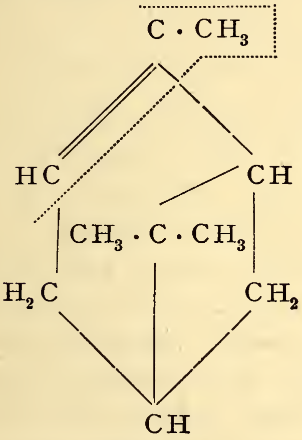
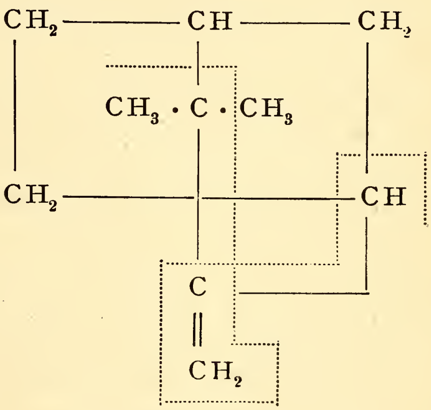
[1]) Berliner Berichte **36** (1903), 3575.

[2]) Berliner Berichte **35** (1902), 2995. — Report April **1903**, 83.

In the course of the examination of compounds with the radical $C_3H_5$, it has now been found that the chain $C_3H_5$, if it represents a propenyl-group $\cdot CH:CH\cdot CH_3$, yields oxidation-products with mercuric acetate; but if it is an allyl-group $\cdot CH_2\cdot CH:CH_2$, yields mercuric addition-products. In perfect agreement with this are the products obtained from pinene and camphene, and in the following formulæ for the two terpenes the above-mentioned groups are clearly shown.

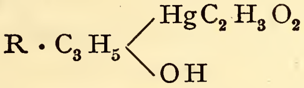


Pinene



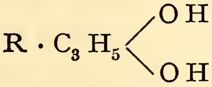
Camphene

Compounds with an allyl-group, such as methyl chavicol, methyl eugenol, safrol, etc. therefore give addition-products which are composed according to the general formula



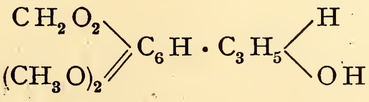
$$R\cdot C_3H_5\left\langle\begin{matrix}HgC_2H_3O_2\\OH\end{matrix}\right.$$

and consist of two isomers each. On the other hand, substances with a propenyl-group, such as anethol, methyl isoeugenol, and isosafrol, form oxidation-products in the form of glycols of the composition



$$R\cdot C_3H_5\left\langle\begin{matrix}OH\\OH\end{matrix}\right.$$

with separation of the characteristic leaflets of mercurous acetate. All addition-products yield again the original compound on reduction with zinc and soda liquor. An exception hereto is apiol, whose mercuric addition-product is reduced to the body



$$\left.\begin{matrix}CH_2O_2\\(CH_3O)_2\end{matrix}\right\rangle C_6H\cdot C_3H_5\left\langle\begin{matrix}H\\OH\end{matrix}\right.$$

a crystalline compound of the melting point 29,5° to 30,5°, with a slight apiol odour. The oxidation-product of isoapiol corresponds to the glycols obtained from isosafrol and methyl isoeugenol.

It is well known that for this simultaneous distillation of two non-miscible liquids, the formula $\frac{P}{P^1} = \frac{MF}{M^1F^1}$ applies, in which P and $P^1$ represent the quantities by weight of the two substances distilling over in the unit of time, M and $M^1$ their molecular weights, F and $F^1$ the steam-pressure during the distillation. On the strength of this proposition E. Charabot and J. Rocherolles[1] have subsequently determined, experimentally as well as by calculation, what influence an alteration in the temperature has on the ratio $\frac{P}{P^1}$, and they found that, according to the selection of the liquids distilling simultaneously, this value is either larger or smaller than 1. When water is distilled simultaneously with limonene, geraniol, linalool, citronellol, or methyl heptenone, it advances with increasing temperature towards 1, whilst with pinene, benzene, isopentane, or normal hexane, with increasing temperature, it falls towards 1. In other words, of the above-named substances, such as linalool, etc. when distilled simultaneously with water more will pass over at ordinary pressure than at reduced pressure; on the other hand, in order to obtain the same result with substances such as pinene, etc., it will be necessary to perform the simultaneous distillation of one of these bodies with water, at reduced pressure. The two last-named chemists have lately[2] applied these conditions to the distillation with water vapour which is of such enormous importance for the manufacture of essential oils, and they distinguish the following two cases, after tests as described: 1. Water vapour passed through turpentine oil which in a vessel was kept at a lower temperature than the combined boiling point of water and turpentine oil (about 98°). Here, while the oil was simultaneously heated to the combined boiling temperature of water and turpentine oil, a condensation of steam naturally took place, and with it a distillation of two non-miscible liquids. This phenomenon was therefore identic with the one mentioned above. 2. Another result, however, was obtained with the test when the temperature of the oil was raised above the common boiling temperature of water and oil (i. e. above 100°). Here, of course, no condensation of steam took place.

The formula $\frac{P}{P^1} = \frac{M\varphi}{M^1h}$ is here sufficiently exact; h represents the tension of the water vapours (equal to the pressure in the vessel), $\varphi$ the tension of the oil vapour saturated with steam, with regard to the temperature of the mixture of the vapours of the two liquids. It

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[1] Compt. rend. **135** (1902) 175.
[2] Compt. rend. **138** (1904), 497.

follows that the value $\frac{P}{P^1}$ may vary within very wide limits. It will increase, on the one hand, if the pressure in the apparatus diminishes, and therefore when a vacuum is employed, and on the other hand, if the temperature of the oil which is to be distilled is raised.

These facts, however, are not new to the essential oil industry. The more simple case, in which the steam passes through the oil present in the copper and heated by the jacket or worm, has been employed in practice as long as water vapour in tension has been used.

With regard to the other case, that of distillation in vacuo with direct introduction of steam into the heated oil, — this has been used in our factory on the largest scale for more than a decade. And we do not believe that we are mistaken if we say that also in other essential oil factories this method of distillation is already known.

In our next Report we hope to deal further with these interesting examinations.

On the essential oil industry of the United States in the year 1902, Pietrusky[1]) gives some particulars based on the Twelfth Census Report of the United States. Natural oils are produced at 97 places, giving employment to 167 workmen; the comparatively small number of the latter is explained by the fact that the oil-production is carried on chiefly by farmers in their houses, with very simply constructed retorts, which, in many cases, are portable. Of the most important oils, such as peppermint, sassafras, and wintergreen oils, the methods of production, yields, and quantities produced are given. The manufacture of synthetic oils is carried on in four factories; the same number of works produce vanillin. The import and export figures for the year 1898 to 1902 are very remarkable; whilst the value of the imports of essential oils increased from 1,51 to 2,09 million dollars, the value of the exports decreased from 201 000 dollars in 1898 to 166 000 dollars, but reached the former level again in 1902. The export of peppermint oil, however, has continuously fallen off, from 145 000 lbs. in 1898 to 36000 lbs. in 1902.

## Pharmacologico-physiological notes.

G. Pégurier[2]) recommends the prescription of menthol for internal administration in the form of mixtures shaken with gum arabic — for example, menthol 0,03 to 0,05 gm., syrup. gummos. 120,0 gm. —, as such mixtures are always identical, and menthol can be properly divided in this manner.

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[1]) Chem. Industrie **26** (1903), 618.

[2]) Apotheker-Zeitung **19** (1904), 54.

The valerianic acid esters of borneol and menthol, whose action has been described in several communications, possess therapeutical interest.

Bornyl valerianate, known as a constituent of valerian oil, has been examined for its therapeutic action by L. Hirschlaff¹). He employed it with patients who suffered from functional nervous symptoms of the systems of circulation and digestion, and of the central nervous system. The remedy was well tolerated, and was found to be reliable and harmless in nervous complaints of all kinds, and specially in nervous affections of the heart.

According to Kerner²), menthyl valerianate is an analeptic with a certain action, which is taken not unwillingly, and which when employed as an enema acts instantly. It deserves special attention as an antinervous remedy, as it also acts as a stomachic. Against sea-sickness it has proved a prophylactic.

E. Varenne, J. Roussel, and L. Godefroy³), have, like S. Laloue, lately arrived at the conclusion, after physiological examinations made during the last three years, that anethol and also anise oil, even in doses of 3 gm. per kilogram weight of the animal, i. e. quite important doses, do not produce the slightest toxic symptoms. The authors believe to be justified in accepting already on the strength of the chemical constitution of anethol, that it possesses an antiseptic analgetic action. It has been proved in practice that in certain disturbances of the stomach and intestinal canal, an infusion, tincture, etc. of anise has an excellent effect. The experiments were made with rabbits and dogs, and after continued administration of anethol, these animals were in a perfectly normal condition and showed no symptoms of disease. The above-named scientists have also studied the action of anethol on themselves, and were unable to detect any injurious consequences whatever. It is stated that the removal of anethol from the organism, by the lungs and urine, already commences in 10 to 15 minutes after administration. The authors believe to have discovered during their experiments a reaction for anethol, which consists of this, that the oil to be examined (3 cc) is heated with 2 to 3 cc glacial acetic acid and 5 cc fuming hydrochloric acid. The occurrence of a green colour points to the presence of anethol. The isomeric methyl chavicol is said to produce under the same conditions an amethyst-red colour.

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¹) Allgem. med. Central-Ztg. **47** (1903). According to Therap. Monatshefte **18** (1904), 43.

²) Klin. therap. Wochenschrift **1903**, 29. According to Pharm. Centralhalle **44** (1903), 917.

³) Compt. rend. **137** (1903), 1294.

On the value of spices for nutrition, Liebreich[1]) makes some communications; we would select for special attention those which deal with mustard. The action of mustard in the process of digestion is probably almost exclusively that of mustard oil, which in small quantity acts as a bactericide, without, however, disturbing the functions of the digestive ferments. In the presence of mustard oil, therefore, the digestion proceeds normally; but if a change in the digestion occurs through putrefaction-bacteria, the vitality of the latter is arrested or destroyed in the presence of mustard oil, by which the chemical force of the digestion is promoted in a marked degree. In addition to this function of the mustard, it has the property of producing an increased secretion of the gastric juice by the irritating action of the essential mustard oil. The mustard oil is becoming resorbed, and is also capable of exerting in small non-toxic quantities a more distant desinfecting action on the blood and the other tissues.

The medicinal applications of turpentine oil mentioned by Kobert in our last Report, can now be supplemented by the following.

Chéron[2]) directs attention to a method of subcutaneous injection of turpentine oil for producing local abscesses (so-called sterile suppurations) in septicæmia which had already been employed in 1891 by Fochier. In his experiments Chéron followed exactly Fochier's directions by injecting in the flank or arm 1 cc of a sterilised solution of turpentine oil. In the majority of the cases observed, a local reaction became apparent 5 to 6 hours after injection by the occurence of inflammation, and after a few days the collection of sterile pus could be observed. The ulcers rarely opened spontaneously, but were cut open as soon as the skin commenced to shrivel up, even when complete absence of fever was not observed. As soon as the evolution of an abscess was arrested, and the diseased state still apeared to be serious, a second injection was made and a further abscess produced, and so on. The therapeutic value of the process can be estimated from the recorded clinical observations of puerperal fever. Although with some of the patients treated according to this method the injections of turpentine oil did not have the desired effect, because they had been made at too late a stage, and the patients died, — yet in the cases which recovered the recovery must undoubtedly be attributed to the use of the injection. In all the cases where recovery took place, there were observed on the day of the injection or on the following day, a diminishing of the fever and of the pulsations, and an improvement in the general condition. In view of the harmless character, the ready

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[1]) Therap. Monatshefte **18** (1904), 65.

[2]) L'obstétrique **7** (1902), 398.

application, and the effect observed in some cases, the method should be tested further, as it is here a question of combating an infection-disease against which one had up to now often been powerless.

The view recently discussed in a treatise by E. Fromm and P. Clemens[1]) that sabinol, during its passage through the animal organism, attaches itself to a reducing substance which differs from ordinary glycuronic acid, possibly a penturonic acid, has after all been found to be erroneous. For it was subsequently[2]) found, that the acid isolated from the urine of animals poisoned with sabinol, is identic with the ordinary glycuronic acid which was at first expected. For further information we must refer to the original treatises.

## Phyto-physiological Notes.

It is well known that essential oils are a product of vegetal metabolism. For this reason it is interesting to learn that when the oils act externally on the plants, they have been found to be powerful poisons towards the latter. This, namely, is the result arrived at by A. Heller[3]) in his thesis "On the action of essential oils and some allied bodies on the plant". The experiments were made by submitting germ-plants and parts of plants under bell-shaped glass shades, with certain precautions, to the action of the bodies to be examined. As such were used essential oils and hydrocarbons in the form of vapour, liquid paraffin, and resins dissolved in turpentine oil, olive oil, or paraffin. The former were vaporised on paper folded in the shape of a fan, the latter introduced by means of a strip of paper into an incision made in the stem. The result of the experiment is essentially as follows: the toxic effect of the essential oils is very powerful. In the liquid state, or when dissolved in water, they act less powerfully. Oil-producing plants have a higher resistance to their own oil than strange plants. The oil vapour enters the plant by the gas channels, dissolves in the imbibition-water of the membrane, and in this manner reaches the interior of the cell. The cuticula renders the action slower, but does not arrest it. A dry membrane offers less protection than an imbibed one. Volatile hydrocarbons show the same action as essential oils. The absorption of dissolved resins in the living cell does not appear to be possible with artificial supply. Paraffin is not absorbed in the living cell by mosses and fungi.

The information on the presence of essential oils in hepatica, which up to the present was very scarce, has been enriched somewhat by a

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[1]) Zeitschrift für physiologische Chemie **40** (1903), 251.

[2]) Zeitschrift für physiologische Chemie **41** (1904), 243.

[3]) Thesis, Leipzig, **1903**.

thesis by Carl Ernst Julius Lohmann[1]). From the work, entitled "Contribution to the Chemistry and Biology of Hepatica", we abstract the parts on essential oils which are of interest to us.

From all the hepatica examined by the author (*Fimbraria Blumeana, Pellia epiphylla, Metzgeria furcata, Fegatella conica, Marchantia polymorpha, Mastigobryum trilobatum, Lunularia vulgaris, Targionia hypophylla, Aneura palmata, Madotheca platyphylla)*, essential oils could be obtained by steam distillation. The yields fluctuated between 0,01 and 0,9 $^0/_0$ of the dry substance. The odour of the oils reminded of the respective mosses. In view of the small quantities — frequently it was a question of only a single drop, but very little could be ascertained about the chemical character. The author determined by analyses the ratio of carbon to hydrogen as 1,51 to 1,61, and from this he deduced the fact that the oils belonged to the terpene-series. The oil of *Mastigobryum trilobatum* which was examined most in detail (of this about 8 gm. = 0,9 $^0/_0$ were available), had at 16° the specific gravity 0,972, and deflected the plane of polarised light to the right. It boiled at 270° to 285°. In the residue there remained a brown-coloured viscid liquid which solidified into colourless needle-shaped crystals. Dried between filtering paper, they melted at 78° to 85°. With acetic acid and concentrated sulphuric acid the oil gives a red colouration. In ethereal solution it absorbs bromine, but it does not yield a crystallised bromide.

With regard to the usefulness of the essential oils, the author agrees with Detto[2]) that they form a protection against animals.

## Hydrocarbons.

For the hydration of terpenes, Semmler[3]) had recommended the use of sodium and alcohol and had been able to accomplish thereby reductions in the case of hydrocarbons with so-called conjugated double-linkings. Semmler had further mentioned the possibility that the capacity for reduction of unsaturated phenol ethers is dependent upon the proximity of the aliphatic double-linking in the benzene-nucleus, and he arrived at the conclusion that these two contiguous double-linkings were capable of reacting like a conjugated system. This view is opposed by Klages[4]) who demurs to the equalisation of an aliphatic double-linking and one of the three double-linkings of the ring on which the benzene character depends. From his earlier as well as his more recent work, Klages concludes that the reduction of the vinyl, or the propenyl side-chain, essentially depends upon the character of the radicles linked in the side-chain and also in the

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[1]) Thesis, Jena 1903.

[2]) Report October **1903**, 82.

[3]) Berliner Berichte **36** (1903), 1033. — Report October **1903**, 83.

[4]) Berliner Berichte **36** (1903), 3584.

benzene-ring. Thus, the grouping $>C = C(CH_3)_2$, which also occurs in terpinolene, cannot be reduced into unsaturated benzene homologues (styrenes) nor in phenol ethers. If a hydrogen atom of the carbon atom of the side-chain linked to the benzene-ring is displaced by an alcohol radical, a reduction only occurs in the case of styrene-like hydrocarbons, whilst the corresponding phenol ethers undergo hardly any change. On the other hand, the vinyl and propenyl groups are always reduced readily. Klages further concludes that the reduction-capacity depends upon the position of the benzene-rest towards the double-linking, from the behaviour of the olefines, of which, for example, hexadecylene only attaches hydrogen to one of the double-linked carbon atoms after the entrance of a phenyl-group.

In view of the well-marked difference between the otherwise closely-allied styrenes and phenol ethers, Semmler's conclusion cannot be maintained in its entirety. In connection with these observations Klages supplies experimental proofs of the facility with which various vinyl phenol ethers of the o-, m- and p-series can be reduced.

Pinene. In continuation of our Report¹) on the publication by Gray, Henderson and Smith dealing with oxidation of pinene with chromyl chloride, we may add that the authors have meanwhile made a detailed communication on the same subject²). The formula of the ketone which occurs in the oxidation is not $C_9H_{14}O$, as mentioned in the first work, but $C_{10}H_{14}O$.

Camphene. With regard to the mercury compound formed with mercuric acetate, see page 101.

Sesquiterpenes. O. Schreiner³) continues in a number of essays his monographs of the sesquiterpenes. He deals especially in detail with caryophyllene, its history, occurrence, and physical and chemical constants, and in addition discusses cedrene, clovene, conimene, cubebene, galipene, guajene, gurjunene, heveene, humulene, and ledene.

## Alcohols.

Nerol. H. v. Soden and W. Treff⁴) have made some further communications with regard to nerol, the geraniol-like alcohol discovered by Hesse and Zeitschel⁵) in neroli oil. They declare that

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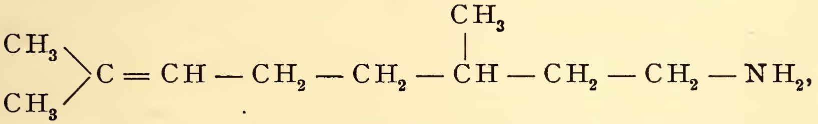
¹) Report October **1903**, 85.
²) Journ. Chem. Soc. **83** (1903), 1299.
³) Pharm. Arch. **6** (1903), 103, 116, 129. Pharm. Rev. **22**, 2 (1904), 60.
⁴) Chemiker-Zeitung **27** (1903), 897.
⁵) Journ. für praktische Chemie II. **66** (1902), 481. Report April **1903**, 54.

they have succeeded in producing nerol now absolutely free from geraniol, and give the following constants for this alcohol:

$d_{15^\circ} = 0{,}8813$; $\alpha_D \pm 0^\circ$; boiling point 226° to 227° at 755 mm; 125° at 25 mm.

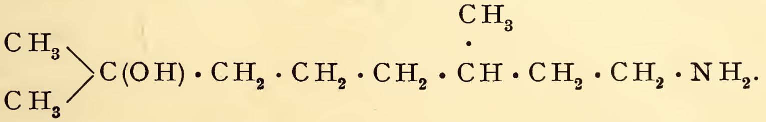
This compound absorbs four atoms bromine and has the composition $C_{10}H_{18}O$. The melting point of the diphenyl urethane was found at 52° to 53°, whilst Hesse and Zeitschel gave 73° to 75°. With regard to the manner in which v. Soden and Treff have obtained nerol free from geraniol, nothing is stated on account of patent rights. On the occasion of our experiments with nerol1) we showed that the melting point of the diphenyl urethane mentioned by Hesse and Zeitschel was probably not correct; for we found that the urethane produced according to Hesse and Zeitschel was a mixture, whose melting point lying about 60° could be raised by repeated recrystallisation from petroleum ether to 81°, the melting point of the diphenyl urethane of geraniol. This supposition has therefore been proved to have been justified.

Citronellol. L. Bouveault2) designates as rhodinamine a base $C_{10}H_{19}NH_2$ which he obtained on reducing geranium acid nitrile with sodium and alcohol. It is a colourless liquid with a fish-like odour, which also reminds faintly of roses, and which boils at 105° (15 mm pressure). The specific gravity $d\frac{4^\circ}{0^\circ} = 0{,}839$. The salts of this base dissolve very readily in water, and have a soap-like appearance. When oxalic acid ester is allowed to act on the base, a uniform oxamide $(CO \cdot C_{10}H_{20}N)_2$, melting at 96°, is formed. The constitution of rhodinamine can only be as follows:



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=CH-CH_2-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}H-CH_2-CH_2-NH_2,$$

that is to say a citronellol or rhodinol whose hydroxyl-group has been substituted by an amide-group. When an ethereal solution of the amine with caustic potash was dried, rhodinamine was converted with absorption one molecule of water into the compound $C_{10}H_{23}NO$, which must be regarded as a tertiary amino alcohol:



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot \overset{\displaystyle CH_3}{\overset{\cdot}{C}}H\cdot CH_2\cdot CH_2\cdot NH_2.$$

Its boiling point lies at 140° (15 mm pressure); $d\frac{4^\circ}{0^\circ} = 0{,}910$.

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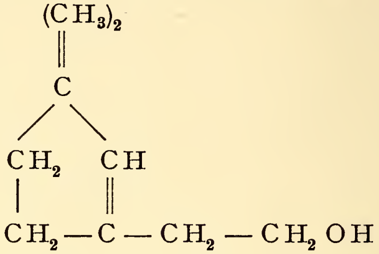
1) Report April **1903**, 63.

2) Bull. Soc. chim. III. **29** (1903), 1046.

If the ethyl ester of inactive campholenic acid is reduced according to the method indicated by Bouveault and Blanc, there is obtained (as Béhal[1]) found), a new alcohol campholenol, isomeric with borneol, which has a faint camphor odour, and shows the following constitution:



Boiling point (760 mm) = 215° to 216°; $d_{20^\circ} = 0{,}9006$; $n_{D20^\circ} = 1{,}47101$.

When boiled with 6 % sulphuric acid, the alcohol is converted into an oxide $C_{10}H_{18}O$ of the melting point 180° to 182°; $d_{19^\circ} = 0{,}9173$; $n_{D19^\circ} = 1{,}46071$. Béhal explains this reaction by the addition of water to the double-linking, and subsequent loss of water from the $\gamma$-glycol formed.

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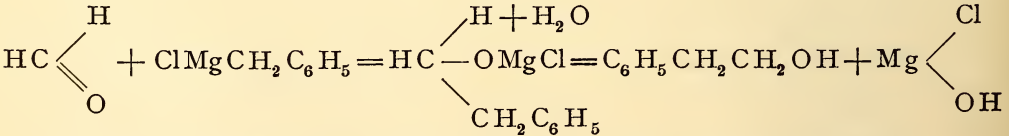
Phenyl ethyl alcohol. The general method of production of primary alcohols by reduction of the corresponding acid esters, published by Bouveault and Blanc[2]), is interesting to us in so far, as it has led to a new process for obtaining the phenyl ethyl alcohol present in rose oil. It is obtained by allowing a solution of one molecule phenyl acetic ester in 3 to 4 times the quantity of its weight of absolute alcohol, to fall in drops on a quantity of sodium calculated for six atoms. It is then heated for several hours on an oil bath, until the sodium has disappeared, if necessary with adding more alcohol. After cooling, water is added, and the ester which is not attacked is saponified. The alcohol and phenyl ethyl alcohol are then distilled off with steam, when the latter is at once obtained in the pure state.

A method for producing phenyl ethyl alcohol published almost at the same time by Grignard[3]), which is said to be based on the following equation:



$$HC\begin{matrix}\diagup H\\ \diagdown\!\!\diagdown O\end{matrix} + ClMgCH_2C_6H_5 = HC\begin{matrix}\diagup H + H_2O\\ -OMgCl\\ \diagdown CH_2C_6H_5\end{matrix} = C_6H_5CH_2CH_2OH + Mg\begin{matrix}\diagup Cl\\ \diagdown OH\end{matrix}$$

was found to be erroneous, as proved by Tiffeneau and Delange[4]),

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[1]) Compt. rend. **138** (1904), 280.

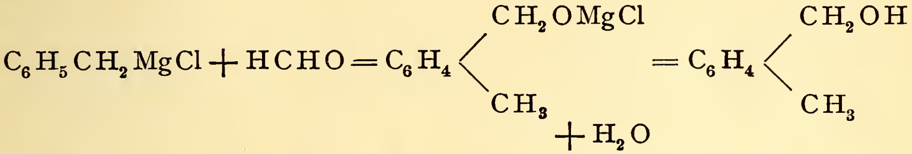
[2]) Compt. rend. **136** (1903), 1676, and **137** (1903), 60.

[3]) Bull. Soc. chim. III. **29** (1903), 953.

[4]) Compt. rend. **137** (1903), 573.

because the alcohol expected is not formed in this case, but on the other hand the isomeric crystalline ortho-tolyl alcohol, whose boiling point almost coincides with that of phenyl ethyl alcohol (219°). The melting points of the phenyl urethanes of both alcohols also lie together (79° to 80°).

According to Tiffeneau and Delange, the reaction proceeds as follows:



$$C_6H_5CH_2MgCl + HCHO = C_6H_4\left\langle\begin{matrix}CH_2OMgCl\\ \\CH_3\end{matrix}\right. + H_2O = C_6H_4\left\langle\begin{matrix}CH_2OH\\ \\CH_3\end{matrix}\right.$$

This abnormal influence on the reaction is said to be characteristic of formaldehyde which comes into application as trioxy methylene.

## Aldehydes.

Citronellal. As a continuation of their work on the influence of the double-linking on the rotatory power of optically active substances, H. Rupe and W. Lotz[1]) have attempted to produce condensation-products of citronellal with acetic acid and acetone. It was then found that by the entrance of a double-linking in one of the four groups of the asymmetric carbon atom, the original dextrorotation of the aldehyde changes into lævorotation; whilst the combination of a double-linking with the carboxyl-group produces a powerful lævorotation, that with a carbonyl-group brings about a less powerful one. Citronellidene acetic acid, obtained by condensation of citronellal with malonic acid in the presence of pyridine, is an odourless, thick oil of the boiling point 175,5° to 177,5° (14 mm pressure). The physical constants are: $d\frac{20^\circ}{4^\circ} = 0{,}9326$; $\alpha_D = -6{,}06^\circ$; $[\alpha]_D = -6{,}49^\circ$. The nickel, cobalt, and silver salts are suitable for analysis. The methyl ester of the acid, a colourless, fairly mobile liquid, has a characteristic and pleasant odour. It boils at 135° to 137° (14 mm pressure); $d\frac{20^\circ}{4^\circ} = 0{,}8177$; $\alpha_D$ (in 9,72 % alcoholic solution) $= -0{,}76^\circ$; $[\alpha]_D = -9{,}56^\circ$. With aqueous hydrobromic acid the acid reacts with formation of an oily monohydrobromide. A dihydrobromide $C_{12}H_{22}O_2Br_2$, also oily, is formed with hydrobromic and glacial acetic acids.

As a second condensation-product the authors obtained citronellal acetone, which of course was already known — if only in the patent literature. It is advisable to carry out the condensation by means of dilute caustic alkalis. The best way is to use for 20 gm. aldehyde, 36 gm. acetone and 150 gm. of a 1 % soda liquor. The mixture is

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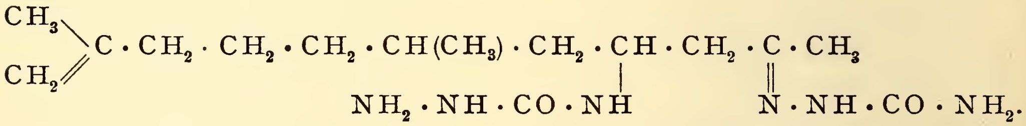
[1]) Berliner Berichte **36** (1903), 2796.

constantly shaken for 12 to 15 hours. The product is a colourless, mobile oil, with a faint odour reminding of the aldehyde. It boils at 142° to 144,5° (14 mm pressure); $d_{4^\circ}^{20^\circ} = 0{,}8737$; $\alpha_D = -\ 2{,}36^\circ$; $[\alpha]_D = -\ 2{,}70^\circ$.

With this ketone now the authors have made the interesting observation that it unites under certain conditions with two molecules semicarbazide. H. Rupe and P. Schlochoff[1]) have subsequently followed this reaction further, applied to other $\alpha$-$\beta$-unsaturated ketones, when they found that, within certain limits, the above-named ketones have a general capacity of adding, in addition to the semicarbazide rest chained to the carbonyl-group, a second molecule semicarbazide to the double-linking situated in the $\alpha$-$\beta$-position. These "semicarbazide-semicarbazones" are well-characterised bodies, which can throughout be recrystallised from water. The derivative of citronellal acetone melts at 167°; the following formula may illustrate its constitution:



$$\left.\begin{array}{l}CH_3\\CH_2\end{array}\right\rangle C\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot \underset{\displaystyle NH_2\cdot NH\cdot CO\cdot NH}{\underset{|}{CH}}\cdot CH_2\cdot \underset{\displaystyle N\cdot NH\cdot CO\cdot NH_2.}{\underset{\|}{C}}\cdot CH_3$$

Concentrated hydrochloric acid dissolves the compound instantaneously; dilute hydrochloric acid splits it up on boiling into ketone and semicarbazide. Attempts to produce the corresponding compounds of benzal acetone, cinnamoyl acetone, and pulegone, led to no result. From this the authors conclude that the addition of a second molecule semicarbazide to the double-linking of $\alpha$-$\beta$-unsaturated ketones only occurs when there is neither a phenyl-group nor another double-linking in their proximity. The examination of the above reaction is being continued.

## Ketones.

C. Harries[2]) has now occupied himself for many years with the study of the reactions of unsaturated ketones, and in a recent number of Liebig's Annalen he has arranged the voluminous material, for the purpose of more readily finding the way in the matters relating to this subject. Harries distinguishes two large principal groups of unsaturated ketones: 1st. ketones with double-linking in $\alpha$-$\beta$-position; 2nd. ketones with double-linking not situated in $\alpha$-$\beta$-position. Whereas the behaviour of the bodies belonging to the second category as a rule behave like saturated ketones, the bodies of the first group differ from

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[1]) Berliner Berichte **36** (1903), 4377.

[2]) Liebig's Annalen **330** (1904), 185.

these completely in many notable reactions. For instance, sodium bisulphite attaches itself to the $\alpha$-$\beta$-double-linking with formation of a hydrosulphonate. Hydroxylamine and semicarbazide show the same behaviour under certain conditions. The reduction and oxidation allow an insight into the nature of the reaction-products. The experiments made by Fittig and Baeyer have shown that the double-linkings of unsaturated acids endeavour to change from the $\beta$-$\gamma$- into $\alpha$-$\beta$-position. The same tendency seems also to exist in unsaturated ketones, as is shown by the conversion of dihydrocarvone into carvenone, of pulegone into isopulegone. Zinc dust and glacial acetic acid, or soda liquor, reduce only the $\alpha$-$\beta$-double-linking; sodium and alcohol also the keto-group, — whilst a double-linking not situated in the $\alpha$-$\beta$-position as a rule cannot be reduced. Dilute solution of permanganate oxidises unsaturated ketones into keto-glycols, from which di-ketones are formed by loss of water. Many unsaturated ketones also change already by the oxygen of the air, i. e., they are auto-oxidised. When carvone, for example, was shaken with alcoholic baryta liquor and air, the formation of $\Delta^6$-menthenedione (2,6) was observed, whose dioxime was also obtained from carvone oxamine-oxime by oxidation. The separation of two unsaturated ketones was accomplished in two cases. In the one case it was a question of mixture of $\alpha$-$\beta$- and $\beta$-$\gamma$-unsaturated ketones (pulegone and isopulegone). Here, the property of the $\alpha$-$\beta$-unsaturated ketone of becoming polymerised on reduction with aluminium amalgam, was used to effect the separation. In the second case, where the object was the separation of two $\alpha$-$\beta$-unsaturated ketones (carvone and $\Delta^6$-menthenone-[2]), it succeeded by conversion of the carvone into carvacrol over the hydrobromide compound, and removal of the same by means of dilute soda liquor. A discussion of the nature of the double-linking in connection with the above experiments concludes the theoretical part of the treatise.

M. Konowalow[1]) has continued his work on the nitrification of terpene ketones, and included in it fenchone, pulegone, dihydrocarvone, and carvenone. Fenchone when heated with nitric acid to 120° to 130°, forms a nitro-product $C_{10}H_{15}(NO_2)O$ of the melting point 86° to 87°, which is soluble in alkali, and which can be reduced with zinc and glacial acetic acid into an amine, and a nitrofenchone insoluble in alkali, of the melting point 96,5° to 97,5°, wich on reduction yields oxyfenchone. When pulegone was nitrified, products soluble and insoluble in alkali were obtained, — of the latter, compounds

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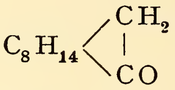
[1]) Journ. Russ. phys. chem. Soc. **35** (1903), 903. According to Chem. Centralblatt **1904**, I. 282.

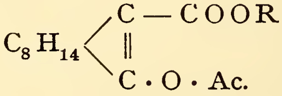
of the melting point 123°, 84° to 86°, 96° to 98° and 64° to 72°. Dihydrocarvone and carvenone also react with nitric acid, with formation of nitro-products. Isomerisation of the ketones did not occur in the above reactions.

Camphor. In his last (VIII) communication on recent experiments with campho-carbonic acid, Brühl[1] summarises the results of his entire work on this subject. Camphor



$$C_8H_{14}\left<\begin{array}{l}CH_2\\ \vert\\ CO\end{array}\right.$$

shows in many of its derivatives the tendency to the formation of enol-forms. With camphor itself, and its alkyl derivatives, the ketone-form only occurs, but with the acid derivatives, and especially with campho-carbonic acid and substances allied thereto, the occurrence of both forms has been observed; thus, the acids and their esters react in non-dissociating solvents, such as ether and benzene, as keto acids (or esters), and in hydrolysed media (water, alcohol) as enol-bodies. The alkylised esters again occur only in ketone form. The nitrile of methyl camphocarbonic acid, the methylcyanocamphor of Haller and Minguin, takes both forms simultaneously. The substitution of the labile hydrogen atom of camphocarbonic acid, or of the two methylene hydrogen atoms of camphor, by organic acid radicals, increases the tendency to produce enolised forms; in almost all cases compounds are formed of the formula



$$C_8H_{14}\left<\begin{array}{l}C - COOR\\ \Vert\\ C\cdot O\cdot Ac.\end{array}\right.$$

Pulegone. By saturating a strongly cooled solution of pulegone in petroleum ether with vapours of nitric oxide, or with nitrous vapours (from starch and nitric acid), P. Genvresse[2] succeeded in producing a nitrosite of pulegone. The oily reaction-product which volatilises with difficulty with steam, becomes solid after a week, and can be obtained, by repeated recrystallisation from alcohol, in the form of a colourless compound with a silky lustre, of the melting point 68° to 69°. A solution of the substance in chloroform deflects the polarised light 23° 13′ to the right (at 23°). The fact that a solution of this body in benzene or chloroform does not discolour bromine, proves that the $N_2O_3$-group has become attached to the double-linking. With phenol and sulphuric acid, the nitrosite shows Liebermann's nitroso-reaction.

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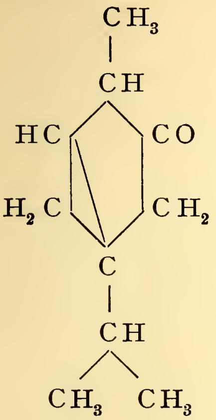
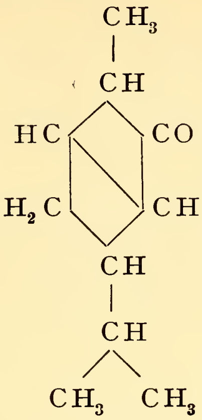
[1] Berliner Berichte **36** (1903), 4292.

[2] Compt. rend. **137** (1903), 494.

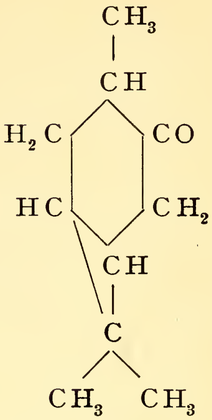
Thujone, tanacetone. Up to the present, the following formulæ have been proposed for tanacetone:



Semmler

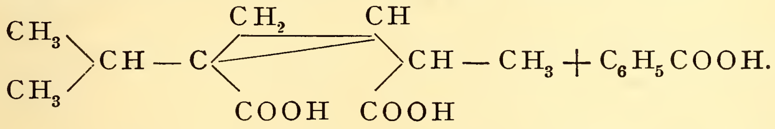


Fromm



Kondakow.

In a recent work, Semmler[1]) objects to the constitutional formulæ drawn up by Fromm and Kondakow. Against the latter it is only mentioned for the present that through it tanacetone is drawn into closer relation to carone, which would render various conversions difficult to explain. Between Semmler's and Fromm's formulæ, the presence or absence of a methylene-group in addition to the carbonyl-group, can be decisive. As Semmler now, by condensation of tanacetone with benzaldehyde, could produce a benzylidene tanacetone, (boiling point 178° at 9 mm; $d_{20^\circ} = 1{,}0298$; $n_{D20^\circ} = 1{,}5728$), this proves in favour of his formula that a methylene-group is contiguous to the carbonyl-group. The degradation-products show that no conversion has taken place during the condensation. Benzylidene tanacetone can be split up by oxidation with potassium permanganate, into homotanacetone dicarbonic acid and benzoic acid:



$$\begin{array}{l}CH_3\\CH_3\end{array}\!\!> CH - C \begin{array}{c}CH_2 \quad\quad CH\\ \\ COOH \quad COOH\end{array} CH - CH_3 + C_6H_5COOH.$$

This acid yields an anhydride, exactly like tanacetone dicarbonic acid; it has no double-linking, and is not attacked by potassium permanganate in the cold. The acid $C_{10}H_{16}O_4$, obtained by Wallach by oxidation of tanacetone with alkaline bromine solution, is possibly identic with homotanacetone dicarbonic acid. Of the derivatives of benzylidene tanacetone which are also described, the product obtained by the action of hydroxylamine (melting point 138° to 140°) is interesting in so far as it is no oxime, but an addition-product.

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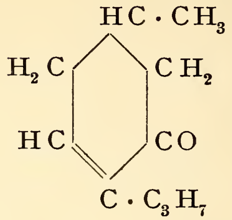
[1]) Berliner Berichte **36** (1903), 4367.

In order to prove by further experiments the formula accepted for menthenone:



O. Wallach[1]) reduced menthenone with sodium and alcohol into menthol, and showed that dibromomenthenone, when heated, yields thymol, with loss of hydrobromic acid. Both results agree with the above formula.

Menthone. At the 75th Meeting of the Society of German Scientists and Physicians, at Cassel, E. Beckmann[2]) reported on his studies relating to the menthol-series. Natural l-menthol, on careful oxidation with Beckmann's mixture, yields l-menthone, which can be converted with concentrated sulphuric acid into d-menthone. Dilute acids and bases produce a mixture of d- and l-menthone. Similar mixtures are also obtained from d-menthone.

From the possible 4 isomeric menthones, 8 menthols can be derived theoretically, of which, however, in practice, on reduction, the natural l-menthol is always produced in the largest quantity. In addition to the menthols, there is formed on reduction with sodium in indifferent media, menthopinacone (melting point 95°) which can be oxidised with Beckmann's chromic acid mixture into d-menthone. When the reduction is made in alcoholic solution this body is not formed.

A separation of the isomeric menthols did not succeed. On the other hand, the attempt to arrive at isomeric amines and isomeric menthols by reduction of the menthone oximes, had the desired result. The bases could be separated by fractional crystallisation from benzene of the picrates and hydrochlorides of the amines. In this manner a pure d-menthylamine hydrochloride could be separated from d-menthone oxime, which could be converted into a new d-menthol by means of nitrous acid. The separation of the amines succeeded also by fractional crystallisation of their benzoates from alcohol. The more readily soluble benzoates yielded on saponification d-menthylamine. Finally the author also succeeded in separating d-menthol as a more readily soluble benzoyl-compound from the menthol-mixtures which are formed by reduction of the menthones. The

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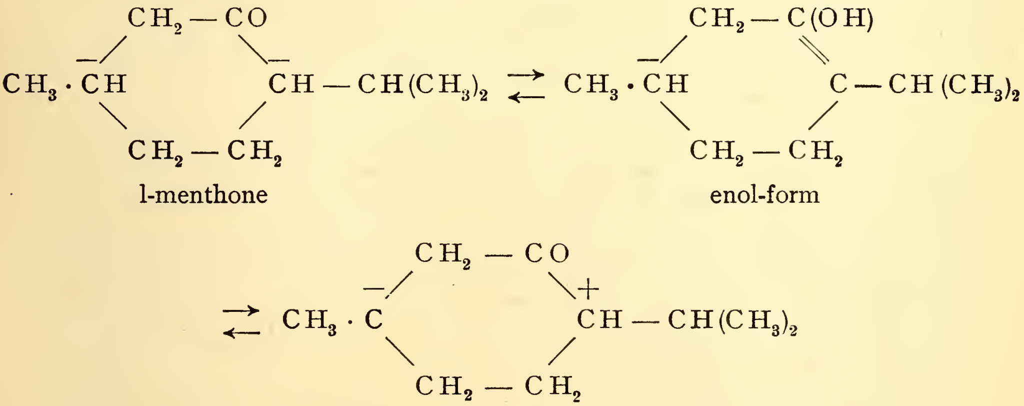
[1]) Nachr. k. Ges. Wiss. Götting. **1903**, part **4** (abstr. according to Chem. Centralbl. **1903**, II. 1324).

[2]) Pharm. Ztg. **48** (1903), 780.

d-menthylamine previously obtained by Wallach is not identic with the one obtained in this case, as on treatment with nitrous acid it does not yield menthol, but menthene.

Pulegone, which contains two hydrogen atoms less than the allied menthone, could be converted by Beckmann into a new "iso-lævo-menthone", by attaching hydrobromic acid to the double-linking, and substituting the bromine by hydrogen by means of zinc dust and alcohol. It is a colourless oil, and has the same rotation as the well-known l-menthone. Its oxime, however, does not melt at 59°, but at 85°. Boiling point and odour are approximately like those of the menthone which can be inverted into d-menthone. All its properties show, that it is structurally identic with the menthones hitherto obtained.

As Andres and Andreef showed years ago, l- and d-menthone-oxime yield on reduction l- and d-menthylamine respectively; Wallach and Kuthe obtained from d-menthone, by heating with ammonium formate, a mixture of both bases which could be separated by formates. More recent examinations by Tutin and Kipping[1] show, that the hitherto accepted view, that the l- and d-menthones produced by oxidation of menthol with bichromate are optical antipodes, is incorrect, as the oximes of both ketones are lævorotatory, in spite of the fact that the latter turn 25° to the left or right. For this reason Tutin and Kipping believe that the action of sulphuric acid, according to its strenghth, effects a more or less large racemisation of the l-menthone, and they explain this by a partial enolisation, as shown by the following formulæ in which the minus sign stands for lævo- and the plus sign for dextro-rotation:



l-menthone

enol-form

"d-menthone",
l-isomenthone.

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[1] Journ. Chem. Soc. **85** (1904), 65.

Tutin and Kipping consider it very probable that dilute sulphuric acid already yields these two menthones on oxidation, and the oximes of two ketones, to which therefore belong the configurations — — and — +, on the reduction by which a third asymmetric carbon atom is formed, must yield 4 optically active amines: from the ketone — —, the bases — — — and — + —, and from the ketone — +, the bases — — + and — + +. The authors assume that the same conditions will prevail in the formation of menthylamine from menthone and ammonium formate, on the supposition that the high temperature of the reaction does not affect the direction of the rotatory power of the asymmetric carbon atom carrying the methyl-group. In this case, four more amines of the configurations + — —, + + —, + — +, and + + + would be formed in addition to the above-mentioned four bases; the result would then be an optically inactive mixture of eight bases, whose rotations would neutralise each other. With regard to the nomenclature of the individual amines, it should be noted that Tutin and Kipping give to true læve-menthone the configuration — —, and to true dextro-menthone the symbol + +. The ketone which can be produced from the first-named ketone by means of alkalis or acids would then have the configuration — +, and the name l-isomenthone. The two bases to be obtained from l-menthone are named l-menthylamine and l-neomenthylamine, — those obtained from l-isomenthone, l-iso- and l-isoneomenthylamine. The four bases from d-menthone are distinguished in the same manner.

Of the four bases from lævo-menthone mentioned by Tutin and Kipping, l-menthylamine — — — is formed in the largest quantity. Of the three others, two are very indifferent, the fourth undergoes partially a racemisation of the $CH_2 \cdot NH_2$-group; as in this case the base yields no menthylamine — — —, the configuration which belongs to it and to its products of racemisation, is that of a base belonging to the iso-series — ± +.

The very troublesome separation of the individual bases, which is described in detail in the original work, was accomplished by fractional crystallisation of various acid derivatives, such as the hydrochlorides, and also of the d-camphor and d-bromcamphor sulphonates, or the formyl and benzoyl compounds. Every one of the bases was identified by pure, uniform salts in respect of rotatory power, melting point etc.

Semmler¹) reports on more recent derivatives of menthone, camphor-phorone and pinophorone.

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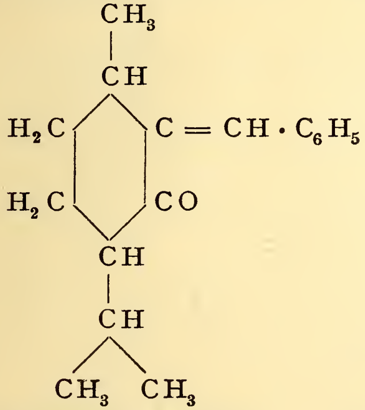
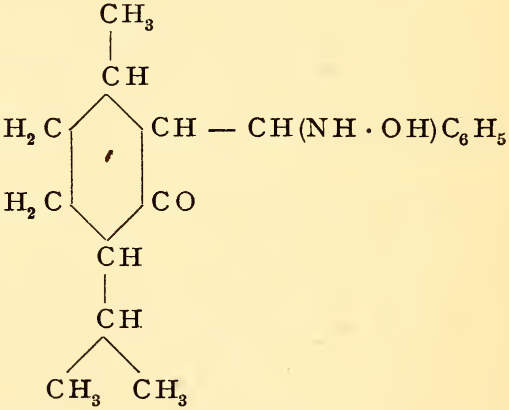
¹) Berliner Berichte **37** (1904), 234.

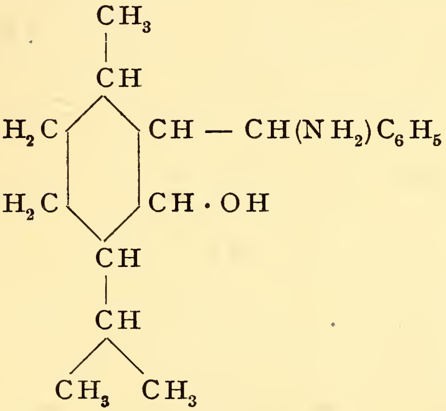
a) Menthone. By condensation of benzaldehyde with menthone in alkaline solution, he obtained a product of the boiling point 193° (15 mm) the specific gravity 1,0145, and the index of refraction 1,549. He allowed hydroxylamine to act on this benzylidene menthone and obtained a hydroxylamine addition-product (melting point 162°) which is soluble in acids, and is again precipitated by alkalis. From this is formed by reduction dihydrobenzylidene mentholamine. If the crude material had been an oxime, the reduction-product would no longer have contained oxygen. Semmler has drawn up the following constitutional formulæ for these bodies:



Benzylidene menthone



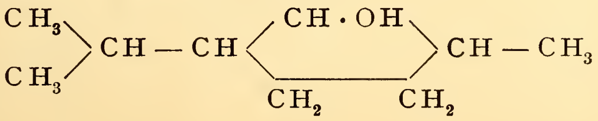
Benzylidene menthone hydroxylamine.



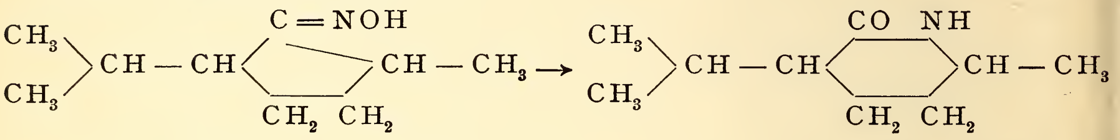
Dihydrobenzylidene mentholamine.

Benzylidene menthone can be reduced to dihydrobenzylidene menthol, and the latter can then be oxidised into dihydrobenzylidene menthone.

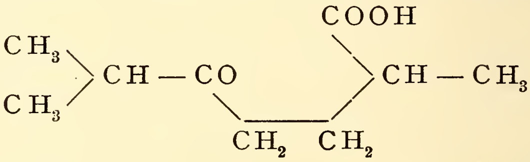
b) Camphorphorone. If camphorphorone is reduced with sodium and alcohol, dihydrocamphoryl alcohol is formed. Boiling point 185° to 192°, $d_{20^\circ} = 0{,}899$; $\alpha_D = 1{,}4604$. Semmler expresses the constitution of this body by the following formula:



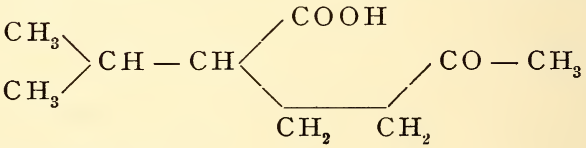
The phenyl urethane of the alcohol melts at 82°. When heated with dry oxalic acid, it yields an unsaturated hydrocarbon $C_9H_{14}$, and in agreement with the above constitutional formula it can be oxidised with chromic acid into a ketone whose boiling point lies at about 184° to 185°. The semicarbazone of the ketone melts at 196° to 197°; the oxime (melting point about 79°) is very readily converted into the isomeric piperidone.



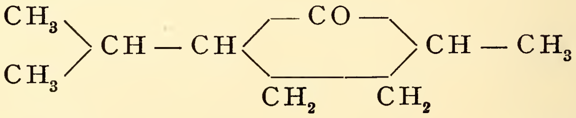
The oxidation of the ketone with potassium permanganate yielded two ketonic acids, which were separated by the semicarbazones. 1. ketonic acid $C_9H_{16}O_3$ from the semicarbazone of the melting point 167° to 168°. On further oxidation it yields α-methyl glutaric acid (melting point 77°) and has therefore the following constitution:



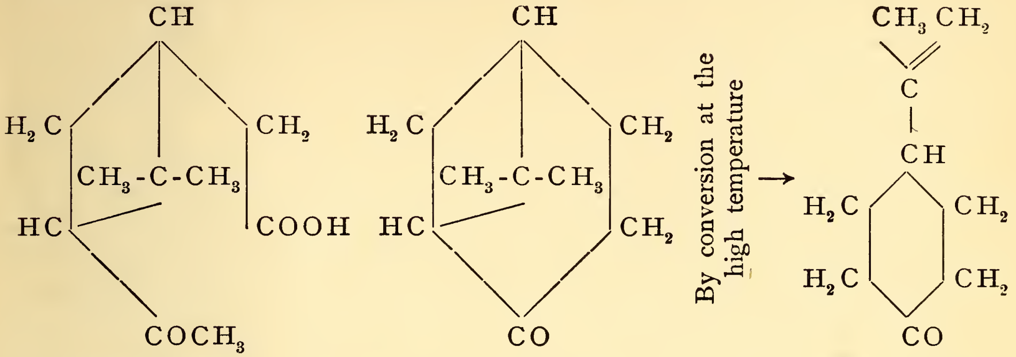
2. ketonic acid from the semicarbazone of the melting point 140°. By oxidation with sodium hypobromite it yields isopropylglutaric acid $C_8H_{14}O_4$, and with potassium permanganate isopropylsuccinic acid (melting point 117°). The following constitution therefore belongs to it:



and to dihydrocamphorone:



c) Pinophorone. Pinophorone was obtained by Semmler in addition to acetone and an unsaturated hydrocarbon $C_9H_{14}$, by distillation of calcium pinonate. It boils at 203° to 205°, has the specific gravity 0,9284, and the refractive index 1,4805. The semicarbazone melts at 157° to 158°. When it is decomposed, hydrocarbon is partly formed. The oxime, like that of camphorphorone, is converted instantly with mineral acids into piperidone $C_9H_{15}NO$, which can be split up into an amido acid $C_9H_{17}NO_2$. It follows from these reactions that the carbonyl-group of the ketone is situated in the nucleus. Pinophorone is unsaturated. The double-linking remains in existence, even when the body is reduced to pinocamphoryl alcohol $C_9H_{16}O$. The author deduces the following constitutional formula for pinophorone:



Pinonic acid Primary ketone Pinophorone

Repeated attempts had already been made to split up camphorphorone analogous to pulegone, into acetone and 1, 2-methyl pentanone, but up to the present without result. O. Wallach[1] now has observed, that when calcium camphorate is distilled, preferably when mixed with moist soda-lime, camphorphorone is split up in not inconsiderable quantity. The same reaction occurs also if camphorone mixed with water is dropped on melted caustic potash. The 1, 2-methyl pentanone obtained by this method, regenerated from pure semicarbazone (melting point 174° to 176°), boils at 140° to 141°, d = 0,917, $n_{D20°}$ = 1,4348, and yields readily on oxidation γ-acetyl butyric acid $C_6H_{10}O_3$; melting point of the hydrate 35° to 36°; melting point of the semicarbazone 170° to 171°.

The following constants are given for pure camphorphorone regenerated from the semicarbazone of the melting point 196° to 197°: boiling point 199° to 201°; d = 0,93; $n_{D20°}$ = 1,4807. This phorone forms with semicarbazide, in addition to the normal semicarbazone, a bisemicarbazone-compound, melting point about 135°, which with picric acid yields a picrate of the melting point 145°. Attempts to isomerise camphorphorone by means of sulphurous acid led to no result.

The same author[2] reports on pulenone (trimethyl 1.4.4. hexanone 5.) in his 62nd treatise on terpenes and essential oils. It is formed when the oxylactone $C_{10}H_{16}O_3$, the first oxidation-product of pulegenic acid, is heated with 33 % sulphuric acid. Sodium and alcohol reduced pulenone to pulenol, a liquid with a menthol-like odour, of the boiling point 187° to 189°, which with carbanile forms a urethane of the

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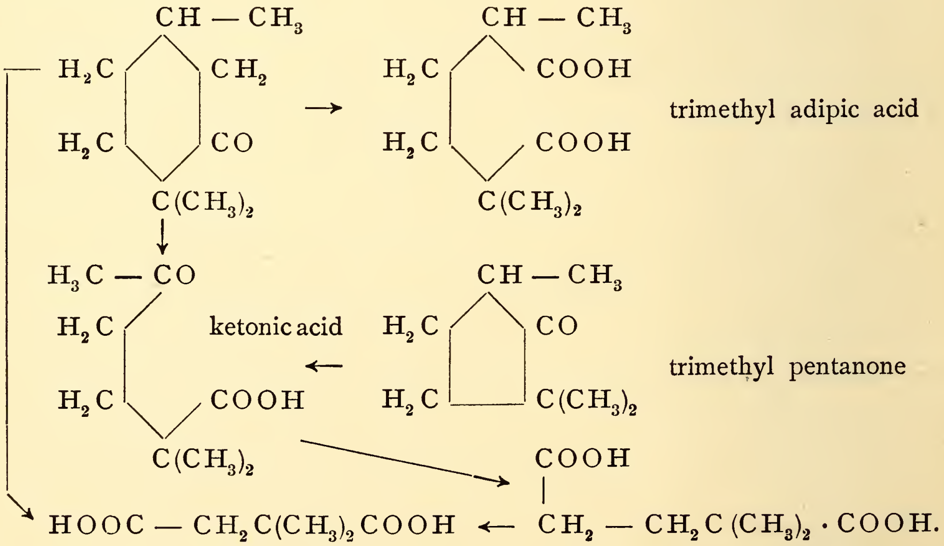
[1] Liebig's Annalen **331** (1904), 318.
[2] Liebig'Annalen **329** (1903), 82.

melting point 84° to 85°. Potassium bisulphite splits off water from the alcohol, with formation of a hydrocarbon $C_9H_{16}$, pulenene (boiling point 60° to 65° [12 mm]), whose nitrosate melts at 98° to 99°, whilst zinc chloride yields an isomeric hydrocarbon boiling at 145° to 150°, which does not form a solid derivative with amyl nitrite and nitric acid.

Whilst the oxidation of pulenone with potassium permanganate in addition to oxalic acid and acetic acid yielded only small quantities of acids which could throw a light on the constitution of the ketone, there could be isolated, by means of chromic acid anhydride in solution of sulphuric acid, first a bicarboxylic acid $C_9H_{16}O_4$ of the melting point 114° to 115°, secondly, a ketonic acid $C_8H_{14}O_3$ of the melting point 49° to 51° (melting point of the semicarbazone 150° to 151°), thirdly as-dimethyl succinic acid $C_6H_{10}O_4$ (melting point 140°). The bicarboxylic acid $C_9H_{16}O_4$ could be identified as *α, β, β*-trimethyl adipic acid by means of conversion into *α, α, α'*-trimethyl pentanone (boiling point 152° to 153°, melting point of the oxime 60° to 62°; melting point of the semicarbazone 150° to 151°), and oxidation thereof into the ketonic acid obtained above and further into *α, α*-dimethyl glutaric acid (melting point 82°). The following summary may illustrate the reaction.



Pulenone oxime (boiling point 117° [12 mm]; melting point 94° to 95°), when treated with phosphorus oxychloride is converted into an isoxime of the melting point 96° to 97° and the boiling point 145° to 150° (27 mm), which with acids yields, with loss of water, nonylenic acid nitrile (boiling point 89° to 90° [10 mm]; 216° to 217° [760]). The latter is also formed direct from the oxime on treatment with phosphorus oxychloride and phosphorus pentachloride.

The corresponding nonylenic acid boils at 143° to 147° (23 mm) and is oxidised by permanganate into acetone and $\beta$-methyl glutaric acid (melting point 85° to 86°) which leads to the following constitution: $C(CH_3)_2C = CH \cdot CH_2 \cdot CH(CH_3) \cdot CH_2COOH$, a result agreeing fully with the oxidation-products of pulenone.

Some time ago already Wallach[1]) reported on a reaction, on the strength of which he succeeded in displacing the oxygen of saturated ketones from one position in the molecule to another.

Wallach[2]) has now also solved this problem successfully with 1-3-methyl cyclohexanone as an example. On a previous occasion we have already referred to the formation of 1-2-methyl cyclohexanone[3]) from 1-3-methyl cyclohexanone. By reduction with sodium and alcohol, this unsaturated ketone is converted into the saturated alcohol belonging to it, 1-2-methyl cyclohexanol, which again can be oxidised with chromic acid into 1-2-methyl cyclohexanone. The 1-2-position of the methyl and carbonyl-groups was determined by oxidation of the ketone into $\delta$-acetyl valerianic acid $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$ and further into normal adipic acid.

Ionone. For the purpose of separating $\alpha$- and $\beta$-ionone by means of their hydrosulphonic acid compounds, Chuit[4]) recommends the following method. In a warm solution of the sodium salts of the two isomeric acids he dissolves common salt; there occurs gradually a separation of the more difficultly soluble $\alpha$-ionone-sodium hydrosulphonate which is deposited on the bottom in the form of beautiful white crystals. The $\beta$-compound remains in solution, and after recrystallisation by decomposition with alkalis, can be converted into absolutely pure $\alpha$-ionone, which is said to have a decidedly finer odour than ordinary commercial ionone. According to Chuit the two pure isomers show a distinct difference with regard to the odour; $\alpha$-ionone possesses a more flowery odour, and reminds more of orris, $\beta$-ionone is said to reproduce the odour of the violet flower more perfectly. The reaction-product from pseudo-ionone can, according to Chuit, also be enriched by one or the other isomer, by the action of cold concentrated sulphuric acid, which produces chiefly $\beta$-ionone, or also by weaker acids, such as hydrochloric and phosphoric acids, at low

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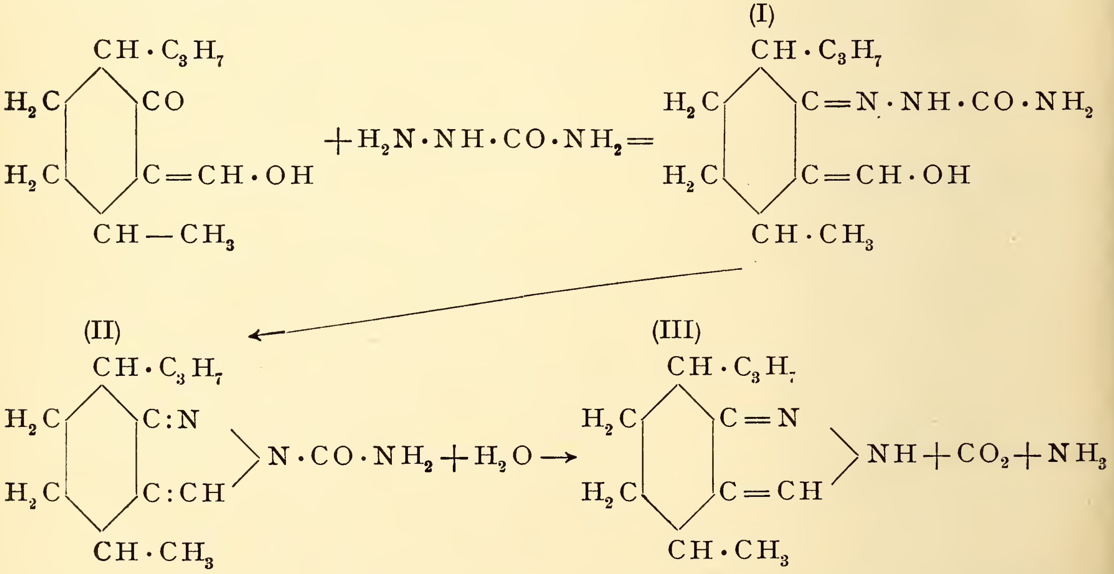
[1]) Liebig's Annalen **324** (1902), 112. Comp. Report October **1902**, 88.
[2]) Liebig's Annalen **329** (1903), 368.
[3]) Berliner Berichte **35** (1902), 2822. Comp. Report April **1903**, 90.
[4]) Rev. Gén. de Chimie; acc. Chemist and Druggist **63** (1903), 1054.

temperatures ($\alpha$-ionone). The most important physical constants of the two ionones are given below:

| | $\alpha$-ionone | $\beta$-ionone |
|---|---|---|
| Boiling point at 12 mm: | 127,6° | 134,6° |
| $d_{15^\circ}$: | 0,9338 | 0,9488 |
| $n_D$: | 1,50001 (17,2°) | 1,52008 (17,5°) |
| melting point of the thiosemicarbazone | 121° | 158° |

The conversion of terpene ketones into cyclic bases has again been studied in detail by Wallach[1]), as is proved by two treatises both representing a rich contribution of great value for chemical systematics. Cyclic oxymethylene ketones react readily with semicarbazide solution (I); the semicarbazones thus obtained split off water, either voluntarily, or after addition of small quantities of mineral acids (cyclic semicarbazones) (II), these are decomposed by boiling with dilute sulphuric acid into carbonic acid, ammonia, and the corresponding pyrazol base (III). Taking menthone as an example, the conversions would take place in the following manner



Acyclic oxymethylene ketones react in an analogous manner excepting that oxymethylene acetone condenses with two molecules semicarbazide.

The same scientist[2]) reports further on a new cyclic base from methyl heptenone. Methyl heptenylamine absorbs not only one, but

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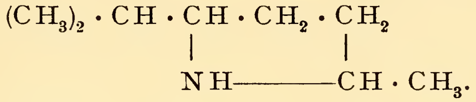
[1]) Liebig's Annalen **329** (1903), 109.

[2]) Nachr. k. Ges. Wiss. Göttingen **1903**, part **4** (according to Chem. Centralbl. **1903**, II. 1324).

also two molecules hydrochloric acid; the hydrochloride thereby formed yields, when heated in addition to a hydrocarbon $C_8H_{14}$, a base $C_8H_{17}N$ of the boiling point 150° to 151°, and the density 0,823 (at 20°), to which probably the following constitution belongs:

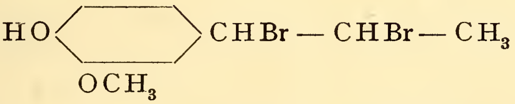


## Phenols and phenol ethers.

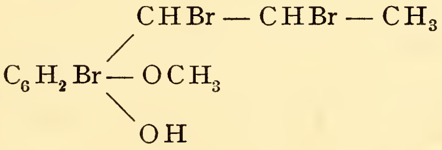
L. Brunel[1]) has succeeded in reducing phenols to cyclohexanols. For this purpose he passes phenol, thymol or carvacrol, in a current of hydrogen over nickel heated to 170° to 200°. The cyclohexanol thus obtained forms a phenyl urethane of the melting point 82°; hexahydrothymol boils at 214°, hexahydrocarvacrol at 218° to 219°.

In continuation of his previous work on halogenised phenols, Zincke[2]) has studied the action of bromine on isoeugenol. The behaviour of the bromine derivatives of these phenols is entirely analogous to that of p-vinyl phenol.

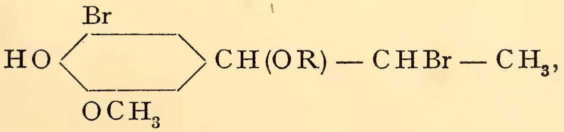
Isoeugenol dibromide



shows completely the character of a pseudo-phenol and reacts with aqueous acetone, with alcohols, and with acetic acid with loss of hydrobromic acid and formation of mostly oily bodies, of which only the solid acetyl derivative shows the true phenol character. These bodies have partly already been produced by Auwers and Müller[3]) and described by them. Monobromisoeugenol dibromide



reacts in its derivatives partly as a true phenol soluble in alkali, — as in the oxy and alkoxy compounds:



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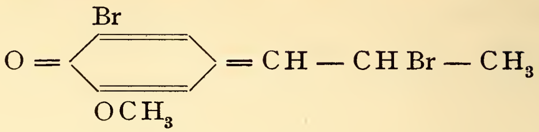
[1]) Compt. rend. **137** (1903), 1268.

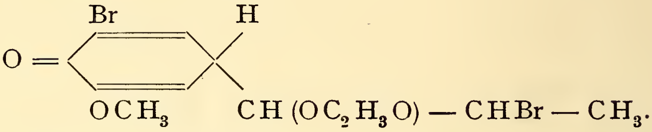
[2]) Liebig's Annalen **329** (1903), 1.

[3]) Berliner Berichte **35** (1902), 114. Report April **1902**, 95.

partly as a pseudo-phenol, as with the quinone



and with the acetyl derivative



The higher brominated products, di- and tribromisoeugenol dibromide, agree with the monobromo derivative with regard to their phenol or pseudo-phenol character.

**Aubépine (Anisic aldehyde).** This preparation, the basis of the hawthorn-perfume, is obtained as a by-product in the manufacture of coumarin, and is now so low in price, that the consumption has increased considerably. At the same time, it remains an article of subordinate importance, and one of those perfumes which must be used with discretion so as not to appear obtrusive.

We must point out that anisic aldehyde, when exposed to the air, oxidises readily into anisic acid, and should therefore be kept in well-closed bottles, if possible filled completely.

**Benzyl acetate.** This body, which we were the first to introduce into commerce, has recently gained in interest, since we succeeded in producing it at a very moderate price. It forms a constituent of natural and artificial oils of jasmine and ylang ylang, and on account of its ready solubility is very suitable for the manufacture of cheap extract and Eau de Cologne preparations with a low alcohol-content.

Our benzyl acetate is absolutely free from chlorine.

**Borneol (Borneo camphor).** In the manufacture of this body a decided advance can also be recorded. In consequence of this, the cutting of the price continues vigorously, and the end will be that nobody will be any the better for it. The same thing happens with all articles whose importance is overestimated.

**Citral.** The criterion for the value of this article is the greater or smaller degree of purity of the product. It is well known that citral was discovered and named by us in 1888. Although its usefulness was at first questioned and deprecated, it is now universally employed for the manufacture of concentrated lemon oils, essences and extracts, and may be called practically indispensable.

The price moves with that of lemongrass oil. There is no other raw material of equal richness. When citral is kept, either in the pure state or in the form of a mixture, it should be protected from heat and sunlight.

**Coumarin.** Since the price has gradually been ruined by new competitors who have decidedly overestimated the consumption, all interest in this article appears to have died away. When judging the prices, the quality of the various products, which are not by any means all equal, should be taken into consideration. Our coumarin has reached the highest degree of perfection by repeated recrystallisation.

It is a well-known fact that many chemical bodies undergo changes by the action of light, and especially of direct sunlight. In the case of colourless organic bodies or solutions thereof, this can frequently be observed by the occurrence of a more or less strong yellow coloration. The examinations of Ciamician and Silber[1]) have shown that coumarin is also subject to such changes. Both crystallised coumarin, and also that in alcoholic solution, are polymerised in sunlight in the course of a few weeks into hydrodicoumarin (melting point 262°), with yellow colouration. As this body dissolves with difficulty in alcohol, it separates out in crystalline form from the coumarin solutions. The formation of this odourless substance causes a continuous decrease of the aroma.

For this reason it does not appear advisable to keep coumarin or its solutions for a prolonged time exposed to the light; under all circumstances a cool, dark place should be much preferred.

With regard to similar occurrences in heliotropin, further details will be found under that heading.

**Eucalyptol.** The slight difference in price between the crude oil of the globulus species and pure eucalyptol has, as we foresaw, brought about a great demand for the latter, so much so, that the execution of large orders was now and then somewhat delayed.

This crisis, however, has passed, since new installations for the manufacture have been brought into operation.

**Eugenol.** The value moves up and down with that of clove oil, and everything said about the latter applies to the former. The demand was brisk, corresponding to the advancing market.

**Geraniol.** The use of this product, which we were the first to introduce into commerce, has in the course of time grown to large dimensions. Geraniol plays an important part in nature. It forms a constituent of

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[1]) Berliner Berichte **36** (1903), 4266, and **35** (1902), 4130.

oils of rose, citronella, geranium, linaloe, lemongrass, lavender, neroli, palmarosa, ylang ylang, and others; but it has this disadvantage that in the pure state it readily oxidises when exposed to the atmosphere, — on the other hand, when mixed with other essential oils it keeps well.

**Heliotropin.** Since our last Report the fall in the price of this article has been arrested. The manufacturers have reached the extreme limits of their art, and the perfumer can look with complacency on the end of this competition.

The prevailing idea that the heliotropin of previous times, produced from the piperidine of pepper, is in point of quality superior to the one now obtained from safrol, is, in our opinion, due to prejudice. The earlier product was doubtless not better than the present one; but, in order to meet all wishes, we carry since some time an extra quality, which has been submitted to a special purification-process. This process is a matter of considerable expense, and consequently necessitates an important addition to the price.

Several complaints relating to the yellow discolouration which has occurred with solutions of heliotropin, have induced us to make some experiments in this direction. We submitted 10 % water-white alcoholic solutions of heliotropin, in bottles of equal capacity which were filled to different heights and were partly left open, to the action of diffused sunlight, and have thereby obtained the following results. Bottles filled right up to the neck and closed, after standing for a period of five months, showed some yellow discolouration hardly worth mentioning. In the other bottles, the colouration increased with the volume of air enclosed, and passed over into brown where the bottles had been left open. In the latter, heliotropin crystals had separated out on the bottom and a brown resinous crust in the neck. In bottles which have only become slightly discoloured, the colouration increases if they are now and then opened and again closed up. It therefore appears that, apart from the light, the air also exerts a pronounced influence on the keeping qualities of heliotropin-solutions, and it should for this reason be avoided to expose such solutions to the light in incompletely filled bottles. Crystallised, and especially melted heliotropin, is in the dry state subject to the same changes. Even the purest product becomes yellow or brown through the influence of light. This can be observed when a glass-jar filled with heliotropin crystals is placed near a window. The side placed towards the window will in a short time be found to have changed in the manner indicated. This is an occurrence which can only be prevented by keeping the article in a cool, dark place.

**Hyacinth.** Our hyacinth "Schimmel & Co." occupies without contradiction a favoured place among the preparations which are found in commerce under a similar name, and has in point of quality nothing in common with the ordinary commercial products. It possesses the odour of the fresh blossom in the most complete and concentrated form, and is an exact imitation of the natural product. It consists partly of chemical bodies, and partly of natural perfumes, and is free from alcohol or other diluents.

**Linalol.** Owing to scarcity of linaloe oil, the manufacture had to be kept within restricted limits. We have recently again had an opportunity of observing how necessary it is to exercise caution with regard to preparations offered at very low prices. A linalol, introduced into commerce by a French firm under the name “linalol rosé”, attracted our attention on account of its cheapness, as it was offered at a price (25 francs per kilo) which could at most only apply to linaloe oil. A closer examination of a small sample showed that it was nothing but a rectified linaloe oil. There is, therefore, no justification to call such a product “linalol”, — on the contrary, such a name can only be designated as directly misleading.

**Linalyl acetate.** This body is used for the production of a highly concentrated and readily soluble bergamot oil, as is required for Eau de Cologne containing little alcohol, and other cheap extracts for export; in the hands of a clever perfumer it can be employed for a variety of purposes.

**Menthol, recryst. pure.** Japanese crude menthol has during the last six months played an important part, especially in the months which preceded the outbreak of the war. When this had taken place, attempts were immediately made, as usual, to bring about a rise, in order to dispose with the greatest possible amount of profit of the important shipments and stocks which were on the way or had accumulated at the European markets. But, strange to say, the “bulls” met with no response on the part of those who had to carry on the trade in the smaller delivery-channels. On calm consideration it had to be admitted that the transport of goods between Japan and Germany can hardly be touched by the war, but that, on the contrary, the neutral German steamship lines would carry on their business without hindrance and restriction. For this reason every cause of alarm disappeared, and the movements of the prices since October even show an uninterrupted decline. We quoted recrystallised menthol

| | | | |
|---|---|---|---|
| at the middle of | October | 54 | marks per kilo |
| „ „ „ „ | November | 54 | „ „ „ |
| beginning „ | January | 48 | „ „ „ |
| „ „ | February | 45 | „ „ „ |
| „ „ | March | 44 | „ „ „ |
| „ „ | April | 46 | „ „ „ |

According to recent reports from Japan, the stocks of crude menthol have lately become reduced by heavy shipments, so that a further drop in the prices is out of the question, and, on the contrary, a rise of several marks in the near future is probable. This has absolutely nothing to do with the political complications. The statistical figures of the shipments of crude menthol from Japan during the year 1903 are found on page 73 of the present Report.

**Musk, artificial.** The fact that the German patents have now expired has been a two-fold advantage to the perfumery-industry. In the first place, the price has fallen to about one twentieth of the previous one, and secondly, a sensible state of affairs has now arisen as regards the quality. The admixture of antifebrin which used to take place has now completely ceased. We take a lively interest in this article, and supply — if perhaps not at the lowest cut prices, — a really remarkable quality of extra-fine perfume, which has met with universal approbation. It dissolves in 95 % alcohol in the proportion of 1 in 200. But in order to meet also higher requirements with regard to solubility, we have now introduced under the name extra-soluble a kind which forms a solution with 95 % alcohol in the proportion of 1 in 80, and which renders it possible to make concentrated tinctures, — a fact to which we would here call attention.

**Safrol.** We were able to make a slight reduction in the selling prices of this article owing to very important and advantageous contracts for camphor oil. Since these purchases were concluded, the camphor monopoly Act has been passed, and the future value of this raw material is now as uncertain as that of camphor. It is probable that the intended permanent rise in the price of the latter will also extend to the oil, and that sooner or later safrol will also advance in price.

In consequence of the high price of sassafras oil there is a very strong demand for safrol.

**Terpineol.** Although the high prices of turpentine oil really justify an increase in the quotations, we are in the pleasant position of reducing our prices, since we have succeeded in introducing important improvements in the manufacture, and in employing these to advantage.

We beg to draw special attention to the quotations in our lists. We need not refer to the fact that our product supplies the highest which can be obtained in point of quality.

**Thymol.** The Japanese war has brought about a very strong demand for this antiseptic which is so esteemed in the Far East. If this should continue or perhaps even increase, a rise in the prices is not improbable. For the present ajowan seed has not yet been touched by the existing state of affairs.

Shipments of Ajowan-seed from Bombay in 1903: —

| | | |
|---|---|---|
| to America | 100 | cwts. |
| „ Germany | 8443 | „ |
| „ Egypt | 98 | „ |
| Total | 8641 | cwts. |

**Vanillin.** This product, which had suffered a fall in the value never dreamt of, has suddenly again come into favour owing to the well-known position of clove oil, which is used almost exclusively as the raw material. The lowest value of the leading brands was about 36 marks, and if it is considered that since then the prices of clove oil have advanced more than 100 $^0/_0$, the present selling price of 54 marks may still be called moderate.

A communication contained in the circular of a Hamburg vanilla merchant stating that Tahiti vanilla is usually prepared with vanillin, was new to us.

We recently had a vanillin under examination in our laboratory, which had been offered by a German firm to a firm in France at such a disproportionately low price, that it was looked upon with great suspicion. The examination answered the expectations: the preparation was greatly adulterated, as not less than about 25 $^0/_0$ boric acid had been added to the vanillin. Previously adulterations with benzoic acid, antifebrin, sugar, acetisoeugenol, and coumarin had been detected. The series of adulterants for vanillin has now been enlarged by an interesting member.

In continuation of Bourquelot's work on the oxidation of certain phenols by means of oxydases contained in some species of fungi, Lerat[1]) allowed the expressed juice of fungi of the species *Russula* to act for 24 hours, at ordinary temperature, on an aqueous solution of vanillin 1 : 50. Cloudiness occured very rapidly; it increased when a current of air was passed through, and was in the course of time deposited on the bottom in the form of a precipitate. This was almost insoluble in the usual solvents, but dissolved readily in alkalis, and melted at 302° to 305°. On further examination, the body was recognised as the dehydrodivanillin produced by Tiemann by the action of ferric chloride on vanillin; both substances yielded the same dimethyl ether of the melting point 135° to 136°. By treating vanillin

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[1]) Journ. Pharm. Chim. VI. **19** (1904), 10.

with the oxydases of gum arabic, Lerat also obtained dehydrodivanillin. The oxidation effect is therefore with vanillin the same as Bougault had established for morphine, which under the same conditions yielded dehydrodimorphine.

In his work on spices and their adulteration, Rühle¹) gives a short review of the commercial qualities and substitutes of genuine vanilla. The best kind of genuine vanilla, the fruit of *Vanilla planifolia* gathered before it has become quite ripe, is the long Mexican (up to 25 cm. long, 6 to 8 mm. wide, 3 to 4 mm. thick), but this is of scarcely any consequence for the European trade; the shorter Mexican *Cimarrona* or wild vanilla falls a long way behind it in quality. For the European trade, the Bourbon Vanilla and that from German East Africa, whose cultivation is on the increase, come chiefly under consideration. Of less value is the vanilla from Mauritius, Java, the Fiji Islands, and the Seychelles. As substitutes of genuine vanilla, the fruit of *Vanilla aromatica* which has no aroma, and of a few other species of vanilla are employed, which partly contain, besides vanillin, also piperonal, and which are placed on the market as vanillons. To these belong the broad vanilla, and also the La Guyara, Guayana, and Brazilian vanillas, of which the former contains 0,4 to 0,7 % vanillin, whilst genuine vanilla contains 1 to 2,75 % vanillin, which, however, by itself is no factor for judging the quality of vanilla. As adulterants, extracted or bad vanilla are used, to which a vanilla-like odour and a better appearance are given by rubbing on balsam of Peru or benzoic acid solution.

Two years ago the Soekaboem Agricultural Society in West Java had offered a prize for the best Java vanilla. Greshoff²) publishes in a long work the result of the competition in which 15 contributors took part. The samples of vanilla sent in, 50 pods of each, were submitted by the Director of the Colonial Museum at Haarlem to the judgment of several experts; as such acted a wholesale dealer in vanilla, an apothecary, a druggist, a chemist and a chocolate manufacturer. As tests for the quality of the vanilla which was judged chiefly from the point of view of saleability and commercial value, the following properties were principally considered: appearance, colour, length of the individual pods, efflorescence of crystals, aroma, fulness, moisture, etc. The result of the very detailed comparison, in which the 15 samples obtained between 55 (best) and 9 (worst) "marks", should be read in the original work; on the whole the opinions of

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¹) Chem. Zeitschrift **3** (1903), 177.

²) Pharm. Weekblad **40** (1903), 981.

the experts agree fairly well. The chemical examination referred to the relation between weight and length of pods, the determination of the content of total volatile substances, of extract, vanillin, and the residual ashes. It is interesting to note that the average vanillin-content was 6,9 %, that of the best sample being 7,6 %, against 2,7 % of the worst; the maximum-content of 10,1 % was shown in the specimen which received the 11th place. Further, the methods are mentioned according to which the two best qualities which had carried off the prizes had been produced; and it is a remarkable fact that these show a marked difference in the period and manner of heating. The pods of the sample which received the first prize, for example, were dipped in boiling water for only ten seconds, whereas the other one was boiled for three minutes in water and then for another minute in poppy oil; the further method of preparation does not show any marked difference. The remaining communications of Greshoff with reference to the relations between vanilla and vanillin, and also on the methods of determining the latter, contain nothing worthy of notice.

**Schimmel & Co.**

J. J. Weber, Leipzig.