THE CHEMICAL SYNTHESIS

OF

VITAL PRODUCTS

THE CHEMICAL SYNTHESIS OF VITAL PRODUCTS AND THE INTER-RELATIONS BETWEEN ORGANIC COMPOUNDS

BY

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VOL. I

HYDROCARBONS, ALCOHOLS AND PHENOLS, ALDEHYDES, KETONES, CARBOHYDRATES AND GLUCOSIDES, SULPHUR AND CYANOGEN COMPOUNDS, CAMPHOR AND TERPENES, COLOURING-MATTERS OF THE FLAVONE GROUP

LONDON
EDWARD ARNOLD
41 & 43 MADDOX STREET, BOND STREET, W.
1904

PREFACE

The present work, the aim and objects of which are set forth in the introductory chapter, originated in the year 1895, when, in the course of preparing an address as President of the Chemical Section of the British Association at Ipswich, I had occasion to take stock of the present state of knowledge of synthetical chemistry[1]. I have been encouraged from time to time by various chemical and biological friends, among whom I would especially mention Dr. Horace Brown, Mr. Francis Darwin, Professors J. R. Green, W. D. Halliburton, Marshall Ward and W. P. Wynne, to proceed with a compilation which, in the midst of many other occupations and with very little leisure time, has necessarily been a somewhat arduous task.

As it stands, this contribution to chemical literature represents the result of fragmentary labour carried on at odd intervals during the last nine years. From the nature of the conditions under which I have been compelled to carry on the work, and in view of the wide domain which it covers, it will, I am afraid, be found imperfect in many respects, both with regard to omissions and inclusions. Encouraged, however, by the belief that no similar work has hitherto been undertaken, and that the time has arrived when a complete presentation of the synthetical achievements of modern Organic Chemistry would be of service to investigators here and abroad, I have decided to offer the book in its present form for whatever value may be attached to it as a work of reference. I am not without hope that it may be found of service as a step towards the foundation of a more exact science of Biochemistry.

Commencing in 1895 with simply a tabular list of synthetical products, it was soon found that the scope of the treatise would have to be considerably enlarged in order to give an adequate account of the distribution in nature of the vital products and of the numerous synthetical processes. Concurrently with the progress of the work a constant supervision over current literature had to be kept up in order that new discoveries might be interpolated as they were announced. The rapid

[1] Rep. Brit. Assoc., Ipswich, 1895, p. 648.

progress of discovery in this field must be held responsible for what might be regarded as many anachronisms of treatment in the text of the work.

It was my ambition at the outset to have kept pace with the extension of our knowledge up to the completion of the whole work, but the ever-increasing demands upon my time and energies have compelled me to abandon this project and to consider the literature as closed at the end of 1902. An Appendix comprises the more important syntheses which have been effected during the printing of this volume. In order to avoid unnecessary delay it has also been decided to issue the work in two volumes. The second of these is in rough draft, and will be completed for publication as soon as practicable.

If asked, as I frequently have been during the progress of the work, what position synthetical chemistry occupies with respect to the doctrines of Vitalism or Neovitalism, I think it advisable to place upon record the opinion that the present achievements in the domain of chemical synthesis furnish no warrant for the belief that the chemical processes of the living organism are in any sense transcendental, or that they must be regarded as belonging to a class of special material transformations which human science will never be able to reproduce. Such an admission as the latter would be tantamount to a proclamation of Neovitalism; but the whole history of organic synthesis, from the time when it was declared that organic compounds could be obtained only by living agency, is opposed to any such conclusion[1]. But although the doctrine of a special 'vital force' has received its deathblow at the hands of modern science, and although there is no warrant for the belief that the physics or chemistry of animals and plants is ultra-scientific, yet it must not be lost sight of that the synthetical possibilities of the living organism have brought us face to face with modes of chemical action of which we are as yet profoundly ignorant.

Those who consider that the triumphs of chemical synthesis have finally disposed of Vitalism in any form will do well to bear in mind that, until the chemist has shown that his synthetical methods are identical with Nature's methods, there is just as much scope for endeavouring to penetrate the chemical vital mysteries as there was in the days when it was believed that every 'organic' compound

[1] See on the other hand Dr. Lionel S. Beale's Introductory Lecture on 'The Foundations of Medical Science,' delivered at King's College on Oct. 4, 1895. 'The Lancet,' Oct. 19, 1895.

required an animal or a plant for its production. If this is lost sight of amidst the overwhelming mass of material accumulated by the great army of workers in the field of Carbon Chemistry—if we have produced thousands of compounds which do not and probably never will be found to exist in living organisms; if we have gone so far beyond Nature as to make it appear unimportant whether an organic compound is producible by vital chemistry or not, we are running the risk of blockading whole regions of undiscovered modes of chemical action by falling into the belief that known laboratory methods are the equivalents of unknown vital methods.

The whole contents of this work will show how little warrant there is for assuming such an attitude as the above. Rather than interpose such a barrier to future investigation it would be better to return to the initial position and to ask critically how far chemical synthesis has as yet thrown light on the physiological processes of animals and plants. It is evident that no synthetical process of a pyrogenic character is of any particular biochemical interest. The fundamental synthesis *par excellence*—the photosynthesis which plants are enabled to accomplish, and in the course of which carbon dioxide is absorbed by an organic compound and the product or products decomposed with the liberation of oxygen—is as yet without a laboratory parallel. It has also long been recognised that many hydrolytic decompositions in the living organism which result in the formation of definite products are due to enzyme action. Such actions can generally be imitated by laboratory methods, but the analogy between the natural and the laboratory process disappears when it is considered that as yet no organic nitrogenous hydrolysing agent of the nature of an enzyme has ever been synthesised.

Still more recently has it been shown to be probable that certain up-grade syntheses in the living organism, i. e. the coalescence of simpler to more complex molecules, may also be the result of enzyme action[1]. Here again it may be said that the process might be imitated by the use of chemical reagents, but the actual vital method has not been reproduced in the laboratory. In emphasising these differences between laboratory synthesis and synthesis in the living organism it has appeared to me that some further stimulus might be given to biochemical investigation, and this consideration has had much weight in

[1] Croft Hill, Trans. Ch. Soc., 1898, 73, 634; Ber. Deutsch. ch. Gesell. 1901, 34, 1380; Kastle and Loevenhart, Am. Ch. Journ. 1901, 26, 533; Hanriot, Comp. Rend. 1901, 132, 212; Emmerling, Ber. Deutsch. ch. Gesell. 1901, 34, 3810; Fischer and E. F. Armstrong, Sitzungsber. Pr. Akad. Berlin, 1901, 123; Ber. Deutsch. ch. Gesell. 1902, 35, 3144.

determining the completion of the task which was commenced nine years ago.

The general survey of synthetical chemistry made possible by the present work will help to bring into prominence the extreme importance of the chemist and physiologist working hand in hand for the future advancement of knowledge in this domain. Had time and space permitted, I should have liked to discuss from the chemical point of view the different hypotheses which have from time to time been advanced by chemists and physiologists in explanation of the vital synthesis of various compounds or groups of compounds. Such discussion, even had I possessed the necessary qualifications as a physiologist, would however have further delayed publication. This part of the work may well be left over for future treatment, and will gain rather than suffer in importance by allowing the facts to accumulate and mature. I am not without hope that the present *résumé* will materially assist any future discussion of the problems of Biochemistry. As it stands, the work must be taken simply for what it professes to be—a bare record of the synthetical achievements of generations of workers arranged with a distinct biochemical bias.

At the outset I had also contemplated the interpolation of chemical reactions and schemes, showing by the usual formulæ the genetic relationships between each vital product and its generators. This likewise was abandoned when it was realised that such additions would have expanded the work to an inordinate size, and, further, that the chemical mechanism of these transformations was often imperfectly understood or had been explained only in a tentative way. Here again, therefore, it has been thought better on the whole to limit the work to statements of fact only, because, while the production of one compound from another is an actual achievement, the chemical explanation of the process must necessarily, with the development of our theoretical notions, be subject to modification. As exercises in chemical theory the pages of this compilation will be found to furnish an overwhelming mass of material, and the original publications from which the facts have been gleaned can always be consulted by those who wish to enter more fully into this aspect of the subject.

In offering this book as a work of reference embodying only records of facts, it must of course be understood that my task has been simply that of a compiler, and that I do not hold myself responsible for any of the statements made by investigators. It is not in any sense to be regarded as a critical work, and my whole object has been simply to

bring practical workers, whether chemists, physiologists, or technologists, into communication with the various authorities quoted. For this reason full references have been given for every record of the natural occurrence of the compounds and of the methods employed for their synthetical production. As it has been found impossible to read every paper in full in the original, it is also necessary to caution those who use this volume that many of the papers contained in difficultly accessible publications have been seen only in the abstracts published in the 'Chemisches Central-Blatt,' the 'Journal of the Chemical Society,' the 'Journal of the Society of Chemical Industry,' and in the 'Journal of the Federated Institutes of Brewing.' The page given in the references must not therefore be quoted in all cases without further verification as the actual page of the original paper in which the statement occurs, but simply as a reference to the page of the publication on which the original paper is to be found.

The vital products recognised in this volume are those compounds of definite chemical composition which are known to be produced as the result of the vital activities—for the most part normal—of animals and plants, including of course the heterogeneous assemblage of micro-organisms. As explained in the introductory chapter, considerable latitude has been allowed in the interpretation of the term 'vital product'; but it is to be understood that the syntheses of these compounds as recorded are in every case *complete* in the chemical sense. It is necessary to call attention to this point because in many instances it may appear that where one vital product (*X*) has been recorded as a generator of other vital products (*A*, *B*, &c.), the compound *X* having originally been synthesised from *A* or *B*, that we have got out of *X* nothing more than was originally put into it, and that there has accordingly been presented a case of 'circular reasoning,' or, in other words, an incomplete synthesis. In all such cases, however, it will be found that *X* can be obtained from generators other than *A* or *B*, and that the synthesis of *X* is therefore independently complete. The importance of recording the inter-relations of *X*, *A*, and *B* is fully explained in the subsequent pages.

A compilation such as the present would have been for me an impossible undertaking without the free use of the standard works of reference, and I must in the first place acknowledge my indebtedness to Beilstein's 'Handbuch der organischen Chemie' and its Supplements; to Watts's 'Dictionary of Chemistry,' Morley and Muir; to Thorpe's 'Dictionary of Applied Chemistry'; and to Roscoe-Schor-

lemmer's 'Lehrbuch der organischen Chemie,' by Brühl and his collaborators. In addition to these general works, many treatises dealing with special branches of the subject have been found of extreme value:—

For physiological chemistry, 'Lehrbuch der physiologischen Chemie,' by Hammarsten, and the American translation by Mandel; also 'The Chemical Basis of the Animal Body,' by Sheridan Lea.

For enzymes, 'The Soluble Ferments and Fermentation,' by J. Reynolds Green.

For fermentation, 'Die Mikroorganismen der Gärungsindustrie,' by Jörgensen; also 'Technical Mycology,' by Franz Lafar, German and English editions; 'Die Gärungsorganismen,' by Klöcker; 'Die Fermente und ihre Wirkungen,' by Oppenheimer; 'Die Zersetzung stickstofffreier organischer Substanzen durch Bakterien,' by Emmerling.

For terpenes, 'The Chemistry of the Terpenes,' by Heusler, translation by Pond.

For ethereal oils, 'Die aetherischen Oele,' by Gildemeister and Hoffmann; also 'Les Huiles essentielles,' by Charabot, Dupont, and Pillet, and 'Odorographia,' by Sawer.

For carbohydrates, 'Die Chemie der Zuckerarten,' by E. O. v. Lippmann; 'Kurzes Handbuch der Kohlenhydrate,' by Tollens; 'Les Sucres et leurs principaux dérivés,' by Maquenne.

For glucosides, 'Die Glykoside,' by Van Rijn.

For colouring-matters, 'Die Chemie der natürlichen Farbstoffe,' by Hans Rupe.

For alkaloids, 'Ueber die Erforschung der Konstitution und die Versuche zur Synthese wichtiger Pflanzenalkaloide,' by Julius Schmidt.

For ptomaines, 'Ueber Ptomaïne,' by Brieger.

Some of the sections in the German edition of Roscoe and Schorlemmer's treatise above referred to are in themselves special monographs, and some of the lectures in the Stuttgart series, entitled 'Sammlung chemischer und chemisch-technischer Vorträge,' have also been found of much value, and are quoted under their respective titles.

Mr. E. M. Holmes, F.L.S., has been good enough to revise the lists of plants referred to in the present volume, and I desire to express my thanks to this well-known authority for the valuable assistance thus given.

R. M.

July, 1904.

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LIST OF SYNTHETICAL PRODUCTS

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4. Normal Heptacosane.
5. Normal Hentriacontane.
6. Cymene.
7. Styrene.
8. Metastyrene.
9. Dipentene and Limonene.
10. Terpinene.
11. Lævo-isoterpene.
12. Naphthalene.

Alcohols and Terpene Alcohols.

13. Methyl Alcohol.
14. Ethyl Alcohol.
15. Normal Propyl Alcohol.
16. Isopropyl Alcohol.
17. Normal Butyl Alcohol.
18. Isobutyl Alcohol.
19. Tertiary Butyl Alcohol.
20. Normal Primary Amyl Alcohol.
21. Normal Secondary Amyl Alcohol.
22. Isoamyl Alcohol.
23. Normal Hexyl Alcohol.
24. Isohexyl Alcohol.
25. Active Hexyl Alcohol.
26. Normal Heptyl Alcohol.
27. Isoheptyl Alcohol.
28. Normal Primary Octyl Alcohol.
29. Nonyl Alcohol.
30. Secondary Hendecatyl Alcohol.
31. Normal Primary Dodecyl Alcohol.
32. Normal Primary Tetradecyl Alcohol.
33. Cetyl Alcohol.
34. Octadecyl Alcohol.
35. Dimethylheptenol.
36. Geraniol.
37. Linaloöl.
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39. Terpineol.
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42. Isopulegol.

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51. Mannitol.
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55. Saligenin.
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153. d-Arabinose.
154. Dextrose. **155.** Lævulose.
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158. Populin.
159. Methylarbutin.

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166. Allyl Isothiocyanate.
167. Crotonyl Isothiocyanate.
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ABBREVIATED TITLES OF PUBLICATIONS QUOTED

American Chemical Journal	= Am. Ch. Journ.
American Journal of Pharmacy	= Am. Journ. Pharm.
American Journal of Physiology	= Am. Journ. Physiol.
American Journal of Science	= Am. Journ. Sci.
Annalen der Chemie (Liebig's)	= Ann.
Annalen der Physik, &c., Gilbert	= Gilb. Ann.
Annalen der Physik, &c., Poggendorff	= Pogg. Ann.
Annales Agronomiques	= Ann. Agronom.
Annales de Chimie et de Physique	= Ann. Chim.
Annales de l'Institut Pasteur	= Ann. Inst. Past.
Annales des Sciences Naturelles	= Ann. Sci. Nat.
Annals of Botany	= Ann. Bot.
Archiv für experimentelle Pathologie und Pharmakologie	= Arch. exp. Path.
Archiv für die gesamte Physiologie des Menschen und der Thiere	= Pflüger's Arch.
Archiv für Hygiene	= Arch. Hyg.
Archiv der Pharmazie	= Arch. Pharm.
Atti della Reale Accademia dei Lincei : Rendiconti	= Atti Real. Accad.
Beiträge zur chemischen Physiologie und Pathologie	= Beit. ch. Physiol. u. Path.
Berichte der Deutschen botanischen Gesellschaft	= Ber. Deutsch. bot. Gesell.
Berichte der Deutschen chemischen Gesellschaft	= Ber.
Berichte der Deutschen pharmazeutischen Gesellschaft	= Ber. Deutsch. pharm. Gesell.
Biedermann's Centralblatt für Agrikulturchemie, &c.	= Bied. Centr.
Bollettino Chimico Farmaceutico	= Boll. Ch. Farm.
Botanische Zeitung	= Bot. Zeit.
Bulletin de l'Académie Royale des Sciences, &c. de Belgique	= Bull. Acad. Roy. Belg.
Bulletin de l'Association Belge des Chimistes	= Bull. Assoc. Belg.
Bulletin de la Société Chimique de Paris	= Bull. Soc.
Bulletin de la Société Mycologique de France	= Bull. Soc. Mycol.
Centralblatt der medizinischen Wissenschaften	= Centr. med. Wiss.
Centralblatt für Bakteriologie und Parasitenkunde, &c.	= Centr. Bakter.
Centralblatt für Physiologie	= Centr. Physiol.
Chemical News	= Ch. News.
Chemiker-Zeitung	= Ch. Zeit.
Chemische Industrie, Die	= Ch. Ind.
Chemisches Central-Blatt	= Ch. Centr.
Chemist and Druggist, The	= Ch. Drug.
Comptes Rendus hebdomadaires des Séances de l'Académie des Sciences	= Comp. Rend.
Dingler's polytechnisches Journal	= Ding. poly. Journ.
Electrical Review	= Elect. Rev.
Elektrochemische Zeitschrift	= Elektro. Zeit.
Gazzetta chimica Italiana	= Gazz.
Geschäftsbericht von Schimmel & Co., Leipzig	= Schimmel's Ber.
Jahresbericht über die Fortschritte der Chemie, &c. (Berzelius)	= Berz. Jahresber.
Jahresbericht über die Fortschritte der Chemie, &c.	= Jahresber.
Journal of the American Chemical Society	= Journ. Am. Ch. Soc.
Journal of the Chemical Society of London	= Journ. Ch. Soc.
Journal für Chemie und Physik, Gehlen	= Gehlen's Journ.
Journal of the Federated Institutes of Brewing	= Journ. Fed. Inst.
Journal de Pharmacie et de Chimie	= Journ. Pharm.

Journal für praktische Chemie	= Journ. pr. Ch.
Journal of the Russian Physical and Chemical Society (in Russian)	= Journ. Russ. Soc.
Journal of Physiology	= Journ. Physiol.
Journal of the Society of Chemical Industry	= Journ. Soc. Ch. Ind.
Landwirtschaftlichen Versuchs-Stationen, Die	= Landw. Versuchs-Sta.
Monatshefte für Chemie	= Monats.
Moniteur Scientifique	= Mon. Sci.
Pharmaceutical Archives	= Pharm. Arch.
Pharmaceutical Journal	= Pharm. Journ.
Pharmaceutical Review	= Pharm. Rev.
Pharmaceutische Rundschau	= Pharm. Rund.
Pharmazeutische Zeitung	= Pharm. Zeit.
Philosophical Magazine	= Phil. Mag.
Philosophical Transactions of the Royal Society	= Phil. Trans.
Proceedings of the Chemical Society of London	= Proc. Ch. Soc.
Proceedings of the Physiological Society	= Proc. Physiol. Soc.
Proceedings of the Royal Society of London	= Proc. Roy. Soc.
Recueil des Travaux Chimiques des Pays-Bas	= Rec. Tr. Ch.
Revue de Chimie Industrielle	= Rev. Ch. Ind.
Revue générale de Chimie pure et appliquée	= Rev. gén. de Chim.
Sitzungsberichte d. k. Preussischen Akademie der Wissenschaften, Berlin	= Sitz. Pr. Akad.
Stazioni sperimentali agrarie Italiane, Le	= Staz. sper. agrar.
Transactions of the Chemical Society of London	= Trans. Ch. Soc.
Transactions of the Pathological Society	= Trans. Path. Soc.
Wochenschrift für Brauerei	= Woch. Brau.
Zeitschrift für analytische Chemie	= Zeit. anal. Ch.
Zeitschrift für angewandte Chemie	= Zeit. angew. Ch.
Zeitschrift für anorganische Chemie	= Zeit. anorg. Ch.
Zeitschrift für Biologie	= Zeit. Biol.
Zeitschrift für Chemie	= Zeit. Ch.
Zeitschrift für die chemische Industrie	= Zeit. ch. Ind.
Zeitschrift für Elektrochemie	= Zeit. Elektroch.
Zeitschrift für das gesamte Brauwesen	= Zeit. ges. Brau.
Zeitschrift für physikalische Chemie	= Zeit. physik. Ch.
Zeitschrift für physiologische Chemie (Hoppe-Seyler's and subsequently)	= Zeit. physiol. Ch.
Zeitschrift für Zucker-Industrie in Böhmen	= Zeit. Zucker-Ind. Böhm.

INTRODUCTORY

I. HISTORICAL

The history of organic chemical synthesis has been so frequently dealt with by previous writers that it is unnecessary to discuss the subject in detail from this point of view. In so far as the existence of a special 'vital force' was considered necessary to explain the formation of organic compounds by the living organism, it is generally conceded that Wöhler, by his synthesis of urea from ammonium cyanate in 1828, was the first to deliver a serious blow against the doctrine in question. As a pioneer in the same field our own countryman, Henry Hennell, must, as I ventured to plead in 1895[1], be accorded a place not inferior to that of Wöhler as being among the first to produce an organic compound independently of the living organism. The English chemist succeeded in synthesising alcohol from olefiant gas at practically the same time that his great German contemporary had excited the interest of the whole chemical world by his synthesis of urea.

Important as was the latter discovery, it must not be forgotten that at the time of its announcement the synthesis was not what would now be termed 'complete,' because the cyanide from which the cyanate was prepared was then obtained by fusing nitrogenous organic matter with an alkaline carbonate, so that it might have been said that the carbon and nitrogen were both of vital origin. The synthesis of alcohol by Hennell was equally incomplete, because the olefiant gas had been obtained by the pyrogenic decomposition of organic material, viz. oil, so that in this respect the two syntheses were on precisely the same level.

Since alcohol was not in 1828 recognised as a vital product in the same sense that urea was so regarded, it will be easily understood why the synthesis of the former failed to arouse any particular interest at the time; the discovery did not clash with the current notions of Vitalism. As Hennell's contribution to chemical synthesis had of late years been allowed to fall into oblivion, I thought it desirable in 1895 to remind chemists once again of his claim to take rank among the early pioneers in this field. The plea has not, however, been allowed to pass unchallenged, for no less an authority than M. Berthelot, one of the most active and distinguished among the later workers at the subject of chemical synthesis, has denied Hennell's claim to have been the first to synthesise alcohol[2]. Under these circumstances it will be

[1] Brit. Assoc. Rep. Ipswich, 1895, p. 649.

[2] Comp. Rend. 1899, 128, 862.

perhaps desirable to state more fully the facts upon which the English chemist's claim is based:—

In 1826 Faraday published a paper entitled, 'On new Compounds of Carbon and Hydrogen, and on the Products of the Decomposition of Oil by Heat[1],' in the course of which he states: 'I find also that sulphuric acid will condense and combine with olefiant gas, no carbon being separated, or sulphurous or carbonic acid being formed, and this absorption has in the course of eighteen days amounted to 84·7 volumes of olefiant gas to one volume of sulphuric acid. The acid produced combines with bases, &c., forming peculiar salts, which I have not yet had time, but which it is my intention, to examine.'

The following year, on March 9, Brande communicated to the Royal Society a paper by Hennell bearing the title: 'On the Mutual Action of Sulphuric Acid and Alcohol, with Observations on the Composition and Properties of the resulting Compound[2].' In this paper the author shows that he possessed very clear notions concerning the nature of the sulphovinates, and he gives analyses of 'oil of wine' as well as of the potassium salt of sulphovinic acid. He refers to some sulphuric acid which had been given to him by Faraday as having absorbed eighty times its volume of olefiant gas from oil gas, this being no doubt the specimen mentioned by Faraday in the previous paper. He identified sulphovinic acid in the foregoing preparation, and proved it by a comparison of the potassium salt with potassium sulphovinate obtained from 'oil of wine[3].' It is true that he gives no analysis of the potassium salt from Faraday's acid, but he had already shown evidence of his familiarity with this salt, and he declares the identity of the salts from the two sources in most distinct terms.

It is impossible to arrive at any other conclusion than that Hennell was aware that he had obtained sulphovinic acid from olefiant gas. In 1828 a second paper was communicated to the Royal Society (read June 19) under the title: 'On the Mutual Action of Sulphuric Acid and Alcohol, and on the Nature of the Process by which Ether is formed[4].' In this second paper, among other experiments, he distilled sulphovinic acid with water and a little sulphuric acid, and proved that it was decomposed into sulphuric acid and alcohol: and not only this, but he also showed that *the whole* of the alcohol and sulphuric acid which originally entered into the composition of the sulphovinic acid could be recovered by distillation with water. It is true that the sulphovinic acid used in his second series of researches was not obtained from olefiant gas, but this cumbersome mode of preparation was obviously unnecessary in view of the circumstance that he had already satisfied himself that the products were identical. There can be no reasonable doubt that the claim advanced on behalf of Hennell as the first to synthesise alcohol from olefiant gas must be admitted to

[1] Phil. Trans. 1825, p. 448.
[2] *Ibid.* 1826, Part III, p. 240.
[3] *Loc. cit.* p. 245.
[4] *Ibid.* 1828, p. 365.

be fully borne out by the critical examination of the papers referred to, and this conclusion has recently been upheld by Fritzsche, who also points out that these results were known to contemporary Continental chemists [1].

II. NATURE OF THE COMPOUNDS REGISTERED AS VITAL PRODUCTS

The term 'vital product' has been adopted in preference to the designation 'natural product,' which first suggested itself because the latter, strictly interpreted, includes also mineral or inorganic compounds. In working out the details presented in the following pages much consideration has had to be given to the question as to which compounds should be regarded as of vital origin. In works dealing with organic or physiological chemistry it is generally stated or implied that such compounds are formed by the living plant or animal, as the result of the physiological activities of its various organs or tissues. It is also understood, in accordance with modern views, that the seat of such physiological activity is the cell. Although this conception of the nature of a vital product at first sight appears to bring the term within easily definable limits, it soon became evident when the individual products came under consideration that from the chemical point of view, apart from the question of the physiological mechanism by which the compounds are formed, some more precise understanding would have to be arrived at. Thus in many cases it is necessary to register a vital product not under one heading as a simple molecule, but under two or more headings if the compound is obviously built up of, and is easily resolvable into, two or more compounds of less molecular complexity.

By way of illustration, it is doubtful whether either methyl alcohol or salicylic acid occurs in nature in the free state; but the ester, methyl salicylate, is the chief constituent of the oil of wintergreen (*Gaultheria*), and is contained in the ethereal oils of large numbers of other plants. It is further probable that methyl salicylate does not itself exist in the plants in the free state, but in the form of a glucoside, gaultherin. The glucoside is therefore, strictly speaking, alone entitled to registration. Similarly with respect to alizarin, which does not exist as such in the plant, but in the form of the glucoside ruberythric acid. In cases such as these, which are typical of a large class, the product has been regarded as having been synthesised, and compounds such as methyl alcohol, salicylic acid, and alizarin have been regarded

[1] Journ. pr. Ch. [2] 65, 597. The references to 'Poggendorff's Annalen' given are 9, 21; 14, 282. The latter, which relates to Hennell's second paper, is given also in Beilstein's 'Handbuch,' Vol. I, p. 222, but, strangely enough, has been corrected in the Supplement (Vol. I, p. 72) so as to make it appear as though M. Berthelot's reclamation had been admitted.

as vital products, although the glucoside itself may not have been hitherto synthesised in all cases.

The necessity for this treatment will be recognised when it is considered that the constituent atomic complexes of easily resolvable molecules are very likely hereafter to be found in the free state in nature, and in many instances are actually known, as in the case of glucose, to exist as individual compounds. Thus, to mention another example, hydroquinone (quinol) [71] was at first entered as occurring only in the form of the glucoside arbutin. While this work was in course of preparation it was announced by Hesse (Ann. **290**, 317), that this phenol occurs in the South African 'sugar bush,' *Protea mellifera*. As the products from animals and plants are more and more investigated it is certain that such instances will be multiplied.

On considering the published records as to the occurrence of vital products it also became evident that in very large numbers of cases it was extremely doubtful in what form the compound was actually produced by the animal or plant. In other words, it is uncertain whether many compounds isolated, identified, and recorded as of natural occurrence may not have resulted from the resolution of more complex and unstable molecules by the action of enzymes or of the chemical reagents employed in their extraction—whether in fact they may not have resulted from secondary changes or decompositions taking place after removal from the organism. In view of this state of affairs it must be admitted that a vital product is not so easily definable as appears at first sight, and that in the present condition of knowledge it is not always possible to say whether a particular compound is of biochemical origin or whether it is a secondary product. Under these circumstances it has been deemed advisable, in order to make this work as comprehensive as possible, to assume that the complex of atoms present in the molecule of the vital product as isolated is of biochemical origin, even if the compound is not directly synthesised as such by the animal or plant.

This view will no doubt commend itself to both chemists and physiologists. From the chemical standpoint it is certainly justifiable to believe that if a complex molecule is so unstable as to break down readily into simpler molecules, the atomic groupings present in the latter pre-exist in their generator. Moreover, molecular instability is a phenomenon of degree, and it has been found practically impossible to define the conception narrowly in terms of the agents necessary for causing the resolution of the compounds. It is not possible, for example, to draw a hard and fast line between, on the one hand, the action of enzymes and of acids or alkalies at ordinary temperatures, and, on the other hand, the action of acids or alkalies at high temperatures, or even, in the case of the more stable cyclic compounds, the action of fused alkali. For this reason the conception of a vital product has been enlarged so as to include every atomic complex

which, without unduly straining the facts, there is reason for believing to be present in the products resulting from vital synthesis, the other condition for ensuring inclusion in this work being of course that the complex has been synthesised in the laboratory. The question whether the agent which reveals the presence of the complex is a mild or a violent one is for the purposes of the present treatment considered only as of subordinate importance.

The liberal extension of the term 'vital product' thus claimed has, it is hoped, been used judiciously, and not pushed to an unwarranted degree. All that can be said is that in the present state of knowledge, where so much doubt surrounds the chemical history of the antecedents of vital products, full advantage has been taken of this doubt on behalf of this compilation. Should it be proved hereafter that any particular compound is the result of secondary synthesis, and that its atomic complex is not formed by the living organism, it can easily be removed from the list.

The importance of including every possible complex, whether it is obviously present in the vital product or whether its presence is inferred only, will be more fully recognised if it is pointed out that the inferred existence of any particular group of atoms in the molecule becomes converted into a demonstrated fact, when, as in many of the cases recorded, the compound has been produced synthetically from a generator which is known to contain the group in question. A few examples will serve more fully to illustrate the nature of the difficulties which have had to be met, and will furnish further justification for the mode of treatment adopted:—

Furfural [**126**] has been found in the aqueous distillate from many ethereal oils from plants as well as in some of the oils. It has been detected also in certain fermented liquors, such as whisky, &c. It is doubtful whether this compound is really a biochemical product, since it may have been produced by the breaking down of more complex antecedents (pentoses, &c.) during the process of distillation. This question has been much discussed of late by technical chemists, and the balance of opinion is against its being a product of alcoholic fermentation. Nevertheless this aldehyde has been included because it may be fairly said that the complex of atoms which so easily closes up with the formation of this heterocyclic molecule pre-exists in the vital compound or compounds which are its generators. Should any of these generators be hereafter synthesised it is possible that furfural may be made use of in their synthesis.

Again, orcinol [**75**] has not yet been found in the free state in any plant, but many complex acids found in lichens yield this phenol with varying degrees of facility, from simply boiling with water, alkaline carbonates, or baryta water, to fusion with caustic alkali. It is therefore evident that the orcinol complex is contained in these lichen acids, and should any of these compounds ever be synthesised it is certain

that orcinol or a derivative would have to be as it were built into the structure of the molecule. This phenol, which has of course been completely synthesised, has therefore been included among the vital products, and it is not at all improbable—in view of the facility with which some of the lichen acids furnish the compound by chemical treatment and even by bacterial action—that it may yet be found in the vegetable kingdom.

Resorcinol [70] presents a similar case, only the evidence that the complex is contained in vital products such as pæonol [133], euxanthone [136], &c., has been in the first place obtained by the more violent method of fusing with alkali. It is hardly likely that this phenol will be ever found in the free state in plants, but it must nevertheless be regarded as a vital product, since it has been proved by synthesis as well as by the action of heated alkali that resorcinol is one of the generators of both pæonol and euxanthone.

For similar reasons the pyrogallol [84] complex is regarded as being present in gallic acid, &c., the phloroglucinol [86] complex in many colouring-matters of the pyrone group, and so forth. Another instructive example is furnished by hydrojuglone [90] from the walnut, *Juglans regia*. This compound is known to be a derivative of naphthalene, and as it contains the naphthalene complex the syntheses of this hydrocarbon are given in connexion with the phenol. While these pages were undergoing final revision it was announced by v. Soden and Rojahn (Pharm. Zeit. 47, 779) that the hydrocarbon itself had been found in certain vegetable ethereal oils.

III. ORGANIC CHEMISTRY FROM THE BIOCENTRIC STANDPOINT

The general tendency of the present work is to bring Carbon Chemistry back to the point from which it departed three-quarters of a century ago, when the leading discovery of the synthesis of urea by Wöhler showed that organic compounds could be formed without vital intervention. Without desiring to reopen the question of the existence of a special 'vital force,' it may be well to call the attention of those physiologists who appeal to the achievements of synthetical chemistry as conclusive evidence against the existence of such a force to the fact—so distinctly brought out by the summary of experimental results herein recorded—that the testimony of pure chemistry cannot, *as it at present stands*, be legitimately interpreted into a direct negation of Vitalism in any form. This negation may, and probably will, be made possible in the future when our chemical methods have been made to approximate more closely to the vital methods.

In the meantime it must not be forgotten that there is at present but little reason for believing that our laboratory methods have much analogy with the processes which go on in the living organism. All

that can be said is that the chemist has realised that which vital chemistry had been realising long before his entry into the field—that such and such atomic groupings are stable and capable of free and definite existence, and to this knowledge he has added the fact that vast numbers of other atomic groupings are also capable of free and definite existence. An impartial survey of the facts will, however, serve to show how far we still are from realising vital chemical processes in the laboratory. The fact that alcohol can be synthesised from carbon and hydrogen through acetylene, &c., has no direct bearing on the formation of alcohol from sugar by the zymase of the yeast-plant. When we can transform sugar into alcohol in the laboratory at ordinary temperatures by the action of a synthesised nitrogenous organic compound; when we can convert glucose into citric acid in the same way that *Citromyces* can effect this transformation; when we can build up heptane, or cymene, or styrene, or when we can produce the naphthalene or anthracene complex in the laboratory by the interaction of organic compounds at ordinary temperatures, then may the chemist proclaim with confidence that there is no longer any mystery in vital chemistry.

It is clear that if chemistry be regarded from what may be called the biocentric point of view, the complete synthesis of an organic compound by pyrogenic methods or by the action of violent reagents is of comparatively little importance. On the other hand, the transformation of one vital product into another by laboratory processes—even if these are at present not actually analogous to the physiological processes—may furnish information of the highest biochemical significance. The treatment of organic chemistry in this work has accordingly been entirely subordinated to the biocentric view of the subject. The book is not to be regarded simply as a catalogue of synthetical products and processes; neither does it profess to be a practical laboratory guide to the preparation of organic compounds, although, by virtue of its contents, it necessarily comprises both kinds of information. Physiologists will find herein a record of the achievements of synthetical chemistry, chemists will be enabled to ascertain the natural mode of occurrence of organic compounds, and technologists will no doubt find it useful to have the chemical generators of such products as are of industrial value brought conspicuously under notice.

The importance of emphasising the relationships between the vital products themselves will be realised when it is pointed out that the future development of our knowledge of the chemistry of the living organism must depend largely upon the detection of the chemical antecedents of these products. The discussion of the results of chemical synthesis from this point of view does not come within the scope of the present work, but belongs—at any rate in the present state of knowledge—rather to the province of physiology. It is for this reason that the necessity for the chemist and physiologist working

hand in hand has been insisted upon so frequently and so emphatically of late years by both classes of workers[1]. The publication of this volume may possibly contribute towards this much-desired *rapprochement* between the sciences.

So far as modern science has been enabled to deal with the question of the mode of origin of these vital products in the living organism, it must be confessed that hitherto but little progress has been made. The chemist at the present time may be said to be far in advance of the physiologist in his contributions to biochemistry. While large numbers of definite vital products have been isolated, identified, and synthesised in the laboratory, the course of development of these compounds in the organism can hardly yet be said to have been satisfactorily traced in any instance. The practical difficulties associated with this kind of investigation are confessedly very great, but it must be apparent to chemists that the study of the evolution of organic compounds in the animal or plant has the most pressing claims upon the attention of physiologists. With the solution of the problems furnished by such studies our knowledge of vital chemistry, and through this of vital processes generally, is certain to advance by great strides. Perhaps it is not going too far to say that the whole future development of physiological chemistry lies in this direction.

The chemical evolution in the living organism of one definite compound of known constitution, if successfully traced, might lead to the discovery of fundamental principles. It certainly must strike chemists as being somewhat remarkable, in view of the importance of the investigation of such problems, that more systematic efforts have not been concentrated upon them by physiologists. The difficulties surrounding the determination of the origin of such a comparatively simple product as urea in the animal body or oxalic acid in plants, or, again, the study of the origin and fate of amino-acids in the growing plant, which has received so much attention of late years from Schulze and others, will only serve to emphasise the necessity for the vigorous prosecution of research in this field. The evolution of definite products in the growing plant would appear to offer special facilities for investigation, because the course of development of the compounds might be followed by collecting and investigating such well-characterised substances as are contained in many ethereal oils at different stages in the life-history of the plant or of the part of the plant which yields the oil. Some progress in this direction has been made in France by Charabot, whose views concerning the development of the terpene alcohols and ketones, which are referred to under these respective groups, are worthy of special notice as examples of the results of a kind of pioneering work which is much required. Such research constitutes the common meeting ground of chemistry and

[1] See, for instance, Prof. W. D. Halliburton's address to the Section of Physiology at the Belfast meeting of the British Association in 1902. Brit. Assoc. Rep. 1902, p. 771.

physiology, and if the publication of this work should give an impetus to further activity in this region one of its main objects will have been achieved.

The development of physiology along chemical lines is bound to take place at an increasing rate with the progress of discovery, and in the future the two sciences must necessarily become more and more interdependent. If, some decades hence, a work on similar lines to the present should ever be compiled, it may be anticipated with confidence that the laboratory methods for synthesising vital products will have approximated more closely to the physiological processes. It may further be predicted with equal confidence that as greater chemical mastery is acquired over the biochemical processes the number of syntheses of vital products effected in the laboratory will go on increasing at a much greater rate. Molecules of greater and greater complexity will be built up independently of the animal or plant, and the final triumph of synthetical chemistry may be expected to culminate in the synthesis of those complex proteids which constitute such a large proportion of the materials composing the living organism. The complicated nitrogenous colloidal substances which play such an important part in vital chemistry will at that time be no longer subject to the reproach, now frequently aimed by organic chemists who recognise nothing that is not crystalline, of being 'messes,' but will take rank among the definite synthesised vital products. In the meantime the recasting of the data of organic chemistry in this biological mould may help to convince physiologists that considerable progress has been made by chemists towards placing their science on a more exact foundation, since all the vital products registered in this work are perfectly definite and well-characterised compounds of known chemical constitution.

IV. CHEMICAL SYNTHESIS FROM THE BIOCENTRIC STANDPOINT

The consideration of the achievements of synthetical chemistry from the present point of view has necessarily resulted in a mode of treatment differing essentially from that adopted in the current treatises. The term 'synthesis' as used in organic chemistry is generally assumed, if not explicitly stated, to mean the building up of a carbon compound from compounds of lesser complexity. If the simpler molecule is capable of being produced directly from its elements the synthesis is said to be *complete*. It is evident, however, that in the living organism two kinds of chemical change are going on—an up-grade or building-up process from simpler to more complex molecules, and a down-grade or breaking-down process from complex to simpler molecules. From the chemical as well as from the physiological point of view it appears that a large proportion, if not a large

majority, of the vital products hitherto synthesised are of the nature of down-grade materials, or, in other words, waste products resulting from the degradation of more complex antecedent compounds. It is probable that in many cases the waste material is a final product of the breaking down of several different antecedent compounds.

For the foregoing reasons the term synthesis as used in this work has been given a wider meaning so as to comprise both up-grade and down-grade products. From the established point of view, for example, the formation of acetic acid from methane *via* methyl chloride and cyanide, &c., is regarded as a true synthesis, the simpler molecule having given rise to the more complex. But from the present point of view the formation of methane from acetic acid by heating acetates with alkali is just as much a true and complete synthesis of methane as is the formation of this hydrocarbon by the direct union of its elements. The methane of vital origin is a bacterial product resulting from the breaking down of an extremely complex molecule, cellulose. The latter has not yet been synthesised, but if this synthesis should ever be effected the synthesis of methane *via* cellulose would be as complete as the synthesis of the hydrocarbon *via* acetic acid.

The enlarged view of chemical synthesis thus rendered necessary by a contemplation of the facts from the biological standpoint has resulted in a mode of treatment which may at first seem strange and unfamiliar, but it will be found that the method on closer acquaintance is one that cannot but be helpful to chemists as well as to technologists. Not only is prominence given thereby to the actual generators of the various synthesised products, but the inter-relations between the organic compounds themselves is also brought out as a special feature to which, in view of the importance of the subject, emphasis is given by means of the sub-title of the book.

The interest of the present work will, it is anticipated, be found to centre not only in the records that particular compounds can be obtained from such or such generators, but, as already pointed out, more particularly in the information that such compounds are genetically related among themselves. Thus, to take a simple illustration, the relationship of alcohol to aldehyde and acetic acid is of more than purely chemical interest in this work; it is a fact also of biochemical interest, because aldehyde and acetic acid are both vital products, and the relationship is further of technological interest because the acid is industrially producible from the alcohol by biochemical processes. In general terms the genetic relationship of an organic compound to a product sometimes of greater and sometimes of less complexity is a fact which the present mode of treatment is well adapted to reveal, and the essential feature of this treatment is to bring out all such inter-relations within the limits of a reasonably sized work. In many cases, such, for example, as the relationship of alcohol to certain sugars, the living organism may be said to have discovered methods of break-

ing down complex into simpler molecules, which the chemist cannot imitate at present by laboratory methods. In other cases, again, the chemist has discovered relationships in the laboratory which the living organism has long been realising in the vital laboratory. It must be left to the judgement of physiological chemists to decide whether in the case of any particular relationship herein recorded the chemical mechanism of the transformation is similar in the organism and in the laboratory—whether there is any analogy between the processes or whether absolute ignorance must be declared. The consideration of such problems cannot but give an impetus to further inquiry into the chemical activities of animals and plants.

Certain details of treatment which follow from the foregoing considerations may now be dealt with. While following the main divisions, such as hydrocarbons, alcohols, aldehydes, ketones, &c., under which organic compounds are generally grouped, the information which from the present standpoint is considered of the greatest importance is the particular generator which serves as a starting-point in each synthesis. Since the generators under the present scheme are for the most part themselves vital products, the relationships which from the biochemical point of view are of the greatest interest are thus brought into prominence. It was hoped at the outset of this undertaking that it would have been possible to keep to the systematic classification of the generators in the order of the above main divisions, but the rapid progress of discovery made interpolations and rearrangements so frequently necessary that this plan was found to be impracticable in the time available and it had to be abandoned. This departure from what may be considered the logical sequence will not, however, be found of any practical disadvantage in using the work. The systematic sequence has been observed as far as possible, and the synthetical processes have been arranged under lettered paragraphs with the name of the generator printed in italics so as to catch the eye at once in running down the page. Each synthetical product has also a registration number, so that cross-references are easily found when necessary, the registration numbers which serve for such references being printed in thick type in square brackets. The system of cross-references, although throwing some additional trouble on the reader, has been unavoidable in view of the fact that many synthetical products serve as generators for numbers of other products. The repetition of the synthetical processes every time a synthesised compound is mentioned would have added enormously to the labour of compilation, and would moreover have increased the size of the book to an inordinate extent. In order to facilitate reference the registration number of the compound and the initial letters of the paragraphs containing the descriptions of the synthetical processes are also printed at the top of each page.

Among other consequences which follow from this biochemical

treatment of organic synthesis is a complete departure from the usual practice of classifying carbon compounds under types representing certain atomic configurations of molecules. According to this method, with which most students of organic chemistry are familiar, the parent-compound or type is naturally looked upon as the generator of all its derivatives, and is accordingly given the first rank in the order of treatment. According to the present scheme each vital product is in itself a biochemical type quite independently of the chemical type to which it may be referred, and the synthesis of each product, instead of being mentioned incidentally in connexion with the group to which it belongs as a point of minor interest, is here brought into the first rank of importance. In other words, the chemical type is in this work subordinated to the individual compound—a mode of treatment for which every justification will be conceded when it is pointed out that in vital syntheses there are unquestionable genetic relationships between compounds of quite different types.

In fact, a general survey of the present state of synthetical chemistry makes it perfectly clear that the transformations in the living organism have little or no relations to the chemical type, and it is equally certain that the parent-compound or type, which is often the actual generator in the laboratory synthesis, is not the generator in the vital synthesis. Genetic relationships between vital products are thus to the student of biochemistry all-important, because they may be indicative of the actual course of the vital chemical transition from one compound to another, while relationships due to the possession of a common type of molecular structure are of subsidiary importance. Whole groups of phenols, aldehydes, acids, &c., are, for example, derivatives of benzene, and this hydrocarbon is their actual laboratory generator. It may be confidently asserted that the synthesis of these phenols, aldehydes, acids, &c., is not effected by the animal or plant *via* benzene any more than that the formation of alizarin in the madder plant proceeds from anthracene, or that the production of hydrojuglone in the walnut-tree is preceded by the synthesis of naphthalene.

On the other hand, the genetic relationships between compounds of such different types as acetoacetic ester and quinol [71], as diacetyl [113] and quinol, or as γ-acetobutyric ester (from acetoacetic ester and glycerol) and resorcinol [70] are of special interest from our present standpoint, and may prove hereafter to be of real biochemical significance. The subordination of the type to the individual vital product has for the foregoing reasons been consistently carried out, so that benzene, for example, is treated of, as it were incidentally, in connexion with the first compound in the work in which the benzene nucleus occurs, viz. cymene [6], anthracene in connexion with meta-hydroxyanthraquinone [144], &c.

Another result which may be said to be accidental to the present mode of treatment is the disproportionate amount of space allotted to

some compounds as compared with others. As long, however, as it is borne in mind that the importance of a compound is not measurable by the number of pages occupied by records of its mode of occurrence or of its synthetical production but little harm is likely to arise from this circumstance. It will be evident that such discrepancy is due to the fact that some compounds have lent themselves more readily to chemical investigation than others—that some have been found only in a limited number of animal or vegetable products, while others are widely distributed, or again, that some compounds are synthesisable from a few generators only, while others can be synthesised from a multiplicity of generators. Thus cymene [6] and benzyl alcohol [54] occupy the large amount of space that has been devoted to them because they happen to offer the first opportunity for dealing with the syntheses of benzene and toluene respectively, these hydrocarbons being required in many subsequent syntheses. Chemists will, of course, regard such cases in true perspective, although the caution herein conveyed may perhaps be necessary for physiologists who have no special knowledge of organic chemistry. Had benzene and toluene occurred as such in the free state in nature they would of course have been given place among the vital products and had their syntheses recorded in the usual way.

In view of the improbability of the derivatives of such hydrocarbons as benzene or toluene being synthesised from the hydrocarbon by the living organism it has not been even considered justifiable to include their atomic complexes among the vital products. In fact, in the present state of knowledge, it would be impossible to draw up a satisfactory scale showing the importance to the vital economy of the various synthetical products—the more especially since, as already stated, the majority of these are of the nature of down-grade materials. The compounds of fundamental importance in vital chemistry, such as enzymes and albuminoid substances, have not yet been produced in the laboratory, so that chemical synthesis from the biochemical point of view may be said to have been hitherto confined to the lower orders of combination. Even the classification into the main groups of hydrocarbons, alcohols, &c., although convenient for practical purposes, is from the biocentric standpoint purely artificial, and must be taken rather as an expression of imperfect knowledge than of biochemical reality. When with the progress of discovery it becomes possible to construct schemes showing the genetic or evolutional inter-relations among vital products, then will the time be ripe for discussing on a scientific basis the order of importance of the various organic compounds in the cycle of vital operations. When our knowledge has reached this level it may be confidently asserted that the biochemical relationships will be found to be quite different from those at present indicated by the ordinary chemical classification.

V. ADVANTAGES OF THE BIOCENTRIC TREATMENT OF SYNTHETICAL CHEMISTRY

In one sense every definite organic compound known to science may be said to have relationships with every other organic compound. These inter-relations are necessarily extremely complex, being sometimes hypothetical—as in relationships of chemical type—and in other cases real or genetic with few or many intermediate stages. The progress of discovery in this department of chemistry consists largely in substituting genetic for hypothetical relationships, and among the advantages incidental to the mode of treatment adopted in this work may be claimed the bringing into prominence, not only of the relationships between the vital products themselves, but likewise the inter-relations among the intermediate compounds which are transition stages between one synthetical product and another. The relations between the vital products are, as frequently dwelt upon, of special biochemical interest; the relations between the intermediate compounds are of more purely chemical interest. The intermediate stages may or may not turn out to be of biochemical significance; in the present state of knowledge it is desirable that all inter-relationships should be borne in mind, and in view of the ever-increasing complexity of the connexions between organic compounds revealed by chemical discovery it has been felt that some such work as the present would furnish an opportunity of presenting this aspect of the subject in a manner that cannot but be helpful to students from whatever point of view they may be approaching the science.

As already explained, the time is not yet ripe for discriminating precisely between biochemical and purely chemical relationships; the work could not therefore be cast either in a purely physiological mould or in a purely chemical mould, and its present arrangement appeals to both classes of students. In the future it may be possible, when our synthetical methods have come more into line with the biochemical methods, to prepare a treatise on synthetical chemistry in which every vital product shall be genetically connected with every compound to which it gives rise by intermediate compounds, each one of which is also a vital product. In other words, the ideal biochemical treatise of the future may be cast on similar lines to the present work, but for non-vital intermediate stages there will be substituted, by the discovery of new and perhaps quite unsuspected synthetical methods, series, more or less numerous, of vital intermediate compounds. The fact that the intermediate stages are now so largely represented by non-vital compounds is a measure of our ignorance of biochemical processes. In the other direction the ideal treatise on pure chemical synthesis—towards which considerably greater progress has already been made—will contain records of genetic relationships starting, let

us say, from carbon and hydrogen or from calcium carbide and water, and every known organic compound. At present the two modes of treatment have perforce been combined, and it must be left to the judgement of chemists and physiologists respectively to attach the proper weight to such data as they may gather from these pages for the purposes of any particular inquiry.

It may perhaps be considered presumptuous on the part of a writer who lays no claim to be considered a physiologist to caution students of this science that the work now offered does really contain in spirit, if not in the text, the two distinct lines of treatment above indicated, and that there is a danger in making too free use of laboratory relationships between organic compounds as evidence of physiological relationship without direct physiological evidence in confirmation. The extreme difficulty of obtaining such confirmation has already been conceded; nevertheless any chemist who considers some of the physiological speculations which have been advanced of late years cannot but come to the conclusion that genetic relationships established experimentally by chemists have been overstrained in the service of physiology. The ordinary chemical equation representing the genetic relationship of one vital compound to another is apt to delude those who are not experts in chemistry into the belief that it is all-sufficient and that it 'explains' the biochemical process: as a matter of fact *the sign connecting the two sides of the equation stands for the whole unexplored region of biochemical transmutation.*

It may perhaps be urged as a countercharge against chemists that many of the highest authorities have advanced purely chemical explanations of biochemical transformations without sufficient physiological evidence. This must be frankly admitted, but it may be pleaded in excuse that the physiological evidence has not been available—partly owing to the practical difficulties of obtaining it, and partly owing to want of co-operation between the two departments of science. Such speculative advances, however, if taken at their true scientific value and not exalted to the rank of proved theories, can do no harm, and may do much good in advancing biochemical science by acting as suggestions stimulating further observation and experiment in this all-important field.

Not the least difficult task in connexion with the present compilation has been the restriction of the series of intermediate compounds within reasonable limits. Although much judgement has been exercised, it may appear even now that many of the genetic relationships are extremely far-fetched—that the number of intermediate compounds has been multiplied to an unnecessary extent, and that stages have been interpolated which would certainly never be passed through in the course of any practical series of laboratory operations for the synthesis of one compound from another. Again, therefore, it may be necessary to insist that this work is not a practical laboratory guide,

but that its object is to furnish material for evolutional schemes of genetic relationships which are chemically real, however far-fetched they may appear from a laboratory or technical point of view.

Thus, to state the case in an abstract form, a vital product, *X*, is capable of being produced from a certain generator, *A*, by the action of heat or chemical reagents. But *A* by treatment with certain other reagents can be transformed into the compounds *P*, *Q*, *R*, &c., each one of which, or only the last one, say *R*, can by appropriate treatment be converted into *X*. It may be urged against the system adopted in this work that since *X* can be directly obtained from *A*, the intermediate compounds *P*, *Q*, *R*, &c., have been interpolated unnecessarily. This objection is valid from a practical point of view, but if the fact that *X* is obtainable from *P*, *Q*, and *R* were for this reason omitted the genetic relationships between *A*, *P*, *Q*, *R*, and *X* would be lost sight of. Moreover it is possible—and in fact during the preparation of this work numbers of actual cases have occurred—that one or all of the intermediate compounds *P*, *Q*, *R* may be at present, or may be found subsequently to be, synthesisable from some generator other than *A*, let us say *B*, so that *B* then becomes a generator of *X*—a fact that would have been ignored if *P*, *Q*, *R* had not been interpolated between *A* and *X*. It is further possible that some natural source of one of the intermediate compounds, say *R*, might be discovered hereafter, in which case the genetic relationship of the vital product *R* to *A* at one end and *X* at the other would then be deducible from this work. Provision is accordingly made by this treatment not only for the possible development of further chemical relationships through the discovery of new modes of synthesising compounds which are now non-vital intermediate stages, but likewise for the possibility of some non-vital products, at present only used as stepping-stones in the laboratory series of operations, being hereafter found in nature.

In illustration of the advantages of this system—a system in which directness and simplicity of transformation cannot be allowed to determine which synthetical processes shall be included and which excluded —the case of diacetyl [**113**] may be quoted. When the section dealing with quinol [**71**] was first written the generators of diacetyl had to be included among the generators of this phenol. It was afterwards found in the laboratory of Schimmel & Co. that diacetyl is a constituent of certain ethereal oils, so that this compound, at first introduced only on account of its genetic relationship to quinol, thereupon had to be enrolled among the vital products and so, as it were, to have its importance enhanced by having biochemical interest added to its purely chemical interest as an indirect generator of quinol. Had diacetyl been excluded because its connexion with quinol is only of an indirect character an interesting relationship between two vital products would have been lost sight of. The cases in which new synthetical processes for the production of non-vital intermediate

compounds have been discovered during the compilation of this work are too numerous to select special illustrations from; constant interpolations have, as already stated, been necessary to keep pace with the progress of discovery.

In pursuance of the scheme of recording the inter-relations between organic compounds on biochemical rather than on purely chemical lines it has also been found necessary, not only to interpolate whole series of intermediate stages irrespective of practical considerations, but also to record synthetical processes which in many cases yield only a small quantity, or even only a trace, of the final product. In other words, the question of yield, like the question of directness of method, cannot be allowed any weight in presenting the subject of chemical synthesis from the present point of view. It is clear that we are following the natural method in this, because it is tolerably certain that a large number, if not a large majority, of the vital products at present isolated and synthesised are of the nature of by-products, having no quantitative relationship to their generators that could be stated—even if we knew what these generators were—in the form of chemical equations which could be said to express the whole truth. No less is it certain that many of the vital compounds herein dealt with arise from the breaking down of many antecedent generators, and the final product results from the accumulation of traces of the compound derived from several sources.

It may fairly be urged that the inclusion of processes which result only in a trace of the final product diminishes the value of this work from the technological point of view. Even here, however, it is claimed that the biochemical method, if properly used, may be of great service in chemical technology. In using this as a work of reference in which all the generators of any particular compound are recorded in a systematic manner, the chemist, the physiologist, and the technologist will no doubt each use his judgement in assigning due weight to any particular process. The mere statement of the fact that there is any genetic relationship between one compound and another of industrial importance may furnish a suggestive clue for future investigation. As our knowledge of biochemical processes advances and as our chemical processes are brought more and more into line therewith, it is certain that the manufacture of vital products will derive just as much advantage as will the laboratory methods for synthesising organic compounds which are of no industrial use.

To state the case another way, the fact that a particular generator gives rise to only a trace of some compound of industrial use is a hint given by Nature that the future technologist might work upon to increase the yield and, as it were, to improve upon Nature's own method. The history of the development of industrial organic chemistry furnishes many examples which justify this inclusion of all processes, irrespective of yield. In modern times the synthesis of

indigo, first from benzene and acetic acid *via* phenylglycin, then from naphthalene and acetic acid *via* anthranilic acid (a vital product) and phenylglycin-orthocarboxylic acid, may be quoted as a most instructive illustration. The yield from the first of these generators was insufficient for technological success; the yield from anthranilic acid is sufficient to enable the synthetical to compete successfully with the natural product. In fact, most laboratory syntheses are at first accomplished without any consideration of the question of yield; it is not till the process is taken over by the technologist that this question becomes of importance. The conversion of a laboratory compound into a technological product often reacts also upon the scientific investigation of the compound, leading not only to improvements in methods of production, but likewise to the discovery of new synthetical processes.

The study of synthetical chemistry from the present point of view will furnish numerous examples illustrative of the interdependence of science and technology, and, in fact, many of the syntheses of vital products effected of late years are the direct outcome of the technological value of such products. In view of the relationships between biochemistry and chemical technology, the revelation of which, it is claimed, is intimately associated with the present mode of treatment, it is obvious that patented processes have had to be included in the literature. It is of course beyond the scope of this work to discuss such processes critically, and they have all been included, when having any bearing upon any particular synthesis, for whatever they may be worth industrially. The inclusion of patented processes cannot, however, but contribute towards the utility of the work from the point of view of the chemical technologist.

In one direction a certain latitude has been allowed in dealing with synthesised vital products, to which special attention must be directed in conclusion. In the case of optically active compounds the synthesis is not logically complete till the optical isomeride has been isolated in the laboratory by one or another of the known methods. Nevertheless the synthesis of such optically active compounds has been recorded as an accomplished fact, although the laboratory product is, as is well known, always optically inactive through 'external compensation' (racemism, &c.). In going beyond the facts to this extent it is claimed that the course adopted is, however, but a reasonable anticipation of future discovery. The optically active vital product is actually present in the racemic compound or mixture produced in the laboratory, and it may confidently be expected that some method will hereafter be devised for separating the optical isomerides in the case of synthesised compounds which, being neither acid nor basic nor attackable by biological methods, have thus far remained as unresolved. To illustrate this point by a hypothetical case, dextrotartaric and racemic acids are natural products, the latter alone being, strictly speaking, a synthetical

product. Nevertheless, had racemic acid never been resolved, both dextro- and lævotartaric acids, according to the above principle, would have been claimed as synthetical products in anticipation of the discovery of methods of resolution. To take another actual example, dipentene and dextro- and lævolimonene [9] are all natural products. Dipentene is racemic limonene, and as this compound has been synthesised it is claimed that the limonenes are also synthetical products, although no method for resolving dipentene has yet been devised.

HYDROCARBONS.

1. Methane; Marsh Gas.

CH_4

Natural Sources.

A product of the bacterial fermentation of calcium acetate and lactate, of milk-sugar, glycuronic acid, choline, cellulose, albumin, &c.

Methane fermentation is produced by micro-organisms from the stomach of ruminants and by bacteria occurring in sewage mud. (For methane fermentation of calcium acetate and lactate see Hoppe-Seyler, Zeit. physiol. Ch. **11**, 561; of milk-sugar, Baginsky, ibid. **12**, 457; of albumin, Nencki and Sieber, Monats. **10**, 526; of choline, Hasebroek, Zeit. physiol. Ch. **12**, 148; of cellulose, Mitscherlich, Monats. d. k. Akad. d. Wissensch. Berlin, 1850, 104; Popoff, Pflüger's Arch. **10**, 113; Tappeiner, Ber. **16**, 1734.) The methane fermentation of cellulose has been erroneously attributed to Trecul's *Amylobacter* (Van Tieghem, Comp. Rend. **88**, 205; **89**, 5; Hoppe-Seyler, Zeit. physiol. Ch. **10**, 201; 401; 409; Ber. **16**, 122).

The gases of the intestinal canal, which are evolved especially after a pulse diet, contain methane, possibly resulting from the bacterial fermentation of cellulose (Tappeiner, Ber. **15**, 999; **16**, 1734; 1740; Zeit. Biol. **20**, 52; 215; **24**, 105), of albumin (Ruge, Wien. Sitzungsber. **44**, 739), and of lecithin (Hasebroek, Zeit. physiol. Ch. **12**, 148).

The intestinal gases of man and dogs fed on purely flesh diet also contain methane (Ruge and Planer, quoted by Lafar, 'Technical Mycology,' I, p. 196). Methane is said to have been detected in the breath of calves and of sheep (Reiset, Jahresber. **1863**, 638).

According to Omeliansky (Comp. Rend. **125**, 1131; Ch. Centr. 1900, **1**, 918, from Arch. Sci. Biol. St. Pét. **7**, 411) the cellulose ferment is *Bacillus fermentationis cellulosæ*, but this does not give rise to methane. The latter is produced towards the end of the fermentation by another *Bacillus*, which is not *Amylobacter*. (See also Centr. Bakter. **8**, 193 et seq.) Chalk is essential for the production of methane from cellulose (Omeliansky).

The methane fermentation of milk-sugar is caused by *Bacterium lactis aërogenes* of Escherich = *Bact. aceticum* of Baginsky (Zeit. physiol. Ch. **12**, 461; Emmerling, Ber. **33**, 2477). The development of gases, including methane, by *Bacillus coli communis* cultivated in different media has been studied by Mary E. Pennington and Geo. Küsel (Am. Ch. Journ. **22**, 556).

Methane is among the gases evolved during the 'sauerkraut' fermentation of vegetables and of nutrient saccharine solutions by *Bacterium brassicæ acidæ* of Lehmann and Conrad (Ch. Centr. 1897, **1**, 1098). Also among the gases evolved during the putrefaction of elastin (prepared from the *ligamentum nuchæ* of the ox) by anaerobic microbes (Zoja, Zeit. physiol. Ch. **23**, 236). Methane is evolved during the putrefaction of compressed manure (Dehérain and Dupont, Ann. Agronom. **26**, 273; also Dehérain, Comp. Rend. **99**, 45; and for evolution of methane by anaerobic fermentation of straw, *Ibid.* Ann. Agronom. **10**, 385), and is among the gases given off during the fermentation which takes place in indigo vats and in sugar diffusers (for latter see Lafar's 'Technical Mycology,' I. p. 196). Methane is among the gases evolved during the putrefaction of barley (Lermer, Journ. Fed. Inst. **8**, 509, from Zeit. ges. Brau. **25**, 165).

Synthetical Processes.

[A.] Methane is produced by the direct union of carbon with hydrogen at 1200° (Bone and Jerdan, Trans. Ch. Soc. **71**, 41; **79**, 1042). The carbides of the metals aluminium, beryllium, cerium,

manganese, lanthanum, yttrium, uranium, and thorium, praseo- and neodidymium produced in the electric furnace give methane (in most cases mixed with other gases) when acted upon by water (Moissan, Proc. Roy. Soc. **60**, 156; Bull. Soc. [3] **11**, 1012; **15**, 1285; **17**, 15; Comp. Rend. **122**, 362; 423; 1462; Ann. Chim. [7] **9**, 302; Moissan and Étard, Ann. Chim. [7] **12**, 429; Lebeau, Comp. Rend. **121**, 498; Moissan, Comp. Rend. **131**, 595; Berthelot, Comp. Rend. **132**, 281).

Carbon and hydrogen combine directly to form acetylene when the electric arc passes between carbon poles in an atmosphere of hydrogen (Berthelot, Ann. Chim. [4] **13**, 143; Comp. Rend. **54**, 640; Bone and Jerdan, Trans. Ch. Soc. **71**, 41; **79**, 1042). Or certain metallic carbides, such as those of barium, calcium, strontium, and lithium prepared in the electric furnace, give acetylene when acted upon by water (Moissan, Bull. Soc. [3] **15**, 1285; the production of acetylene from calcium carbide and water was first observed by Wöhler, Ann. **124**, 220: the technical production of calcium carbide is due to Willson, 1894. Wöhler prepared calcium carbide by strongly heating an alloy of zinc and calcium with charcoal: Maquenne prepares barium carbide by heating barium carbonate with magnesium powder and carbon; Ann. Chim. [6] **28**, 266). Acetylene gives methane when passed over finely divided nickel heated to 300° (Sabatier and Senderens, Comp. Rend. **124**, 617) or when heated *per se* to 1150° (Bone and Jerdan, Proc. Ch. Soc. **17**, 164). Or acetylene forms a compound with mercuric chloride (see under acetaldehyde [**92**; **A**]), and this on treatment with iodine and alkali gives iodoform (Le Comte, Journ. Pharm. **16**, 297). From iodoform as under **D** below.

Carbon monoxide and hydrogen give methane under the influence of the silent electric discharge (Brodie, Proc. Roy. Soc. **21**, 245; Ann. **169**, 270). So also (probably) does a mixture of carbon dioxide and hydrogen (Collie, Trans. Ch. Soc. **79**, 1067). Methane is produced by the catalytic action of finely divided heated nickel or cobalt on a mixture of hydrogen with carbon dioxide or monoxide (Sabatier and Senderens, Comp. Rend. **134**, 514; 689).

[**B.**] *Heptane* [**2**] gives methane among the gases produced by heating the hydrocarbon to 900° (Worstall and Burwell, Am. Ch. Journ. **19**, 815).

[**C.**] From *methyl alcohol* [**13**] through methyl iodide and the action of sodium on the moist ethereal solution or of the copper-zinc couple or aluminium amalgam on the alcoholic solution of the iodide (Gladstone and Tribe, Trans. Ch. Soc. **45**, 154; Wright, *Ibid.* **47**, 200; Bone and Wheeler, *Ibid.* **81**, 541). Magnesium amalgam reduces the alkyl iodides more readily than the copper-zinc couple (Meunier, Comp. Rend. **134**, 472). Methyl iodide (or chloride) gives methane by heating with potassium hydride (Moissan, Comp. Rend. **134**, 389). Or from methyl iodide through zinc methyl (Frankland, Ann. **85**, 346; **111**, 62) and decomposition of the latter by water (*Ibid.* Phil. Trans. 1852, **2**, 417; Ladenburg and Krügel, Ber. **32**, 1821), or by alcohol in an atmosphere of nitrogen or hydrogen (Tolkatscheff, Journ. Russ. Soc. **33**, 469). Magnesium methiodide gives methane on decomposition by water (Grignard, Ann. Chim. [7] **24**, 433; Tschugaeff, Ber. **35**, 3912).

From methyl alcohol by passing the vapour over heated magnesium (Keiser and Breed, Ch. News, **71**, 118), or by passing the electric arc through the vapour (Löb, Ber. **34**, 917), or by pyrogenic contact decomposition (Ipatieff, Ber. **35**, 1055; 1060). From methyl alcohol through methyl ether (Dumas and Peligot, Ann. **15**, 12; Kane, Ann. **19**, 166; Ebelmen, Ann. **57**, 328; Erlenmeyer and Kriechbaumer, Ber. **7**, 699; Tellier, Arch. Pharm. **10**, 57). The latter gives methane on passing through a hot tube (Tischtschenko, Ch. Centr. 1900, **1**, 586, from Journ. Russ. Soc. **31**, 784).

[**D.**] From *ethyl alcohol* [**14**] through chloroform (Liebig, Ann. **1**, 198; Soubeiran, Ann. Chim. [2] **48**, 131; Soubeiran and Mialhé, Ann. **71**, 225; Kessler, Journ. Pharm. **13**, 162; Belohoubek, Ann. **165**, 349; Goldberg, Journ. pr. Ch. [2] **24**, 114; for electro-

lytic production of chloroform from potassium chloride and alcohol see Chem. Fab. auf Aktien, Germ. Pat. 29771 of 1884; Ber. **17**, Ref. 624. See also Dony-Hénault, Zeit. Elektroch. **7**, 57). Chloroform gives methane on reduction with zinc dust in alcoholic solution (Sabanejeff, Ber. **9**, 1810; Perkin, Ch. News, **18**, 106) or by potassium amalgam (Regnault, Gerhardt's 'Traité,' **1**, 603). Or by passing chloroform vapour and hydrogen through a hot tube, or by heating chloroform with copper or with potassium iodide and water in a sealed tube (Berthelot, Jahresber. **1857**, 267).

Or from ethyl alcohol through bromoform (Löwig, Ann. **3**, 295; Dumas, Ann. Chim. [2] **56**, 120; Günther, Arch. Pharm. [3] **25**, 373), which is reduced to methane by heating with potassium iodide, water, and copper or zinc (Berthelot, Ann. Chim. [3] **51**, 48), or by the copper-zinc couple (Gladstone and Tribe, Journ. Ch. Soc. **28**, 510). Bromoform yields methane by passing the vapour over heated copper (in an atmosphere of carbon dioxide) or by heating with zinc dust in alcoholic solution (Nef, Ann. **308**, 329).

Or from ethyl alcohol through iodoform (Serullas, Ann. Chim. [2] **22**, 172; **25**, 314; Günther, Arch. Pharm. [3] **25**, 373; Rother, Pharm. Journ. [3] **4**, 593; for electrolytic preparation of iodoform see Chem. Fab. auf Aktien, Germ. Pat. 29771 of 1884; Ber. **17**, Ref. 624; Förster and Meves, Journ. pr. Ch. [2] **56**, 354; Elbs and Herz, Zeit. Elektroch. **4**, 113; also Dony-Hénault, *Ibid.* **7**, 57; Bull. Assoc. Belg. [6] **14**, 247; for production from potassium iodide and alcohol by the action of ozone see Otto, Germ. Pat. 109013 of 1898; Ch. Centr. 1900, **2**, 304). Iodoform gives methane by the action of the copper-zinc couple (Gladstone and Tribe, Journ. Ch. Soc. **28**, 508), or by heating with finely divided silver in an atmosphere of carbon dioxide (Nef, Ann. **308**, 329).

Or from ethyl alcohol through ethyl chloride (Robiquet and Colin, Ann. Chim. [2] **1**, 343; Regnault, *Ibid.* **71**, 355; Kuhlmann, Ann. **33**, 108; Löwig, Pogg. Ann. **45**, 346; Groves, Journ. Ch. Soc. **27**, 637; Krüger, Journ. pr. Ch. [2] **14**, 195; Geuther, Zeit. [2] **7**, 147). The latter gives methane (and acetic acid) when passed over red-hot lime (L. Meyer, Ann. **139**, 282; see also Dumas and Stas, Ann. Chim. [2] **73**, 154, and Nef, Ann. **318**, 1).

Or from alcohol through chloral by chlorination (Liebig, Ann. **1**, 189); also under formic acid [Vol. II]). Chloral in aqueous solution gives methane on heating with zinc or iron dust (Cotton, Bull. Soc. [2] **42**, 622).

Methane is among the gases produced by passing the vapour of ethyl alcohol over heated magnesium (Keiser and Breed, Ch. News, **71**, 118). Ethyl alcohol by the action of aluminium in presence of stannic chloride gives aluminium ethylate (Hillyer and Crooker, Am. Ch. Journ. **19**, 41). The latter gives methane among the products of its decomposition by heat (Tischtschenko, Ch. Centr. 1900, **1**, 585, from Journ. Russ. Soc. **31**, 784).

From ethyl alcohol through ethyl ether (Valentin Rose, Scherer's Journ. d. Ch. **4**, 253; Saussure, Ann. Chim. **89**, 273; Dumas and Boullay, *Ibid.* [2] **36**, 294; Williamson, Journ. Ch. Soc. **4**, 106; Boullay, Journ. Pharm. **1**, 97; Soubeiran, *Ibid.* [3] **16**, 321). The latter gives methane among the products of photochemical oxidation in presence of hydrogen peroxide (Berthelot, Comp. Rend. **129**, 627).

From ethyl alcohol through ethylene by heating with dehydrating agents (Mitscherlich, Ann. Chim. [3] **7**, 12; Ebelmen, *Ibid.* **16**, 136; Erlenmeyer and Bunte, Ann. **168**, 64; **192**, 244; Villard, Ann. Chim. [7] **10**, 389; Newth, Proc. Ch. Soc. **17**, 147). Methane is among the products formed by passing ethylene over finely divided nickel heated in a tube (Sabatier and Senderens, Comp. Rend. **124**, 1358; **131**, 267), by passing a mixture of ethylene and hydrogen over heated freshly reduced cobalt (*Ibid.* **130**, 1761), or by passing through a hot tube (Day, Am. Ch. Journ. **8**, 153).

NOTE:—Ethylene and acetylene are among the products formed when the vapours of primary alcohols such as *methyl* [13], *ethyl* [14], *isobutyl* [18], and *amyl alcohol* [22] are passed over calcium carbide heated to 500° (Lefebvre,

Comp. Rend. 132, 1221). Ethylene or methane or both gases are among the products formed by passing the vapour of ethyl alcohol through hot tubes of glass, platinum, or iron, or over heated metals such as zinc, brass, &c., or certain metallic oxides such as those of zinc, tin, &c. (Jahn, Ber. 13, 987; Ipatieff, Ber. 34, 3579; 35, 1047; also over heated plumbago crucible material, *Ibid.* 1058). Ethylene and acetylene are among the products of the pyrogenic decomposition of the vapour of amyl alcohol [22] (Wurtz, Ann. 104, 242). Ethylene is among the products formed by passing *n-hexane* [23; A, &c.] or *isobutyl alcohol* vapour [18] mixed with air over heated platinum (v. Stepski, Monats. 23, 773).

[E.] *Propyl alcohol* [15] gives methane among the products formed by passing the vapour over heated magnesium (Keiser and Breed, Ch. News, 71, 118), or over heated plumbago crucible material (Ipatieff, Ber. 35, 1059). Or n-propyl alcohol gives iodoform by the action of iodine and alkali (Lieben, Ann. Suppl. 7, 218; 377), and this can be reduced to methane as above under D.

Or from n-propyl alcohol through the aldehyde (propanal) by oxidation (Chancel, Ann. 151, 301; Przybytek, Journ. Russ. Soc. 8, 335; Lieben and Zeisel, Monats. 4, 14). Propanal gives methane among the products of decomposition of its vapour at a high temperature (Tischtschenko, Ch. Centr. 1900, 1, 586; Journ. Russ. Soc. 31, 784).

Or from n-propyl alcohol through n-propyl chloride (see under isopropyl alcohol [16; B]). The latter gives carbon tetrachloride (with the hexachloride) when heated with iodine chloride to 200° (Krafft and Merz, Ber. 8, 1296). The tetrachloride gives methane as below under L.

Or from *isopropyl alcohol* [16], being among the products of pyrogenic contact decomposition (Ipatieff, Ber. 35, 1056).

[F.] *Normal butyl alcohol* [17] gives iodoform by the action of iodine and alkali (Lieben; see above under E). Subsequent treatment as under D.

Or *isobutyl alcohol* [18] gives isobutyl chloride or bromide, and these haloids passed over soda-lime heated to 600° give methane among other products (Nef, Ann. 318, 22, &c.). Methane is among the gases produced by the pyrogenic contact decomposition of the vapour of isobutyl alcohol by certain metals (Ipatieff, Ber. 35, 1052; also Noyes, Beilstein, I, 115) or by plumbago crucible material (Ipatieff, Ber. 35, 1060).

[G.] From *octyl alcohol* [28] through iodoform (Lieben, *loc. cit.*) and then as above under D.

[H.] *Glycerol* [48] gives a small quantity of methane among the products of the dry distillation of the barium compound (Destrem, Ann. Chim. [5] 27, 17; 44; Comp. Rend. 90, 1213).

Or from glycerol through allyl alcohol (see under ethyl alcohol [14; G]), which gives methane among the products of pyrogenic contact decomposition by passing the vapour over certain heated metals (Ipatieff, Ber. 35, 1054). Or from glycerol through *acroleïn* [101] as under HH below.

[I.] From *aldehyde* [92] through iodoform (Lieben, *loc. cit.*) and then as above under D. Or aldehyde gives chloral on chlorination (Pinner, Ber. 4, 256; Wurtz and Vogt, Zeit. [2] 7, 679), and this is decomposed by alkali with the formation of chloroform (Liebig, Ann. 1, 199). The latter, or chloral itself, can be reduced to methane as above under D.

Aldehyde gives methane among the products of the decomposition of its vapour by heat (Tischtschenko, Ch. Centr. 1900, 1, 586; see also Ipatieff, Ber. 34, 3579) or by pyrogenic contact decomposition by the action of certain metals (Ipatieff, Ber. 35, 1049). Methane is among the products of the action of strong aqueous hydriodic acid on aldehyde and many other compounds at a high temperature (Berthelot, Bull. Soc. [2] 7, 60; 9, 8; 91; 178; 265; Jahresber. 1867, 342).

Or aldehyde-ammonia gives methane among the products of its decomposition when heated with a hypochlorite (De Coninck, Comp. Rend. 126, 1042).

[J.] From *acetone* [106] through chloroform or iodoform (Liebig, Ann. 1, 198; Lieben, as above under E; Rother, Jahresber. 1874, 317; Curtman, Beilstein's 'Handbuch,' I, 189; Suilliot and Raynaud, Bull. Soc. [2] 51, 4; Orndorff and Jessel, Am. Ch. Journ. 10, 365), and

subsequent reduction as above under **D**. According to Berthelot (see above under **I**) methane is among the gases produced by the reduction of acetone by heating to a high temperature with strong aqueous hydriodic acid.

Acetone also gives bromoform by electrolysis in presence of potassium bromide and carbonate (Coughlin, Am. Ch. Journ. **27**, 63: compare Elbs and Herz, Zeit. Elektroch. **4**, 113).

[**K.**] *Butyric aldehyde* [**94**] gives iodoform by the action of iodine and alkali (Lieben, as above under **E**).

[**L.**] From *carbon disulphide* [**160**] by passing the vapour mixed with sulphuretted hydrogen over heated copper (Berthelot, Comp. Rend. **43**, 236; Ann. Chim. [3] **53**, 69). Or from carbon disulphide by heating with phosphonium iodide to 120°–140° (Jahn, Ber. **13**, 127).

Or carbon disulphide on chlorination in the presence of iron and iodine and subsequent treatment of the product with bleaching powder gives carbon tetrachloride (Serra, Gazz. **29**, 353). Or carbon disulphide can be converted into the tetrachloride by chlorination (Kolbe, Ann. **45**, 41; **54**, 146; Hofmann, Ann. **115**, 264; Klason, Ber. **20**, 2376; Mouneyrat, Bull. Soc. [3] **19**, 262: for references to technical processes see Conroy, Journ. Soc. Ch. Ind. **21**, 309; Urbain, Eng. Pat. 13733 of 1901; Journ. Soc. Ch. Ind. **21**, 926). Carbon tetrachloride can be reduced to methane in the same way as chloroform (Berthelot, Jahresber. **1857**, 267).

[**M.**] *Phenol* [**60**] gives methane among the products of pyrogenic decomposition (Müller, Journ. pr. Ch. **58**, 1). Or phenol by the action of potassium chlorate and hydrochloric acid gives trichlor-*aa*-glyceric acid, which is decomposed by cold alkaline solutions into oxalic acid and chloroform (Schreder, Ann. **177**, 282).

[**N.**] From *cresol* [**61**; **62**; **63**] by pyrogenic decomposition (Müller, as above under **M**).

[**O.**] From *formic acid* [Vol. II], being among the products of the dry distillation of the barium salt (Berthelot, Jahresber. **1857**, 426) and of the action of heated zinc dust on the vapour of the acid (Jahn, Ber. **13**, 2109).

Or methyl formate on extreme chlorination gives perchlormethyl formate (Hentschel, Journ. pr. Ch. [2] **36**, 100; 214; 305), which is decomposed by aluminium chloride with the formation of carbon tetrachloride (*Ibid.* 308). Subsequent steps as above under **L**.

[**P.**] From *acetic acid* [Vol. II] by heating acetates with barium oxide, with potash-lime or soda-lime (Dumas, Ann. Chim. [2] **73**, 92; Ann. **33**, 181; Von Schlegel, Ann. **226**, 140; Schorlemmer, Ch. News, **29**, 7: compare Ladenburg and Krügel, Ber. **32**, 1820). Also from acetic acid by photochemical decomposition in the presence of uranium salts (Fay, Am. Ch. Journ. **18**, 287). Also by the electrolysis of fused potassium acetate (Lassar-Cohn, Ann. **251**, 358).

Or indirectly from acetic acid through the trichloro-acid by chlorination (Dumas, Ann. **32**, 101). The trichloro-acid gives chloroform on heating with aqueous alkali (*Ibid.* 113; Ann. Chim. [2] **56**, 115).

[**Q.**] *Glycollic acid* [Vol. II] gives methane on distillation with lime (Hanriot, Bull. Soc. [2] **45**, 80; Comp. Rend. **101**, 1156).

[**R.**] *Lactic acid* [Vol. II] gives iodoform by the action of iodine and alkali (Lieben, as above under **E**). Subsequent reduction as before. Or lactic acid gives chloroform on treatment with bleaching powder (Eberhard, Journ. Ch. Soc. **80**, I, Abst. 357). Subsequent reduction as above under **D**.

[**S.**] From *malonic acid* [Vol. II], ethylene being among the products of the electrolysis of the acid potassium salt (Petersen, Ch. Centr. 1897, **2**, 519). Ethylene gives methane as above under **D**.

[**T.**] From *succinic acid* [Vol. II], methane being among the products of electrolysis of an alcoholic solution in presence of sodium hydroxide (Clark and Smith, Journ. Am. Ch. Soc. **21**, 967).

Or indirectly through ethylene by the electrolysis of a strong solution of the sodium salt (Kekulé, Ann. **131**, 79; Clark and Smith, *loc. cit.*; also from

the acid potassium salt, Petersen, Ch. Centr. 1897, **2**, 519; 1900, **2**, 171), and then as above under **D**.

Or succinic acid gives a dibromo-acid on bromination (Kekulé, Ann. **117**, 123; Ann. Suppl. **1**, 352; Bourgoin, Bull. Soc. [2] **19**, 148; Gorodetzky and Hell, Ber. **21**, 1731), and this by treatment with alcoholic potash gives acetylenedicarboxylic acid (Bandrowsky, Ber. **10**, 838; Baeyer, Ber. **18**, 677; 2269), the sodium salt of which gives, on the addition of silver nitrate, silver acetylide (Lossen, Ann. **272**, 140). Acetylene liberated from the latter gives methane as above under **A**.

[**U.**] *Fumaric acid* [Vol. II] combines with bromine to form dibromsuccinic acid (Kekulé, Ann. Suppl. **1**, 131; Baeyer, *loc. cit.*; Kirchhoff, Ann. **280**, 209; Michael, Journ. pr. Ch. [2] **52**, 295). Subsequent steps as above under **T**.

Or fumaric (or maleïc) acid gives acetylene on electrolysis of a strong solution of the sodium salt (Kekulé, Ann. **131**, 85).

Or *maleïc* acid (anhydride) on combination with bromine gives isodibromsuccinic acid (Kirchhoff, Ann. **280**, 207), and this on heating with strong hydrobromic acid gives dibromsuccinic acid (Michael, Journ. pr. Ch. [2] **52**, 324). Subsequent steps as above under **T**. Isodibromsuccinic acid also on treatment with alcoholic potash gives acetylenedicarboxylic acid (Bandrowsky, Ber. **10**, 838), which gives acetylene and methane as above under **T**.

[**V.**] *Azelaïc acid* [Vol. II] gives a small quantity of ethylene among the products of its distillation with soda-lime (Miller and Tschitschkin, Ch. Centr. 1899, **2**, 182). Ethylene gives methane as above under **D**.

[**W.**] *Salicylic acid* [Vol. II] by the action of potassium chlorate and hydrochloric acid gives trichlor-*aa*-glyceric acid, from which chloroform can be obtained (see under **M** above).

[**X.**] From *gallic acid* [Vol. II] through trichlor-*aa*-glyceric acid by the action of potassium chlorate and hydrochloric acid and chloroform, &c., as before (see under **M** above).

[**Y.**] *Methylamine* [Vol. II] gives methane among the products of its reduction by strong aqueous hydriodic acid at a high temperature (Berthelot, as above under **I**).

[**Z.**] *Trimethylamine* [Vol. II] on heating the hydrochloride to 326° decomposes with the formation of methyl chloride (Vincent, Journ. Pharm. [4] **30**, 132; Jahresber. **1878**, 1135). Methyl chloride gives methane among the products of pyrogenic decomposition (Perrot, Ann. **101**, 375), or a solution of the chloride might be reduced as above under **C**.

[**AA.**] *Benzene* (see under cymene [**6**; I, &c.]) by the action of sulphuric acid and potassium chlorate gives trichlorphenomalic acid, $CCl_3 . CO . CH : CH . COOH$ (Carius, Ann. **142**, 129; Kekulé and Strecker, Ann. **223**, 170; Anschütz, Ann. **254**, 152), and this decomposes into chloroform (and maleïc acid) on heating with barium hydroxide solution. For reduction of chloroform to methane see above under **D**.

[**BB.**] From *malic acid* [Vol. II], which gives bromoform by the action of bromine and alkali (Cahours, Ann. **64**, 351). Subsequent steps as above under **D**.

[**CC.**] From *citric acid* [Vol. II], which gives bromoform as above.

[**DD.**] *Ethylamine* [Vol. II] gives methane among the products of pyrogenic decomposition (Müller, Bull. Soc. [2] **45**, 438).

[**EE.**] *Glucose* [**154**] gives an oxime which on reduction yields the base glucamine. The latter gives iodoform with iodine (Maquenne and Roux, Comp. Rend. **132**, 980). From iodoform to methane as above under **D**.

[**FF.**] From *isovaleric acid* [Vol. II], methane being among the products of the dry distillation of the calcium salt (Dilthey, Ber. **34**, 2115).

[**GG.**] *Isoamyl alcohol* [**22**] gives methane among the products of pyrogenic decomposition by the contact action of certain heated metals on the vapour (Ipatieff, Ber. **35**, 1053).

[**HH.**] From *acroleïn* [**101**] through propinal and acetylene (see under cymene [**6**; XVIII]), and then as under **A** above.

2. Normal Heptane.

$CH_3 . [CH_2]_5 . CH_3$

Natural Source.

Occurs in the exudation of the Californian nut pine, *Pinus sabiniana* (Thorpe, Trans. Ch. Soc. **35**, 296; **37**, 213). Also in the resin of *Pinus jeffreyi* (Blasdale, Journ. Am. Ch. Soc. **23**, 163).

Synthetical Processes.

[A.] From *methyl* and *n-hexyl alcohols* [13; 23] by conversion into the corresponding alkyl iodides and combination of the alkyls by the action of sodium on the iodides in ethereal solution (general method of Wurtz, Ann. Chim. [3] **44**, 275; see also Frankland, Ann. **71**, 171; **74**, 41).

[B.] From *ethyl* and *n-amyl alcohols* [14; 20] as above.

[C.] From *n-propyl* and *n-butyl alcohols* [15; 17] as above.

[D.] *Œnanthol* [97] on reduction with sodium amalgam or zinc dust and acetic acid gives normal heptyl alcohol (Bouis and Carlet, Ann. **124**, 352; Schorlemmer, Ann. **177**, 303; Cross, Ann. **189**, 2; Jourdan, Ann. **200**, 102; Krafft, Ber. **16**, 1723). The alcohol gives n-heptyl iodide on heating with aqueous hydriodic acid (Jourdan, *loc. cit.* 104), and this might be reduced to n-heptane by the usual methods (see under methane [1; C]).

Or. œnanthol by the action of phosphorus pentachloride gives 1 : 1-dichlorheptane = œnanthylidene chloride (Limpricht, Ann. **103**, 81), which by the action of alcoholic potash gives 6-(α)-heptine = œnanthylidene (*Ibid.*; Rubien, Ann. **142**, 294). The latter combines with hydrogen by the 'contact' action of hot finely divided nickel to form heptane (Sabatier and Senderens, Comp. Rend. **135**, 87).

[E.] From *azelaïc acid* [Vol. II] through heptane by heating the barium salt with barium oxide (Dale, Journ. Ch. Soc. **17**, 258).

[F.] From *acetic* and *n-heptoic acids* [Vol. II], a mixture of the potassium salts giving a heptane on electrolysis which is probably normal heptane (Wurtz, Ann. **96**, 372).

Note :—Many synthetical products belonging to the aromatic series are said by Berthelot to give heptane on heating to a high temperature with strong aqueous hydriodic acid, but the constitution of the heptanes thus obtained has not been determined. (See for references under methane [1; I] and under isoheptyl alcohol [27].)

3. Normal Pentadecane.

$CH_3 [CH_2]_{13} . CH_3$

Natural Source.

Possibly a constituent of the essential oil of *Kaempferia galanga* (P. van Romburgh, Proc. K. Akad. Wetensch. Amsterdam, **4**, 618; Journ. Ch. Soc. **82**, I, Abst. 633).

Synthetical Processes.

[A.] From *palmitic acid* [Vol. II] and *methyl alcohol* [13] by distilling the barium salt of the acid in a vacuum with sodium methoxide (Mai, Ber. **22**, 2134).

Or *palmitic* and *acetic acids* on distilling a mixture of the barium salts give 2-heptadecanone (Krafft, Ber. **12**, 1671), and this on oxidation with chromic acid mixture gives pentadecylic acid (*Ibid.*). The latter on heating with hydriodic acid and phosphorus to 240° gives n-pentadecane (*Ibid.* **15**, 1700).

4. Normal Heptacosane.

$CH_3 [CH_2]_{25} . CH_3$

Natural Sources.

Occurs in beeswax (Schwalb, Ann. **235**, 117) and in tobacco leaf (Thorpe and Holmes, Trans. Ch. Soc. **79**, 982; see also Kissling, Ber. **16**, 2432).

Synthetical Process.

[A.] From *myristic acid* [Vol. II] through myristone, by distilling the calcium or barium salt (Overbeck, Pogg. Ann. **86**, 591; Ann. **84**, 290; Krafft, Ber. **15**, 1713); the dichloride by distilling with phosphorus pentachloride, and reduction of the dichloride by heating with aqueous hydriodic acid and phosphorus (Krafft, *loc. cit.*).

Note:—A heptacosane may occur in néroli oil (E. and H. Erdmann, Ber. 32, 1214), but the constitution of this hydrocarbon is at present unknown.

5. Normal Hentriacontane.

$$CH_3[CH_2]_{29}.CH_3$$

Natural Sources.

Occurs with the preceding in beeswax (Schwalb, *loc. cit.*) and tobacco leaf (Thorpe and Holmes, *loc. cit.*).

Synthetical Process.

[A.] From *palmitic acid* [Vol. II] through palmitone by distilling the barium salt (Piria, Ann. **82**, 249); the dichloride as above, and reduction of latter as before (Krafft, *loc. cit.* 1714).

6. Cymene; Paraisopropyltoluene; Paramethylisopropylbenzene; 1-Methyl-4-Methoethylbenzene.

Natural Sources.

In Roman cumin oil from the seeds of *Cuminum cyminum* (Gerhardt and Cahours, Ann. **38**, 70; 101; 345); in oil from the seeds of water-hemlock, *Cicuta virosa* (Trapp, Journ. pr. Ch. **74**, 428; Arch. Pharm. **231**, 212; Ann. **108**, 386); in oil of pepperwort, *Satureia hortensis* (Jahns, Ber. **15**, 816), and of *Satureia thymbra* (Schimmel's Ber. Oct. 1889).

Cymene occurs in oil of true bishop's weed, *Ptychotis ajowán* (Haines, Journ. Ch. Soc. **8**, 28; Müller, Ber. **2**, 130; Landolph, Ber. **6**, 936); in oil of thyme from *Thymus vulgaris* and *T. serpyllum* (Lallemand, Journ. Pharm. **24**, 274; Comp. Rend. **37**, 498; Ann. **102**, 119; Febve, Comp. Rend. **92**, 1290); in oil of wild bergamot from *Monarda fistulosa* (Kremers, Pharm. Rund. **13**, 207; Melzner and Kremers, Pharm. Rev. **14**, 198); and in oil of American horsemint from *Monarda punctata* (Kremers and Hendricks, Pharm. Arch. **2**, 73; Schumann and Kremers, Pharm. Rev. **14**, 223).

According to Faust and Homeyer (Ber. **7**, 1429) cymene occurs in the oil of *Eucalyptus globulus*, but according to Gildemeister and Hoffmann (p. 691) the oil investigated by these chemists could not have been from that species. Cymene occurs in oil of *Eucalyptus hæmastoma* (Gildemeister and Hoffmann, p. 161), in oil of *Thymus capitatus* from S. Spain (Schimmel's Ber. Oct. 1889), in oil of Trieste and Smyrna origanum from *Origanum hirtum* and *O. smyrnæum* (Jahns, Arch. Pharm. **215**, 1; Gildemeister, *Ibid.* **231**, 182), and in Ceylon oil of cinnamon (Schimmel's Ber. April, 1902; Walbaum and Hüthig, Journ. pr. Ch. [2] **66**, 47).

According to Tardy (Bull. Soc. [3] **17**, 580; 660) cymene is contained in the oil of French bitter-fennel, but it more probably resulted from the action of hydrogen chloride on some other constituent of the oil (Gildemeister and Hoffmann, p. 740). According to Klason the oil extracted from pine-wood during the sulphite cellulose process is cymene (Bied. Centr. **27**, 137; Ber. **33**, 2343).

Cymene is contained in the steam distillate from lemon-grass oil from the Indian *Andropogon citratus* (Dodge, Am. Ch. Journ. **12**, 553; Stiehl, Journ. pr. Ch. [2] **58**, 51). Cascarilla oil from the bark of *Croton eluteria* contains cymene

(Fendler, Arch. Pharm. **238**, 671 : see also Ch. Centr. 1900, **2**, 574).

Note:—The cymene said in the older works to be a constituent of so many plant oils is no doubt some other hydrocarbon and was recorded before the discovery of dependable chemical methods for identifying cymene. It is probable also in many cases that the cymene was produced by the action of the reagents employed upon some constituent of the oil and was not pre-existent as such.

Cymene is found in the urine of dogs after repeated doses of sabinol (Hildebrandt, Ch. Centr. 1901, **1**, 53).

Synthetical Processes.

One of the generators of cymene in some of the synthetical processes is benzene, and as this hydrocarbon is also the generator of large numbers of other synthetical products its syntheses are here introduced:—

Syntheses of Benzene.

[I.] From *acetylene* (see under methane [1; A]). The latter polymerises under the influence of heat with the formation of benzene (Berthelot, Comp. Rend. **63**, 479; Bull. Soc. [2] **7**, 303; Ann. Chim. [4] **9**, 469).

Note:—Generators of acetylene (see under methane [1; T; U; &c.]) thus become generators of benzene.

Carbon monoxide combines with potassium at 80° to form a salt of hexahydroxybenzene, the latter being liberated on treatment of the salt with hydrochloric acid (Brodie, Journ. Ch. Soc. [2] **12**, 269; Ann. **113**, 358; Nietzki and Benckiser, Ber. **18**, 1834). Hexahydroxybenzene gives benzene (and diphenyl) on distillation with zinc dust.

Mellitic acid = benzenehexacarboxylic acid can be obtained by oxidising charcoal or other forms of carbon by alkaline permanganate (Schulze, Ber. **4**, 802; 806), by fuming nitric acid (Dickson and Easterfield, Proc. Ch. Soc. **14**, 163), by the electrolysis of dilute acid or alkali with carbon electrodes (Bartoli and Papasogli, Gazz. **11**, 468; Ch. Centr. **1881**, 327), by alkaline hypochlorite (*Ibid.* Gazz. **15**, 446), or by heating with strong sulphuric acid (Verneuil, Bull. Soc. [3] **11**, 121; Comp. Rend. **132**, 1340). Mellitic acid gives benzene when distilled with soda-lime (Baeyer, Ann. Suppl. **7**, 5).

Certain metallic carbides, e.g. of barium, give benzene when heated to 600–800° with an equimolecular weight of the metallic hydroxide (Bradley and Jacobs, Germ. Pat. 125936 of 1898; Ch. Centr. 1902, **1**, 77).

[II.] *Methane* [1] and *heptane* [2] give benzene among the products formed by passing through a hot tube (for heptane see Worstall and Burwell, Am. Ch. Journ. **19**, 815).

[III.] From *ethyl alcohol* [14] through ethylene (see under methane [1; D]). The latter gives benzene among the products formed by passing through a hot tube (Berthelot, Bull. Soc. [2] **9**, 456; Norton and Noyes, Am. Ch. Journ. **8**, 362).

Note:—Generators of ethylene thus become generators of benzene. (See under methane [1; S; T; V, &c.]).

Or from ethyl alcohol through chloroform, bromoform, or iodoform (see under methane [1; D]). Chloroform gives acetylene by passing the vapour over heated copper (Berthelot, Comp. Rend. **50**, 805) or by the action of potassium or sodium amalgam (Kletzinsky, Zeit. [2] **2**, 127; Fittig, *Ibid.*). Iodoform gives acetylene by the action of finely divided silver, zinc, or the copper-zinc couple (Cazeneuve, Comp. Rend. **97**, 1371; Bull. Soc. [2] **41**, 106). Bromoform gives acetylene by similar treatment (*Ibid.* [3] **7**, 70; see also Nef, Ann. **308**, 329). Acetylene gives benzene by polymerisation as under I above.

Note:—Generators of chloroform and iodoform given under methane thus become through acetylene generators of benzene.

Or from ethylene through ethylene bromide and acetylene by the action of alcoholic potash on the latter (Miasnikoff, Ann. **118**, 330; Sawitsch, Comp. Rend. **52**, 157; Ann. **119**, 184; Sabanejeff, Ann. **178**, 111), or by the action of potassium isobutylate on the bromide (Forcrand, Ann. Chim. [6] **11**,

477), or by passing ethylene chloride over hot soda-lime (Wilde, Ber. 7, 352).

[IV.] From *normal* or *isopropyl alcohol* [15; 16] through propylene and allylene (see under benzyl alcohol [54; E]). The latter gives mesitylene when treated with sulphuric acid (Schrohe, Ber. 8, 17). Mesitylene oxidises to trimesic = 1 : 3 : 5-benzenetricarboxylic acid (Fittig, Ann. 141, 153), and this gives benzene on distillation with lime.

NOTE:—Generators of allylene (see under benzyl alcohol [54; F, G, &c.]) thus become generators of benzene. Generators of propylene are given under glycerol [48].

[V.] From *butyl alcohols* normal or iso- [17; 18] through normal or isobutylene or pseudobutylene (see under isobutyl alcohol [18; A]; tertiary butyl alcohol [19; B]; and secondary butyl isothiocyanate [165; A and B]). Butylene or pseudobutylene bromide gives crotonylene on treatment with alcoholic potash (Caventou, Ann. 127, 347; Almedingen, Journ. Russ. Soc. 13, 392; J. Wislicenus and Schmidt, Ann. 313, 211), and this by the action of sulphuric acid gives hexamethylbenzene (Almedingen, *loc. cit.*). The latter on oxidation with permanganate gives mellitic acid (Friedel and Crafts, Ann. Chim. [6] 1, 470), which gives benzene as above under I.

Benzene is a product of pyrogenic synthesis from isobutylene (Noyes; Beilstein, I, 115).

[VI.] *Methyl alcohol* [13] is said to give a small quantity of hexamethylbenzene by the action of zinc chloride (Greene and LeBel, Jahresber. 1878, 388).

A passage from methyl alcohol to benzene is also possible through methyl chloride and the further chlorination of the latter to chloroform (Damoiseau, Comp. Rend. 92, 42). From chloroform through acetylene as above under III.

[VII.] From *carbon disulphide* [160] through carbon tetrachloride (see under methane [1; L]). The latter is reduced by zinc and dilute sulphuric acid to chloroform (Geuther, Ann. 107, 212).

[VIII.] From *acetone* [106] through mesitylene (see under benzyl alcohol [54; D]), and then as above under IV.

Or from acetone through phorone and pseudocumene (see under orthocresol [61; B]). The latter oxidises to *a*-xylic = methylterephthalic acid and finally to trimellitic = 1 : 2 : 4-benzenetricarboxylic acid (Fittig and Laubinger, Ann. 151, 276; Krinos, Ber. 10, 1494), which gives benzene on fusion with alkali (Barth and Schreder, Ber. 12, 1257).

Or acetone and *formic acid* [Vol. II] condense when the ethyl ester of the latter and the ketone are acted upon by sodium ethoxide. The product is hydroxymethylene-acetone, and this undergoes further condensation to triacetylbenzene, which is oxidised to trimesic acid by nitric acid (Claisen and Stylos, Ber. 21, 1144).

[IX.] From *formic* and *acetic acids* [Vol. II]. A mixture of the esters when acted upon by sodium gives *β*-hydroxyacrylic = hydroxymethylene-acetic = formylacetic acid, which readily condenses to trimesic ester (Piutti, Ber. 20, 537; Claisen and Stylos, Ber. 21, 1146; see also Wislicenus and Bindemann, Ann. 316, 18).

Or a mixture of monochlor- or (better) monobromacetic acid and ethyl formate when acted upon by zinc condenses to trimesic ester, from which the acid can be obtained by hydrolysis (Reformatsky, Journ. Russ. Soc. 30, 280).

Or acetic acid on boiling potassium dichloracetate with potassium acetate solution gives the potassium salt of diacetyldihydroxyacetic = diacetylglyoxylic acid (Doebner, Ann. 311, 129). The latter (salt) condenses with *pyroracemic acid* (see below under XIV) in presence of alkali to phthalidetricarboxylic acid, the aqueous solution of which gives phthalidedicarboxylic acid on boiling. The dicarboxylic acid gives toluene when the barium salt is heated with barium oxide (Doebner, *loc. cit.* 132). Toluene can be oxidised to *benzoic acid* [Vol. II], which gives benzene on distillation with lime.

NOTE:—Generators of toluene are given under benzyl alcohol [54] *passim*.

[X.] From *isobutyric* and *formic acid* [Vol. II]. Isobutyric acid is brominated

(Markownikoff, Ann. **153**, 229; Hell and Waldbauer, Ber. **10**, 448) and a mixture of bromisobutyric ester and formic ester acted upon by zinc. Trimesic (with tetramethyloxyglutaric) ester is formed (Blaise, Comp. Rend. **126**, 1808).

[XI.] From *succcinic acid* [Vol. II] through acetylenedicarboxylic acid (see under methane [1; T]). The acid potassium salt of the latter gives propiolic = propargylic acid on boiling with water (Bandrowski, Ber. **13**, 2340), and this on long exposure to light out of contact with air partially condenses to trimesic acid (Baeyer, Ber. **19**, 2185).

Or from succinic acid through ethylene by electrolysis (see under methane [1; T]), ethylene bromide and acetylene as above under III, and polymerisation as under I.

[XII.] From *fumaric* or *maleïc acid* [Vol. II] through acetylene by electrolysis (see under methane [1; U]).

[XIII.] *Isovaleric acid* [Vol. II] gives mesitylenic acid among other products when the dry sodium salt is mixed with sodium ethoxide and heated to 160° in an atmosphere of carbon monoxide (Loos, Ann. **202**, 321). Mesitylenic acid oxidises to trimesic acid (Fittig, Ann. **141**, 153).

[XIV.] From *tartaric acid* [Vol. II] through pyroracemic acid (see under benzyl alcohol [54; N]). The latter gives uvitic acid (54; I), and this oxidises to trimesic acid (Baeyer, Zeit. [2] **4**, 119; Fittig and Furtenbach, Ann. **147**, 301).

Pyroracemic acid condenses also with *acetaldehyde* [92] or homologues (by heating the mixture with baryta water) to form uvitic = methylisophthalic acid and homologues (Doebner, Ber. **23**, 2377; **24**, 1746). These alkylisophthalic acids all oxidise to trimesic acid.

Note :—Generators of pyroracemic acid are given under benzyl alcohol [54].

[XV.] From *malonic acid* [Vol. II] and *acetal* [93]. The latter is converted into monobromacetal (Pinner, Ber. **5**, 149; Fischer and Landsteiner, Ber. **25**, 2551), and this by interaction with sodio-malonic ester gives acetalmalonic ester (W. H. Perkin, junr., and Sprankling, Trans. Ch. Soc. **75**, 13), which by hydrolysis to acetalmalonic acid and the action of water at 180–190° gives β-aldehydopropionic acid (*Ibid.* 16). The latter on heating with sodium hydroxide solution gives terephthalic acid (*Ibid.* 18), and this gives benzene on distillation with lime.

Or from malonic acid and *ethyl alcohol* [14] and *chloroform* through dicarboxyglutaconic ester by the interaction of chloroform and sodio-malonic ester in alcoholic solution (Conrad and Guthzeit, Ann. **222**, 250; Guthzeit and Dressel, Ber. **22**, 1414). The sodium derivative of dicarboxyglutaconic tetraethyl ester on heating with alcohol at 150° gives the triethyl ester of trimesic acid (Lawrence and W. H. Perkin, junr., Proc. Ch. Soc. **17**, 47).

Note :—Dicarboxyglutaconic ester can also be obtained from sodio-malonic ester and ethoxymethylenemalonic ester (Claisen and Haase, Ann. 297, 86), or from sodio-malonic ester and trichloracetic ester (Ruhemann, Ber. 29, 1017), or from sodio-malonic ester and carbon tetrachloride (Dimroth, Ber. **35**, 2881).

[XVI.] *Malic acid* [Vol. II] by the action of fuming sulphuric acid gives coumalic acid = formylglutaconic anhydride (v. Pechmann, Ber. **17**, 936; Ann. **264**, 272). The methyl ester of the latter is converted into trimesic monomethyl ester by dilute alkali (*Ibid.* Ann. **264**, 294), and this can be hydrolysed and converted into benzene as before.

Note:—Formylglutaconic = hydroxymethyleneglutaconic ester can also be obtained by the action of dilute sulphuric acid on sodium-ethylformylacetate (see above under IX). The ester condenses to trimesic ester on standing (oily form) or on distillation under reduced pressure (Wislicenus and Bindemann, Ann. 316, 18).

[XVII.] *Tiglic acid* [Vol. II] combines with bromine to form a dibromide which by the action of alcoholic potash is converted into β-bromangelic acid. By the extreme action of alkali the latter gives crotonylene (Wislicenus and Henze, Ann. **313**, 243). Subsequent steps through hexamethylbenzene and mellitic acid as above under V.

[XVIII.] From *glycerol* [48] through *acroleïn* [101] by dehydration (Redten-

bacher, Ann. **47**, 120; Van Romburgh, Bull. Soc. **36**, 550; Griner, Ann. Chim. [6] **26**, 367; Aronstein, Ann. Suppl. **3**, 180; Wagner, Journ. Russ. Soc. **16**, 317; Wohl and Neuberg, Ber. **32**, 1352), dibromacroleïn = dibrompropionic aldehyde by combination with bromine (Aronstein, *loc. cit.* 185; Henry, Ber. **7**, 1112; Linnemann and Penl, Ber. **8**, 1097), and the ethyl diacetal by condensing the aldehyde with formiminoether (Claisen, Ber. **31**, 1015). The diacetal on treatment with alcoholic potash gives the diacetal of propargylaldehyde = propinal, the latter being obtained by the action of dilute sulphuric acid on the diacetal (Claisen, *loc. cit.* 1022). Propinal is decomposed by aqueous alkali into acetylene and formic acid (Claisen, *loc. cit.*). From acetylene to benzene as above.

The synthetical processes for the production of cymene are the following:—

[A.] From *benzene*, *methyl* [13], and *normal* or *isopropyl alcohol* [15; 16]. Benzene and normal or isopropyl bromide or the corresponding chlorides condense in the presence of aluminium bromide or chloride respectively to form isopropylbenzene = cumene (Gustavson, Ber. **11**, 1251; R. Meyer, Journ. pr. Ch. [2] **34**, 98; Silva, Bull. Soc. [2] **43**, 317; Claus and Schulte im Hof, Ber. **19**, 3012: see also Kekulé and Schrötter, Ber. **12**, 2280; Konowaloff, Journ. Russ. Soc. **27**, 457; Radziewanowski, Ber. **28**, 1137).

Or monobrombenzene and isopropyl iodide condense to isopropylbenzene on treatment with sodium (Jacobsen, Ber. **8**, 1260).

Isopropylbenzene on bromination in presence of iodine gives parabromisopropylbenzene (R. Meyer, *loc. cit.* 101), and this condenses with methyl iodide under the influence of sodium to form cymene (Widman, Ber. **24**, 439; 1362; see also Jacobsen, Ber. **12**, 430).

Or *toluene* (see above under IX) and isopropyl chloride condense to cymene in contact with aluminium chloride (Silva, *loc. cit.* 321).

NOTE:—Isopropylbenzene may also be synthesised from toluene through benzal chloride by chlorination (Beilstein, Ann. **116**, 336; Beilstein and Kuhlberg, Ann. **146**, 322) and interaction of the latter with zinc methyl (Liebmann, Ber. **13**, 46). Or from *cumic acid* [Vol. II] by distillation with lime or baryta (Gerhardt and Cahours, Ann. Chim. [3] **1**, 87; 372; **14**, 107; Ann. **38**, 88). Or from *isobutyric aldehyde* [94] and *pyroracemic acid* (see above under XIV) through isopropylisophthalic acid, which gives isopropylbenzene on distillation with lime (Doebner, Ber. **24**, 1748). Or from phenyldimethylcarbinol through β-allylbenzene = methovinylbenzene by dehydration; the hydrocarbon gives isopropylbenzene by reduction (Tiffeneau, Comp. Rend. **134**, 845). Also from *acetophenone* and magnesium methiodide through methovinylbenzene and reduction (Klages, Ber. **35**, 2640; 3507; **36**, 620). See also under benzoic aldehyde (**114**; **A**).

[B.] From *dipentene* [9] which gives cymene on heating with phosphorus pentoxide or cymenesulphonic acid by the action of sulphuric acid. Or dipentene (limonene) is combined with hydrogen bromide, the dihydrobromide further brominated and the product debrominated by reduction with zinc dust and hydrochloric acid followed by sodium in alcoholic solution (Baeyer and Villiger, Ber. **31**, 1401).

[C.] From *amyl alcohol* [22] (crude fusel oil) through the pentine or valerylene obtained by the action of alcoholic potash on the amylene bromide (Reboul, Ann. **131**, 238). This pentine on heating to 250–260° gives a divalerylene which is said to yield cymene by the action of bromine (Bouchardat, Comp. Rend. **90**, 1560).

[D.] *Geraniol* [36] gives terpin hydrate $[C_{10}H_{18}(OH)_2 . H_2O]$ by the action of dilute mineral acids (Tiemann and Schmidt, Ber. **28**, 2137), and this on dehydration over sulphuric acid gives terpin $[C_{10}H_{18}(OH)_2]$. The latter gives a dibromide on heating with bromine ($C_{10}H_{16}Br_2$), and this gives cymene on heating with aniline (Barbier, Bull. Soc. [2] **17**, 17; Comp. Rend. **74**, 194).

[E.] *Linaloöl* [37] gives terpin hydrate under the same conditions as geraniol (Tiemann and Schmidt, *loc. cit.*).

[F.] *Terpineol* [39] combines with bromine to form a dibromide which gives cymene on heating with zinc dust. Or terpineol on standing in contact with dilute sulphuric acid gives

terpin hydrate (Tiemann and Schmidt, Ber. **28**, 1781), which can be converted into cymene as above under **D**.

[**G.**] *Cineole* [**40**] (eucalyptol) gives cymene on distillation with phosphorus pentasulphide (Faust and Homeyer, Ber. **7**, 428).

[**H.**] *Menthol* [**41**] gives cymene on heating with copper sulphate solution at 260° (Brühl, Ber. **24**, 3375). Also (with hexahydrocymene and other products) on treatment with strong sulphuric acid (Wagner, Ber. **27**, 1638).

[**I.**] From *thymol* [**67**] by distilling with phosphorus pentasulphide (Pott, Ber. **2**, 121). Or by the action of phosphorus pentachloride on thymol and reduction of the chloride ($C_{10}H_{13}Cl$) with sodium amalgam (Carstanjen, Jahresber. **1871**, 456).

[**J.**] *Citral* [**104**] gives cymene on heating with aqueous hydrochloric acid (Dodge, Am. Ch. Journ. **12**, 561; see also Tiemann, Ber. **32**, 108), with acid potassium sulphate at 170° (Semmler, Ber. **24**, 204), with acetic acid (Barbier and Bouveault, Comp. Rend. **118**, 1051), or on treatment with zinc chloride solution, with hydriodic or sulphuric acid (Verley, Bull. Soc. [3] **21**, 408).

[**K.**] *Citronellal* [**105**] combines with bromine to form a dibromide which gives cymene on heating (Beilstein's 'Handbuch,' III, 475).

[**L.**] From *cumic aldehyde* [**116**] through cumic alcohol (Kraut, Ann. **92**, 66; **192**, 224; Fileti, Gazz. **14**, 498). The latter gives cymene on boiling with zinc dust (Kraut, *loc. cit.*; Jacobsen, Ber. **12**, 434).

[**M.**] *Carvone* [**127**] gives cymene by the action of the sulphides of phosphorus (Kekulé and Fleischer, Ber. **6**, 1088) and among the products formed by passing the vapour over heated zinc dust (Arndt, Ber. **1**, 204).

[**N.**] From *terpinene* [**10**], which forms a nitrite which on reduction with sodium in alcohol gives cymene among other products (Wallach, Ann. **313**, 361; Semmler, Ber. **34**, 715).

7. Styrene; Styrolene; Phenylethylene; Cinnamene.

Natural Sources.

Occurs in liquid storax, a balsam from the *Liquidambar orientalis* of Asia Minor and N. Syria (Bonastre, Journ. Pharm. **17**, 338; Simon, Ann. **31**, 265; Blyth and Hofmann, Ann. **53**, 293; 325). Also in American storax from *Liquidambar styraciflua* (W. v. Miller, Arch. Pharm. **220**, 648) and in the oil from the yellow resin of *Xanthorrhœa hastilis* of Australia (Schimmel's Ber. Oct. 1897; Ch. Centr. 1898, **1**, 258).

Styrene exists as such in storax and is not a product of distillation (Van Itallie, Ch. Centr. 1901, **2**, 856: see also Tschirch and Van Itallie, Arch. Pharm. **239**, 506; 532).

Synthetical Processes.

[**A.**] Among the products formed by the action of heat on *acetylene* [**1**; **A**, &c.] (Berthelot, Comp. Rend. **62**, 905; 947; Ann. **141**, 181). Also among the products formed by passing acetylene over finely divided nickel at 200° (Sabatier and Senderens, Comp. Rend. **134**, 1185). Also by passing *ethylene* [**1**; **D**, &c.] or ethylene and *benzene* vapour [**6**; **I**, &c.] through a hot tube (Berthelot, Bull. Soc. [2] **9**, 456; Zeit. [2] **4**, 384; Ann. **142**, 257; Ferko, Ber. **20**, 660).

Toluene vapour, alone or mixed with ethylene, gives styrene by pyrogenic synthesis (Ferko, *loc. cit.*). Acetylene passed through benzene in presence of aluminium chloride gives styrene (Varet and Vienne, Bull. Soc. [2] **47**, 918; Comp. Rend. **104**, 1375).

Or from ethylene through the bromide and monobromethylene (vinyl bromide) by the action of alcoholic potash (Regnault, Ann. Chim. [2] **59**, 358; Beilstein, Jahresber. **1861**, 609; Glöck-

ner, Ann. Suppl. 7, 109; Semenoff, Jahresber. 1864, 480). Vinyl bromide and benzene condense in the presence of aluminium chloride to form styrene (Hanriot and Gilbert, Jahresber. 1884, 561: see also Anschütz, Ann. 235, 331).

NOTE :—Vinyl bromide is formed also by the combination of acetylene with hydrogen bromide (Reboul, Comp. Rend. 74, 947).

Or from *ethyl alcohol* [14] and *benzene* through ethylbenzene by the condensation of ethyl bromide or iodide with benzene in presence of aluminium chloride (Friedel and Crafts, Ann. Chim. [6] 1, 457). Ethylbenzene gives styrene when the vapour is passed through a hot tube (Berthelot, Zeit. [2] 4, 589; Ferko, Ber. 20, 663).

Or ethylbenzene on bromination at its boiling-point or in presence of light gives 1^1-bromethylbenzene, $C_6H_5 . CHBr . CH_3$ (Berthelot, Bull. Soc. 10, 343; Comp. Rend. 67, 328; Radziszewski, Ber. 6, 492; 7, 141; Anschütz, Ann. 235, 328; Schramm, Ber. 18, 351), and this gives styrene by the action of heat or of alcoholic potash (Thorpe, Proc. Roy. Soc. 18, 123; Radziszewski, Ber. 7, 140). Or ethylbenzene on bromination with two molecules of bromine gives $1^1 : 1^2$-dibromethylbenzene = styrene bromide (Radziszewski, Ber. 6, 493; also Friedel and Balsohn, Bull. Soc. [2] 35, 55), and this on heating with strong alcoholic potash at 120° gives phenylacetylene (Glaser, Ann. 154, 155; Zeit. [2] 5, 97; Friedel and Balsohn, *loc. cit.*; Holleman, Ber. 20, 3080; see also Moureu and Delange, Bull. Soc. [3] 25, 302). The latter can be reduced to styrene by zinc and acetic acid (Aronstein and Holleman, Ber. 22, 1184).

Or ethylbenzene can be converted into phenylacetaldehyde = α-toluic aldehyde and ω-phenylethylamine (see under phenylethyl mustard oil [170; A]). The hydrochloride of the latter gives styrene on distillation (Fileti and Piccini, Ber. 12, 1308).

NOTE :—Generators of ethylbenzene are given under phlorol as follows:—*Tartaric* or *racemic acid* [Vol. II] and *n-propyl alcohol* [15] through ethylisophthalic acid (see under phlorol [64; J]). *Benzoic* and *acetic acids* [Vol. II] through acetophenone (see below under D) and dypnone (see under phlorol [64; K]). Full references to syntheses of ethylbenzene from benzene are given under phlorol [64; A].

Benzene can be converted into acetophenone by various processes (see under benzoic aldehyde [114; A]). The ketone reduces to *methylphenyl carbinol* [58] (Emmerling and Engler, Ber. 6, 1006; Klages and Allendorff, Ber. 31, 1003), and this gives styrene on heating with zinc chloride or by distilling the acetate (E. and E. Ber. 4, 147; Radziszewski, Ber. 7, 140), or by heating with syrupy phosphoric acid (Klages and Allendorff, Ber. 31, 1298).

Or methylethyl carbinol by the action of hydrobromic acid gives 1^1-bromethylbenzene (Engler and Bethge, Ber. 7, 1126), which gives styrene as above.

Or acetophenone and hydrogen sulphide combine in presence of hydrogen chloride to form a trithio-derivative ($C_{24}H_{24}S_3$) which gives styrene on heating (Baumann and Fromm, Ber. 28, 901).

By the action of phosphorus pentachloride acetophenone is converted into the dichloride = $1^1 : 1^1$-dichlorethylbenzene, and this gives phenylacetylene by the action of alcoholic potash or hot lime (Friedel, Comp. Rend. 67, 1192; Morgan, Journ. Ch. Soc. 29, 164; Peratoner, Gazz. 22, 67; Nef, Ch. Centr. 1899, 2, 933). Phenylacetylene can be reduced to styrene as above.

Toluene gives benzyl chloride on chlorination at its boiling-point (see under benzyl alcohol [54; A]), and this by interaction with potassium *cyanide* [172] and reduction of the product gives phenylethylamine (see under phenylethyl mustard oil [170; A]), which gives styrene as above under A.

[B.] *Cymene* [6] gives cumic aldehyde and acid, and isopropylbenzene (see under benzoic aldehyde [114; K]). The latter gives acetophenone among the products of the action of chromium oxychloride (Miller and Rohde, Ber. 24, 1358). Acetophenone gives styrene as above under A.

[C.] From *benzoic aldehyde* [114] and *acetic acid* [Vol. II] and *alcohol* [14] through phenylglycidic acid, α-toluic

aldehyde, and ω-phenylethylamine (see under phenylethyl mustard oil [170; D]).

Or from benzoic aldehyde and *hydrogen cyanide* [172] through mandelonitrile and phenylethylamine (references as before).

Or from benzoic aldehyde and *chloroform* [1; D, &c.], which condense in the presence of alkali to form trichlormethylphenyl carbinol (Jocitsch, Journ. Russ. Soc. **29**, 97). The latter by the action of zinc dust on the alcoholic solution gives styrene (Jocitsch and Faworsky, *Ibid.* **30**, 920).

[D.] From *benzoic* and *acetic acids* [Vol. II] through acetophenone (Friedel, Ann. **108**, 122). Or from benzoic acid and *methyl alcohol* [13] through benzoyl chloride and zinc methyl, which yield acetophenone by interaction (Popoff, Ber. **4**, 720; Ann. **161**, 296); or benzoyl chloride and *sodio-acetoacetic ester* [Vol. II] give benzoylacetoacetic ester, which yields acetophenone among other products on hydrolysis (Bonné, Ann. **187**, 1; Nef, Ann. **266**, 99). Acetophenone gives styrene as above under **A**.

Note :—Since ethylbenzene gives α-toluic aldehyde and the latter phenylethylamine, which is a generator of styrene (see above under A), generators of α-toluic aldehyde become generators of styrene (see below and under phenylethyl mustard oil [170]).

[E.] From *phenylacetic* and *formic acids* [Vol. II] through α-toluic aldehyde [170; H].

[F.] From *β-phenylpropionic acid* [Vol. II] through ω-phenylethylamine [170; I].

[G.] From *phenylalanine* [Vol. II] through ω-phenylethylamine [170; J].

[H.] From *cinnamic acid* [Vol. II], which gives styrene by heating *per se* or with lime or baryta or by heating the copper salt (Gerhardt and Cahours, Ann. Chim. [3] **1**, 96; Ann. **38**, 96; Kopp, Comp. Rend. 53, 634; Simon, Ann. **31**, 265; Howard, Journ. Ch. Soc. **13**, 135; Hempel, Ann. **59**, 318; Miller, Ann. **189**, 338; Krämer, Spilker, and Eberhardt, Ber. **23**, 3269).

Or cinnamic acid on combination with hydrogen iodide gives iodhydrocinnamic = phenyliodopropionic acid, and this gives styrene on boiling with sodium carbonate solution (Fittig and Binder, Ann. **195**, 137).

Cinnamic acid (or ester) combines with bromine to form phenyldibrompropionic acid, which by the action of alcoholic potash is converted into α-brom- = ι^2-bromcinnamic acid and finally into phenylpropiolic acid (Glaser, Ann. **143**, 325; 330; Barisch, Journ. pr. Ch. [2] **20**, 182; Kinnicutt, Am. Ch. Journ. **4**, 26; Stockmeier, Inaug. Diss. 1883, 52; Glaser, Zeit. [2] **4**, 328; Ann. **154**, 140; W. H. Perkin, junr., Trans. Ch. Soc. **45**, 173; Weger, Ann. **221**, 70; Roser, Ann. **247**, 138; Michael, Ber. **34**, 3648: see also Liebermann and Sachse, Ber. **24**, 4113, note). Phenylpropiolic acid on heating with water at 120° or by distilling the barium salt gives phenylacetylene (Glaser, Ann. **154**, 155; Weger, *loc. cit.*: see also Holleman, Ber. **20**, 3081).

Or phenylbrompropionic acid on boiling with sodium carbonate solution gives ω-bromstyrene, which, on heating with alcoholic potash, gives phenylacetylene (Nef, Ch. Centr. 1899, **2**, 933, from Ann. **308**, 264, &c.: for conversion of β-bromcinnamic acid into phenylacetylene see Michael, Ber. **34**, 4226).

Cinnamic acid by the action of iodine in presence of pyridine gives pyridine β-iodocinnamate, which, by the action of sulphurous acid on the sodium hydroxide solution, gives β-iodocinnamic acid. The silver salt of the latter gives phenylacetylene on heating (Ortoleva, Gazz. **29**, 503). Phenylacetylene can be reduced to styrene as above under **A**.

From cinnamic acid through phenyl-α-chlorlactic acid, α-toluic aldehyde, and ω-phenylethylamine (phenylethyl mustard oil [170; A and E] and above under **A**); or through α-oxyphenylpropionic lactone and α-toluic aldehyde [170; E]; or through phenylglyceric acid (benzaldehyde [114; E]), phenyl-β-chlor- or bromlactic acid, and α-toluic aldehyde (phenylethyl mustard oil [170; E]).

[I.] *Benzoylacetic ester* [Vol. II] gives phenyl-β-lactic acid on reduction with sodium amalgam (W. H. Perkin, junr., Trans. Ch. Soc. **47**, 254). This acid

on heating with dilute sulphuric acid gives, among other products, a small quantity of styrene (Erlenmeyer, Ber. **13**, 304).

[J.] From *methylphenyl carbinol* [58] by conversion into the chloride and heating the latter with pyridine at 130° (Klages and Keil, Ber. **36**, 1632).

8. Metastyrene.

$(C_6H_5 . CH : CH_2)_x$

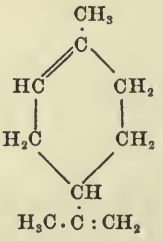
Natural Sources.

Occurs in liquid storax (Kowalewsky, Ann. **120**, 66), and in Siegburgite, a fossil resin found in sandy concretions over deposits of brown coal at Troisdorf and Siegburg (Klinger and Pitschki, Ber. **17**, 2742).

Synthetical Process.

[A.] From *styrene* [7] by polymerisation through heat (Blyth and Hofmann, Ann. **53**, 311; Lemoine, Comp. Rend. **125**, 530; Kronstein, Ber. **35**, 4153) or light (Lemoine, *Ibid.* **129**, 719), by the action of a hot solution of acid sodium sulphite (Miller, Ann. **189**, 341) or of strong sulphuric acid (Berthelot, Bull. Soc. **6**, 296).

9. Dipentene; Inactive Limonene; Cajeputene; Terpilene; Cinene; Diisoprene; Isoterebenthene; Caoutchene.



Natural Sources.

Occurs in Russian and Swedish turpentine oil (Bertram and Walbaum, Arch. Pharm. **231**, 290; Wallach, Ann. **230**, 244; 246); in camphor oil from *Cinnamomum camphora* (Lallemand, Ann. **114**, 196; Wallach, Ann. **227**, 296); probably in oil of cascarilla from the bark of *Croton eluteria*, Bahamas (Brühl, Ber. **21**, 152; compare Thoms, Ch. Centr. 1900, **2**, 574); in kuromoji oil from the leaves of *Lindera fericia*, Japan (Kwasnick, Ber. **24**, 81); in oil of elemi resin from *Canarium* sp.? (Wallach, Ann. **246**, 233; **252**, 102), and in oil of Canadian golden-rod from *Solidago canadensis* (Schimmel's Ber. April, 1897).

Dipentene is contained also in the oil of lemon-grass from the Indian *Andropogon citratus* (Stiehl, Journ. pr. Ch. **58**, 51; Tiemann, Ber. **32**, 834, on authority of Bertram); in oil of bergamot (Charabot, Comp. Rend. **129**, 728); in oil of pine-needle (Bertram and Walbaum, Arch. Pharm. **231**, 296; Wallach, Ann. **227**, 287); in Ceylon citronella oil from *Andropogon nardus* and vars. (Bertram and Walbaum, Journ. pr. Ch. [2] **49**, 16; Schimmel's Ber. Oct. 1899); in small quantity in East Indian geranium or palmarosa oil from *Andropogon schœnanthus* (Gildemeister and Hoffmann, p. 364); *possibly* in oil of bay from *Pimenta acris* (Mittmann, Arch. Pharm. **227**, 529; compare Power and Kleber, Pharm. Rund. **13**, 60); as 'terpinol' (a mixture) in oil from the Californian bay, *Umbellularia californica* (Stillmann, Ber. **13**, 630; Wallach, Ann. **230**, 251); in oil of cubebs from *Piper cubeba* (Wallach, Ann. **238**, 78); *possibly* in oil of black pepper from *Piper nigrum* (Wallach, Ann. **287**, 372); *possibly* in oil of Ceylon cardamom from *Elettaria cardamomum*, var. (Weber, Ann. **238**, 98); and in oil of mace or nutmeg from *Myristica fragrans* (Semmler, Ber. **23**, 1803; **24**, 3818).

Dipentene is contained in oil of *Massoia* bark (Schimmel's Ber. Oct. 1888; Wallach, Ann. **258**, 340; Arch. Pharm. **229**, 116); *possibly* in oil of lime leaves from *Citrus limetta* (Watts, Trans. Ch. Soc. **49**, 316); in oil of fennel from *Fœniculum vulgare* (Schimmel's Ber. April, 1890); in oil of myrtle from *Myrtus communis* (*Ibid.* April, 1889); in kesso oil from the root of Japanese valerian, *Valeriana officinalis* var. *angustifolia*; possibly derived from pinene or terpineol by the action of acid

(Gildemeister and Hoffmann, p. 869); in oils from the Spanish *Satureia thymbra* (Schimmel's Ber. Oct. 1889) and *Thymus capitatus* (*Ibid.*); in oil of frankincense from *Boswellia carteri*, &c. (Wallach, Ann. **252**, 100); in wartara oil, probably from the seeds of *Xanthoxylum alatum* and *X. acanthopodium* (Schimmel's Ber. April, 1900).

Dipentene and d-limonene are contained in the ethereal oil from the bucco-leaf, *Barosma betulina* and *B. serratifolia* (Kondakoff and Bachtschieff, Journ. pr. Ch. [2] **63**, 49). Dipentene is contained (with d-limonene) in mandarin oil (Schimmel's Ber. Oct. 1901; Ch.Centr. 1901, **2**, 1007), and (probably) in oil of pennyroyal from *Mentha pulegium* (Tétry, Bull. Soc. [3] **27**, 186). White camphor oil, néroli oil (Cannes), and oil of petit-grain contain dipentene (Schimmel's Ber. Oct. 1902; Ch. Centr. 1902, **2**, 1207).

Note :—The question of the existence of dipentene as such in plant oils is complicated by the fact that many compounds of the terpene group give this hydrocarbon when acted upon by heat or chemical reagents.

Dipentene is racemic limonene or (possibly) a pseudo-form of limonene (Semmler, Ber. **33**, 1455). d-Limonene = hesperidene, carvene or citrene. The synthetical product is inactive (= dipentene), but the occurrence of the active limonenes is here included in anticipation of some method of resolution of the racemic form being discovered. The dipentene found in some ethereal oils may arise from limonene by the action of the heat applied for distillation.

d-Limonene occurs in oil of sweet orange, Portugal (Wright, Ch. News, **27**, 260; Wallach, Ann. **227**, 287: see also Wright and Piesse, Ch. News, **24**, 147; Flatau and Labbé, Bull. Soc. [3] **19**, 361; Fabris, Journ. Soc. Ch. Ind. **19**, 771), and in the néroli oil from the flowers (Theulier, Ch. Zeit. **26**, 126); in oil of mandarin orange from *Citrus madurensis* (Gildemeister and Stephan, Arch. Pharm. **235**, 583; Flatau and Labbé, *loc. cit.* 364; Fabris, *loc. cit.*: for references to botanical source of mandarin oil see Gildemeister and Hoffmann, p. 626, note); in Italian limetto oil from *Citrus limetta* (Gildemeister, Arch. Pharm. **233**, 174); in oil from the peel of *Citrus medica* (possibly with dipentene: Burgess, 'Analyst,' **26**, 260); in Chinese néroli oil from *Citrus triptera* (Umney and Bennett, Pharm. Journ. [4] **15**, 146); in oil of lemon (Wallach, Ann. **227**, 290); in oil of bergamot (*Ibid.*; also Charabot, Comp. Rend. **129**, 728; Fabris, *loc. cit.* 772); in oil of caraway from *Carum carui* (Schweizer, Ann. **40**, 333; Journ. pr. Ch. **24**, 257; Sauer and Grünling, Ann. **208**, 75; Wallach, *loc. cit.* 291); and in oil of dill from *Peucedanum graveolens* (Nietzki, Arch. Pharm. **204**, 317; Wallach, *loc. cit.* 292).

d-Limonene occurs also in oil of fleabane from *Erigeron canadensis* (Beilstein and Wiegand, Ber. **15**, 2854); in kuromoji oil (see above under dipentene); in néroli oil from orange flowers, *Citrus bigaradia* (Tiemann and Semmler, Ber. **26**, 2711; E. and H. Erdmann, Ber. **32**, 1214); in oil of petit-grain from the young fruit of the same plant (Paraguay oil: Semmler and Tiemann, Ber. **25**, 1186; Charabot and Pillet, Bull. Soc. [3] **21**, 74); in oil of *Massoia* bark (see above under dipentene); possibly in small quantity in oil of spoonwort from *Cochlearia officinalis* (Gadamer, Arch. Pharm. **237**, 92).

d-Limonene occurs also in oils of American horse-mint from *Monarda punctata* and wild bergamot from *M. fistulosa* (Kremers and Hendricks, Pharm. Arch. **2**, 73; 76; Brandel and Kremers, Pharm. Rev. **19**, 200: the hydrocarbon from the latter plant is entered simply as limonene); in oil of Malabar cardamom from *Elettaria cardamomum* (Parry, Pharm. Journ. [4] **9**, 105); in oil of Macedonian fennel (Schimmel & Co.; Gildemeister and Hoffmann, p. 741); in oil of celery from herb and seeds of *Apium graveolens* (Schimmel's Ber. April, 1892); in Ceylon citronella oil (Lana Batu) from *Andropogon nardus* and vars. (Schimmel's Ber. Oct. 1899). Limonene probably exists in the oleo-resin of *Dacryodes hexandra*, Montserrat, W. Indies (More, Trans. Ch. Soc. **75**, 718).

l-Limonene occurs in oil from the needles and cones of *Pinus picea* = *Abies alba* (Wallach, Ann. **227**, 287; **246**,

221; Bertram and Walbaum, Arch. Pharm. **231**, 290; Schimmel's Ber. Oct. 1892; April, 1893); in American oil of spearmint from *Mentha viridis* (Power, quoted by Gildemeister and Hoffmann, p. 852; in Russian oil, Schimmel's Ber. April, 1898; Ch. Centr. 1898, **1**, 991); in Russian peppermint oil (Andres and Andreef, Ber. **25**, 609); in American peppermint oil (Power and Kleber, Pharm. Rund. **12**, 157; Arch. Pharm. **232**, 639); in oil of cascarilla (see above under dipentene; also Fendler, Arch. Pharm. **238**, 671); in oil of rue, probably Algerian (Power and Lees, Trans. Ch. Soc. **81**, 1590); in the oil of *Bystropogon origanifolius*, Teneriffe (Schimmel's Ber. Oct. 1902; Ch. Centr. 1902, **2**, 1208).

The oil from the leaves of *Verbena triphylla* (Grasse) probably contains l-limonene (Theulier, Rev. gén. de Chim. **5**, 324). A limonene is present in the American oil of cedar leaves from *Juniperus virginiana* (Schimmel's Ber. April, 1898; Ch. Centr. 1898, **1**, 990).

Synthetical Processes.

[**A.**] From *terpineol* [**39**] by heating the latter with acid potassium sulphate to 190° (Wallach, Ann. **230**, 258; **275**, 104; **291**, 362).

[**B.**] *Cineole* [**40**] gives a hydrochloride which yields dipentene on dry distillation (Hell and Stürcke, Ber. **17**, 1971; Hell and Ritter, *Ibid.* 1979; Wallach and Brass, Ann. **225**, 298). Also from cineole by heating with benzoyl chloride or by combining with hydrogen iodide and then eliminating hydrogen iodide from the dipentene dihydriodide thus formed (Wallach and Brass, *loc. cit.*; Wallach, Ann. **230**, 255).

[**C.**] *Geraniol* [**36**] by the action of dilute mineral acids gives terpin hydrate (Tiemann and Schmidt, Ber. **28**, 2137). The latter on heating with acid potassium sulphate at 200° gives dipentene (Wallach, as under **A** above).

[**D.**] *Linaloöl* [**37**] also gives terpin hydrate by the action of mineral acids (Tiemann and Schmidt, *loc. cit.*). Formic acid acts on l-linaloöl with the formation of dipentene and terpinene (Bertram and Walbaum, Journ. pr. Ch. [2] **45**, 601; Stephan, *Ibid.* [2] **58**, 109: see also Charabot, Bull. Soc. [3] **23**, 189).

[**E.**] From *carvone* [**127**] through its oxime and dihydrocarvylamine by reduction. The hydrochloride of the latter gives dipentene among other products on treatment with sodium nitrite (Wallach, Kruse, and Kerkhoff, Ann. **275**, 110). Dihydrocarvylamine can also be obtained from carvone by heating with ammonium formate (Leuckart and Bach, Ber. **20**, 105; Wallach, *loc. cit.* 120; Ber. **24**, 3984).

d-Carvone can be reduced by sodium to dihydrocarveol and the latter converted into the xanthic acid dihydrocarvyl methyl ester by means of carbon disulphide and subsequent methylation of the sodium salt. The methyl dihydrocarvyl xanthate on dry distillation gives l-limonene (Tschugaeff, Ber. **32**, 3332; **33**, 735).

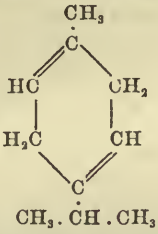
[**F.**] From *normal* or *isopropyl alcohol* [**15**; **16**] and *potassium cyanide* [**172**] through the nitrile of pyrotartaric acid by the interaction of propylene bromide and the cyanide (Simpson, Ann. **121**, 160) and β-methyltetramethylenediamine by reduction (Oldach, Ber. **20**, 1654). The diamine is converted into 3-β-methylpyrrolidine by the dry distillation of the hydrochloride (*Ibid.* 1657), the latter base into β-methyl-N-dimethylpyrrolidylammonium iodide; the latter distilled with solid potash gives a base which combines with methyl iodide to form β-methyl-N-trimethylpyrrolidylammonium iodide, and the latter on distillation with solid potash gives trimethylamine and *isoprene* [$CH_2 : C(CH_3) . CH : CH_2$] (Euler, Ber. **30**, 1989). Isoprene polymerises on heating to 250° or by the action of dilute or alcoholic sulphuric acid with the formation of dipentene (Wallach, Ann. **227**, 295; Bouchardat, Comp. Rend. **89**, 1217).

Note:—All generators of propylene thus become, with potassium cyanide, generators of dipentene.

[**G.**] From *glycerol* [**48**] through allyl chloride (see under benzyl alcohol

[54; F]) and *potassium cyanide* [172] through pyrotartaric nitrile (Pinner, Ber. **12**, 2053) and then as above.

10. Terpinene; $\Delta^{1,4}$-Menthadiene.



For constitutional formula see Harries, Ber. **35**, 1169.

Natural Sources.

In oil of Ceylon cardamom from *Elettaria cardamomum*, var. *major* (Weber, Ann. **238**, 107), and in oil of sweet marjoram from *Origanum majorana* (Biltz, Ber. **32**, 995).

Note:—It is possible that the terpinene does not pre-exist in the oils from these plants, but is formed from some compound in the oils by the heat of distillation (Gildemeister and Hoffmann, p. 178: see also Semmler, Ber. 34, 718).

Synthetical Processes.

[A.] *Dipentene* [9] gives terpinene on treatment with hydrochloric or sulphuric acid in alcoholic solution (Wallach, Ann. **239**, 15; 35). Limonene gives terpinene when distilled with solid arsenic acid (Genvresse, Comp. Rend. **134**, 360).

[B.] *Cineole* [40] gives terpinene by the same treatment (Wallach, Ann. **239**, 22).

[C.] *Terpineol* [39] gives terpinene among other products on heating with dilute sulphuric acid (Wallach and Kerkhoff, Ann. **275**, 106): also on boiling for some time with oxalic acid solution or with anhydrous formic acid (*Ibid.* **291**, 342).

[D.] From *geraniol* [36] through terpin hydrate (see under dipentene [9; C]) and the action of boiling dilute sulphuric acid on the latter.

[E.] From *linaloöl* [37] through terpin hydrate, &c. (see under dipentene [9; D]; also Bertram, Journ. pr. Ch. **45**, 601).

[F.] From *carvone* [127] through dihydrocarveol by reduction. The latter gives terpinene on boiling with dilute sulphuric acid (Wallach, Kruse, and Kerkhoff, Ann. **275**, 113). Dihydrocarvylamine also gives terpinene when acted upon by acid (Wallach, Ber. **24**, 3991) or by distilling the dry hydrochloride (Wallach, &c. Ann. **275**, 120).

11. Lævo-Isoterpene (?).

$C_{10}H_{16}$

Natural Sources.

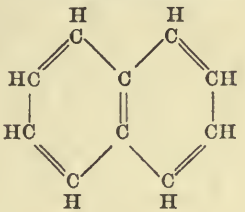
A hydrocarbon corresponding with the above possibly exists in elemi resin from species of *Canarium* and in the resins from *Pinus* and *Abies* (Kuriloff, Journ. Russ. Soc. **21**, 362).

Synthetical Process.

[A.] *Terpineol* [39] gives isoterpene on heating with acetic anhydride to 135–150° (Flawitzky, Ber. **12**, 2356).

Note:—The synthetical product was obtained from l-terpineol acetate prepared by the action of zinc chloride and acetic acid on pinene (Ertschikowsky, Journ. Russ. Soc. 28, 132). The synthesis is thus complete only in so far as the synthesis of l-terpineol is complete. d-Isoterpene is also said to have been synthesised from d-terpineol (Flawitzky, Ber. 20, 1961)

12. Naphthalene.



Natural Sources.

According to v. Soden and Rojahn (Pharm. Zeit. **47**, 779) this hydrocarbon is contained in certain ethereal oils from clove stems and storax bark.

Syntheses of naphthalene are given under hydrojuglone (**90**).

ALCOHOLS

MONOHYDRIC OF FATTY SERIES

13. Methyl Alcohol; Carbinol; Methanol; Wood Spirit.

$CH_3.OH$

Natural Sources.

Methyl alcohol is contained in the steam distillate from meadow grass (Lieben, Monats. **19**, 333); in the distillation water from oil of cloves (Schimmel's Ber. Oct. 1896), from oil of caraway (*Ibid.* Oct. 1899), from vetiver oil from the roots of *Andropogon muricatus* (*Ibid.* April, 1900), from the oil of the fruit of *Heracleum giganteum* (Zincke and Franchimont, Ber. **4**, 822; Möslinger, Ber. **9**, 999; Gutzeit, Ann. **177**, 344) and *H. sphondylium* (Möslinger, Ber. **9**, 998; Ann. **185**, 26), and from oil of tea from leaves of *Thea chinensis* (Van Romburgh, Schimmel's Ber. April, 1897, and April, 1898; Gerber, Mon. Sci. [4] **11**, 880; Ch. Centr. 1898, **1**, 122).

Methyl alcohol occurs also in the aqueous distillate from the unripe fruit of *Anthriscus cerefolium* (Gutzeit, Ann. **177**, 382), from the oil obtained by distilling the leaves of *Indigofera galegoïdes* (Van Romburgh, Schimmel's Ber. Oct. 1894; April, 1896), from oil of bay (Schimmel's Ber. April, 1901), and in the steam distillate from the root of *Acorus calamus* (Schnedermann, Ann. **41**, 374; Kurbatoff, Ber. **6**, 1210; Gladstone, Journ. Ch. Soc. **17**, 1; Geuther, Ann. **240**, 109).

It is doubtful in these cases whether the alcohol exists in the free state in the plant or whether it is produced by the hydrolysis of esters. (For references to the occurrence of free methyl alcohol in juices of plants see Gutzeit, Jahresber. **1879**, 905; Maquenne, Comp. Rend. **101**, 1067; also Lieben as above.)

Methyl alcohol is found in the fermented juice of fruit, such as currants, plums, apples, cherries, grapes, &c. (Wolff, Comp. Rend. **131**, 1323).

Esters of methyl alcohol occur very frequently in volatile plant oils. Methyl esters of fatty acids occur in the fruit of *Heracleum giganteum* and *H. sphondylium;* methyl butyrate probably occurs in the oils from the fruit of *Anthriscus cerefolium* and *Pastinaca sativa* (Gutzeit, Ann. **177**, 344); methyl esters of myristic and (possibly) oleïc acids occur in the oil of orris-root from (?) *Iris germanica* (Tiemann and Krüger, Ber. **26**, 2675: *Iris pallida* and *I. florentina* also furnish orris-root oil: the botanical source of the oil examined by Tiemann and Krüger is not stated).

Methyl salicylate occurs in many plants, notably in oil of wintergreen (as the glucoside gaultherin) from *Gaultheria procumbens* (Cahours, Ann. Chim. [3] **10**, 327; Ann. **48**, 60; **52**, 327; Procter, Am. Journ. Pharm. **14**, 211; Ann. **48**, 66; Kremers, Pharm. Rev. **20**, 350), from the leaves of *G. punctata* (De Vrij, Pharm. Journ. [3] **2**, 503; Köhler, Ber. **12**, 246; Broughton, Pharm. Journ. [3] **2**, 281: the latter refers to the oil from *Andromeda leschenaultii*, probably = *G. punctata*), and from the leaves of *G. leucocarpa*, Java (De Vrij, *loc. cit.*; Köhler, *loc. cit.*).

Methyl salicylate occurs (also as the glucoside gaultherin) in the bark of the sweet birch, *Betula lenta* (Procter, Am. Journ. Pharm. **15**, 241; Schneegans and Gerock, Arch. Pharm. **232**, 437; Power and Kleber, Pharm. Rund. **13**, 228; Kremers, Pharm. Rev. **20**, 350). The oil from the flowers of the meadow-sweet, *Spiræa ulmaria*, contains methyl salicylate (Schneegans and Gerock, Jahresber. Pharm. **1892**, 164) and also the oil from the roots (Nietzki, Arch. Pharm. **204**, 429). According to Beyerinck (Centr. Bakter. **5**, 425) the roots, rhizomes, and lower parts of *Spiræa ulmaria*, *S. filipendula*, and *S. palmata* contain the glucoside gaultherin. Methyl salicylate is present in oil of

rue, probably from Algeria (Power and Lees, Trans. Ch. Soc. **81**, 1587). The oils from the following plants also contain methyl salicylate:—

Spicewood or spicebush oil from the N. American *Laurus benzoïn* (Schimmel's Ber. Oct. 1885 and Oct. 1890); oil from the leaves of *Erythroxylon coca* (Van Romburgh, Rec. Tr. Ch. **13**, 425; Schimmel's Ber. Oct. 1895; April, 1896); oils from roots of *Polygala senega*, var. *latifolia* (Reuter, Arch. Pharm. **227**, 313), *P. variabilis* = *β-albiflora*, *P. oleifera*, and *P. javana* (Van Romburgh, Rec. Tr. Ch. **13**, 421), *P. vulgaris*, *P. calcarea*, and *P. serpyllacea* = *depressa* (Bourquelot, Comp. Rend. **119**, 802; Journ. Pharm. [5] **30**, 96; 188; 433; [6] **3**, 577: according to Bourquelot the roots contain gaultherin); roots of *Monotropa hypopitys* as gaultherin (Bourquelot, Journ. Pharm. [5] **30**, 435; [6] **3**, 577; Comp. Rend. **119**, 802; **122**, 1002); oils from *Viola tricolor*, *Acacia intsia*, *A. pluricapitata*, *A. sarmentosa*, *A. tenerrima*, and *A. farnesiana* (Schimmel's Ber. Oct. 1899; Journ. Soc. Ch. Ind. **18**, 1153); oil of tea (Schimmel's Ber. April, 1898; see also above); ylang-ylang oil (Schimmel's Ber. Oct. 1901; Ch. Centr. 1901, **2**, 1007). Methyl benzoate may also be present in this last oil (*Ibid.*).

The following list of plants containing methyl salicylate is given by Schimmel & Co. (Ber. April, 1900) as having been investigated in the Government Laboratory of the Botanical Gardens at Buitenzorg:—

Anacardiaceæ. *Mangifera* sp.; *Semecarpus* sp.

Anonaceæ. *Cananga odorata.*

Apocynaceæ. *Allamanda hendersoni*; *Chilocarpus densiflorus*; *C. denudatus*; *Melodinus lævigatus*; *M. orientalis*; *Landolphia watsonii.*

Artocarpaceæ. *Cecropia schiedeana*; *Ficus elastica*; *F. benjamina* and var. *crassinervis*; *F. annulata*; *F. geniculata*; *F. pilosa* and var. *chrysocoma*; *F. retusa*, var. *nitida*; *F. xylophylla*; *Streblus mauritianus*; *Slætia sideroxylon.*

Boraginaceæ. *Cordia asperrima.*

Burseraceæ. *Canarium* sp.

Cupuliferæ. *Castanopsis javanica*; and var. *tungurrut*; *Quercus* sp.; *Q. bancana*; *Q. glandulifera*; *Q. junghuhnii*; *Q. teysmannii.*

Euphorbiaceæ. *Antidesma diandrum*; *Adenocrepis javanica*; *Agyneia multiflora*; *Baccaurea* sp.; *Cyclostemon* sp.; *Elateriospermum tokbrai*; *Cluytia oblongifolia*; *Euphorbia* sp.; *Leiocarpus* sp.; *L. arboreus*; *Pierardia dulcis* and other sp.; *Phyllanthus zeylanicus*; *Rottlera dispar*; *Sphenodesme pentandra*; *Trewia* sp.

Gnetaceæ. *Gnetum gnemon* = *β-ovalifolium.*

Myrtaceæ. *Memecylon* sp.

Podocarpaceæ. *Podocarpus chinensis*; *P. nageia.*

Rhizophoraceæ. *Carallia integerrima.*

Rosaceæ. *Rubus sundaicus.*

Rubiaceæ. *Canthium* sp.; *Gardenia schoemannii*; *Nauclea* sp.; *Pavetta angustifolia*; *P. arborea*; *P. barbata*; *P. grandiflora*, vars. *lutea* and *aurantiaca*; *P. littorea*; *P. longiflora*; *P. rosea*; *P. paludosa*; *P. longipes* and other sp.; *Petunga roxburghii*; *Psychotria celastroides*; *Wendlandia* sp.

Styraceæ. *Symplocos* sp.

Ternstrœmiaceæ. *Camellia lanceolata*; *Thea cochinchinensis.*

Tiliaceæ. *Elæocarpus resinosus.*

Urticaceæ. *Gironniera subæqualis* and another sp.

(For localities of species the original must be consulted; see also Journ. Soc. Ch. Ind. **19**, 553.)

The methyl ester of anthranilic acid occurs in néroli oil from the flowers of the bitter orange, *Citrus bigaradia* (Schimmel's Ber. April, 1899; Walbaum, Journ. pr. Ch. [2] **59**, 350; Ber. **32**, 1512; E. and H. Erdmann, Ber. **32**, 1213; **33**, 2061; also Germ. Pat. 5958 of 1898; Hesse and Zeitschel, Ber. **34**, 299; Journ. pr. Ch. **64**, 245; Theulier, Bull. Soc. [3] **25**, 762); also in oil from the peel of the sweet or Portugal orange (Parry, Ch. Drug. **56**, 462; 722; Schimmel's Ber. April, 1900 and Oct. 1900; compare Theulier, Bull. Soc. [3] **25**, 762), in oil of limette

(Parry, *loc. cit.* 993), in oil of *Gardenia* (Parone, Boll. Ch. Farm. **41**, 489; Ch. Centr. 1902, **2**, 703), in Chinese néroli oil from *Citrus triptera* (Umney and Bennett, Pharm. Journ. **69**, 146), and in oil of bergamot leaves (Schimmel's Ber. Oct. 1902; Ch. Centr. 1902, **2**, 1207; Gulli, Ch. Drug. **60**, 995).

The methyl ester of methylanthranilic acid occurs in mandarin oil from the rind of *Citrus madurensis* (Walbaum, Journ. pr. Ch. [2] **62**, 135) and from the leaves (Charabot, Comp. Rend. **135**, 580), and possibly in oil of rue from *Ruta graveolens* (Schimmel's Ber. Oct. 1901; Ch. Centr. 1901, **2**, 1007; see also Houben, Ber. **35**, 3587).

Oil of jasmine from the flowers of *Jasminum grandiflorum* contains methyl anthranilate (Hesse, Ber. **32**, 2616; **33**, 1585; **34**, 291; 2916; Zeit. angew. Ch. 1900, p. 270; see also E. Erdmann, *Ibid.*, and Ber. **34**, 2281, and Germ. Pat. 122290 of 1898: according to Hesse the methyl anthranilate does not pre-exist in the flowers in the free state, Ch. Ind. **25**, 1: compare Erdmann, Ber. **35**, 27).

Methyl cinnamate occurs in the oil from the root, stems, and leaves of *Alpinia malaccensis* (Schimmel's Ber. April, 1899) and in wartara oil, probably from the seeds of *Xanthoxylum alatum* and *X. acanthopodium* (Schimmel's Ber. April, 1900, and May, 1901). Methyl benzoate occurs in oil of cloves (Schimmel's Ber. April, 1902) and in ylang-ylang oil (*Ibid.* Oct. 1901; see also Darzens, Bull. Soc. [3] **27**, 83).

The vegetable alkaloids cocaïne, γ, δ, and ϵ-isatropylcocaïne from the leaves of *Erythroxylon coca*; colchicine from the seeds of meadow saffron, *Colchicum autumnale*; ricinine from the seeds of *Ricinus communis*, and arecoline from the nuts of *Areca catechu* are the methyl esters of complex acid radicles. Methysticin or kawain from kawa-root (*Piper methysticum*) is the methyl ester of methysticinic = 3 : 4-phenediol-1^1-heptylonic acid. Gummigutt resin, the dried sap of *Garcinia morella*, yields a gum which may contain a methyl ester (Tassinari, Gazz. **26**, 249).

Many products obtained from lichens appear to be methyl esters:—

Atranorin or atranoric acid = parmelin from *Lecanora atra*, *L. subfusca*, *L. sordida* and vars. *glaucoma* and *swartzii*, *L. campestris*, *L. thiodes*, *Cladonia rangiferina*, *C. rangiformis*, *Evernia prunastri*, *E. furfuracea*, *E. vulpina*, *Parmelia perlata*, *P. ceratophylla* or *physodes*, *P. tiliacea*, *P. ciliaris* (probably), *P. fuliginosa*, *P. aleurites*, *P. olivetorum*, *P. saxatilis*, var. *phæotropa*, var. *sulcata*, and var. *panniformis*, *P. stellaris*, var., *P. speciosa*, *P. acetabulum*, *P. omphalodes*, *P. perforata*, *P. nilgherrensis*, *P. encausta*, *P. pertusa*, *Parmeliopsis hyperopta*, *Ramalina pollinaria*, *Placodium saxicolum*, var. *compactum*, *P. melanaspis*, *Terecaulon* sp., *Physcia parietina*, *P. cæsia*, *P. pulverulenta* var. β-*pityrea*, *P. endococcina*, *P. tenella*, *P. aipolia*, *Anaptychia ciliaris*, *Sphyridium placophyllum*, *Cetraria fahlunensis*, *C. chlorophylla*, *C. complicata*, *Platysma glaucum*, *Mycoblastus sanguinarius*, *Everniopsis trulla*, *Stereocaulon vesuvianum*, *S. alpinum*, *S. coralloïdes*, *S. salazinum*, *S. incrustatum*, *S. denudatum*, var. *genuinum*, *S. tomentosum*, *S. pileatum*, *S. condensatum*, *S. paschale*, *S. virgatum*, *forma primaria*, *S. ramulosum*, *Hæmatomma coccineum*, and vars. *leiphæmum* and *abortivum*, *Urceolaria scruposa*, var. *vulgaris* (?), *U. cretacea* (?), *Pulveraria* (*Lepraria*) *latebrarum*, *Blastenia arenaria*, var. *teicholytum* = *Callopisma teicholytum*, *Pachnolepia decussata*. (For distribution, synonymy, and nomenclature of these and other lichens see Paternò and Oglialoro, Jahresber. **187**7, 811; Paternò, Gazz. **10**, 157; **12**, 256; Zopf, Ann. **284**, 174; **288**, 38; **295**, 222; 292; **297**, 271; **300**, 322; **306**, 282; **313**, 317; **317**, 120; 139; **321**, 37; **324**, 39; Hesse, Ann. **284**, 157; Ber. **30**, 357; 1983; **31**, 663; Journ. pr. Ch. [2] **57**, 232; 409; **58**, 465; 553; **62**, 321; 430; **63**, 522; **65**, 537: the view that atranorin is a methyl ester is due to Hesse, Journ. pr. Ch. [2] **57**, 232.)

Physcianin = atraric acid = ceratophyllin, a product of decomposition of atranorin, is β-orcinolcarboxylic methyl ester (Hesse, Ber. **30**, 359; 1988;

Journ. pr. Ch. [2] **57**, 287; 422; Ch. Centr. 1898, **1**, 1303: see also under β-orcinol [77]).

Rangiformic acid from *Cladonia rangiformis* (Paternò, Gazz. **12**, 259; Zopf, Ann. **288**, 63; Hesse, Journ. pr. Ch. [2] **57**, 275), and chrysocetraric = pinastric acid from *Cetraria juniperina, C. pinastri, Calycium flavum,* and *Lepraria flava* are methyl esters, the latter of oxypulvic acid (Zopf, Ann. **284**, 107; Hesse, *Ibid.* 176; Journ. pr. Ch. [2] **57**, 307; **62**, 342; **65**, 537; 552, &c.).

Lecidic acid from *Lecidea cinereo-atra* is a methyl ester (Hesse, Journ. pr. Ch. [2] **58**, 508). Caperatic acid from *Parmelia caperata, Mycoblastus sanguinarius*, var. *endorhodea*, and *Platysma glaucum* may be a methyl ester (Hesse, Ber. **30**, 365; Journ. pr. Ch. [2] **57**, 427; Zopf, Ann. **306**, 306; 312).

Parellic acid = psoromic = squamaric and (?) zeoric acid is a methyl ester found in the following lichens:—*Lecanora parella* (*Ochrolechia pallescens*, γ-*parella*), *L. varia, L. sordida*, var. *glaucoma, Placodium crassum*, var. *cæspitosum, P. lagascæ, P. gypsaceum, P. circinatum, Rhizocarpon geographicum*, var. *lecanorina*, and vars. *contiguum* and *geronticum, Stereocaulon coralloïdes* (?), *S. incrustatum, S. vesuvianum, S. denudatum*, var. *genuinum* or *pulvinatum, Catocarpus alpicolus, Roccella intricata, R. tinctoria, Darbishirella gracillima, Cladonia pyxidata, Usnea ceratina, U. barbata* and *florida* (Schunck, Ann. **54**, 274; Spica, Gazz. **12**, 431; Zopf, Ann. **284**, 129; **288**, 59; **295**, 233; 236; 248; 251; 273; 295; **297**, 285; **317**, 110; **321**, 37; Hesse, Journ. pr. Ch. [2] **57**, 272; 274; **58**, 518; **62**, 430; 462; 465; **65**, 537; Ber. **30**, 363; **31**, 663. Hesse was unable to find this acid in *Lecanora parella*, from which it was first said to be obtained by Schunck, and concludes that this last author had some other species in hand; see Ch. Centr. 1902, **2**, 382).

Thamnolic acid from *Thamnolia vermicularis, Cladonia floerkeana*, and *Cladina uncialis* may be a methyl ester (Zopf, Ch. Centr. 1893, **2**, 54; Journ. pr. Ch. [2] **58**, 465; **62**, 441; 446; Ann. **324**, 39).

Vulpic acid is the methyl ester of pulvic acid = diphenylketipic anhydride, and is found in the following lichens:—*Cetraria* (= *Evernia*) *vulpina, C. pinastri, C. tubulosa, C. juniperina, Cyphelium chrysocephalum, Calycium chlorinum, C. chlorellum, C. stenhamari, Parmelia perlata*, American, (Möller and Strecker, Ann. **113**, 56; Bolley, Jahresber. **1864**, 554; Zopf, Ann. **284**, 120; **324**, 39; Hesse, Ann. **284**, 173; Journ. pr. Ch. [2] **57**, 316; **62**, 340; **65**, 537: the later papers of Zopf and Hesse referred to above under atranorin may also be consulted for references to vulpic acid: for references to constitution see also Spiegel, Ann. **219**, 1, &c.).

The methoxy group, $CH_3.O$, is contained in large numbers of natural products belonging to nearly every family of organic compounds. Such compounds are in a sense ethers of methyl alcohol.

Methyl alcohol is among the products of fermentation of glycerol by *Bacillus boocopricus* (Emmerling, Ber. **29**, 2727), of the bacterial fermentation of calcium glycerate (Fitz, Ber. **13**, 1312), and of the fermentation of the juice of the sugar-cane by a special (wild) yeast (Marcano, Comp. Rend. **108**, 955).

Synthetical Processes.

[A.] From carbon, oxygen, and hydrogen, a mixture of carbon monoxide, and the latter giving methyl alcohol among other products under the influence of the electric discharge in an 'ozoniser' (Slosse and Solvay, Bull. Acad. Roy. Belg. **35**, 547; Ch. Centr. 1898, **2**, 421).

[B.] From *methane* [1] by chlorination and the action of aqueous potash on the methyl chloride (Berthelot, Ann. **105**, 241; Ann. Chim. [3] **52**, 101). Methane and air (the mixture containing insufficient oxygen for complete combustion) give methyl alcohol among other products when passed over finely divided copper, asbestos, or coppered pumice (Glock, Germ. Pat. 109014 of 1898; Ch. Centr. 1900, **2**, 304; see also Coquillon in Journ. Soc. Ch. Ind.

19, 684, abst. from Zeit. Spiritusind. **23**, 182).

[C.] From *glycerol* [48], methyl alcohol being among the products formed by the dry distillation of the calcium compound (Destrem, Ann. Chim. [5] **27**, 20; Comp. Rend. **90**, 1213) or by heating the sodium compound above 245° (Fernbach, Bull. Soc. [2] **34**, 146).

[D.] From *formic aldehyde* [91] by heating with strong sodium hydroxide solution (Löw, Ber. **20**, 144) or lime water (*Ibid.* **21**, 271), or by the prolonged action of potassium hydroxide solution at ordinary temperatures (Delépine, Bull. Soc. [3] **17**, 938: see also Comp. Rend. **123**, 120; Bull. Soc. [3] **15**, 997, and Lieben, Monats. **22**, 289).

[E.] From *formic acid* [Vol. II], methyl alcohol being among the products formed by the dry distillation of the calcium salt (Friedel and Silva, Bull. Soc. [2] **19**, 481; Comp. Rend. **76**, 1545; Lieben and Paternò, Ann. **167**, 293; Gazz. **3**, 290).

[F.] From *acetic acid* [Vol. II] by acting with iodine on the silver salt and hydrolysing the methyl acetate formed (Simonini, Monats. **13**, 320; see also Birnbaum, Ann. **152**, 111). Methyl acetate is among the products of electrolysis of potassium acetate in aqueous solution (Kolbe, Ann. **69**, 279), especially in presence of acid (Petersen, Ch. Centr. 1897, **2**, 518). The alcohol is produced by electrolysis from sodium or potassium acetate in presence of sodium perchlorate (Hofer and Moest, Ann. **323**, 284).

[G.] From *methylamine* [Vol. II] by the action of nitrous acid (Linnemann, Zeit. [2] **4**, 284).

[H.] From *trimethylamine* [Vol. II] through methyl chloride by heating the dry hydrochloride (Vincent, Journ. Pharm. [4] **30**, 132). From methyl chloride as above under **B**.

[I.] From *ethyl alcohol* [14] through chloral by chlorination. Methyl chloride is among the products of reduction of chloral by zinc or iron dust in aqueous solution (Cotton, Bull. Soc. [2] **42**, 622).

[J.] From *aldehyde* [92] through chloral (see under methane [1; I]), and then as above under **I**.

[K.] From *malonic acid* [Vol. II] by electrolysis of a solution of the potassium salt (Petersen, Zeit. physik. Ch. **33**, 714).

14. Ethyl Alcohol; Methyl Carbinol; Ethanol.

$CH_3 . CH_2 . OH$

Natural Sources.

Ethyl alcohol is contained in the steam distillate from grass and leaves previously macerated in very dilute sulphuric acid (Lieben, Monats. **19**, 333). According to Berthelot (Comp. Rend. **128**, 1366; see also Devaux, *Ibid.* 1346) alcohol is formed in the tissues of growing plants (wheat and hazel).

Alcohol is formed by the cells of plants from carbohydrates by 'intracellular respiration' when they are insufficiently supplied with oxygen (J. R. Green's 'Soluble Ferments and Fermentation,' p. 327 et seq.; Lafar's 'Technical Mycology,' Vol. II, p. 78; Pasteur, Comp. Rend. **75**, 1054; Lechartier and Bellamy, Comp. Rend. **79**, 949; 1006; **81**, 1129; Brefeld, Landwirth. Jahrbuch, **5**; De Luca, Ann. Sci. Nat. [6], **6**; Müntz, Comp. Rend. **86**, 49; Ann. Chim. [5] **13**, 543; Gerber, Ann. Sci. Nat. [8] **4**: for production of alcohol by intracellular respiration in beet see Strohmer, Zeit. Zucker. **24**, 685; v. Lippmann, Ber. **31**, 677; by peas, Godlewski and Polzeniusz, Bied. Centr. **27**, 135; Journ. Ch. Soc. **74**, II, Abst. 400; **80**, II, Abst. 618; Ch. Centr. 1901, **2**, 595; Mazé, Comp. Rend. **128**, 1608; Ann. Inst. Past. **16**, 195; Takahashi, Bull. Coll. Agric. Tokio, **5**, 243; by deep tissues of woody stems, Devaux, Comp. Rend. **128**, 1346: for general summary see also J. R. Green's address to the Brit. Assoc. Belfast, 1902: for isolation of the enzyme causing anaerobic cellular respiration in higher animals and plants see Stoklasa and Czerny, Ber. **36**, 622).

Ethyl alcohol is formed by yeast as a product of auto-fermentation (Har-

den and Rowland, Trans. Ch. Soc. **79**, 1227).

Ethyl alcohol is contained in the distillate from rose leaves, but this may arise from carbohydrates by fermentation (Eckart, Arch. Pharm. **229**, 355; Ber. **24**, 4205; Schimmel's Ber. Oct. 1892).

Ethyl alcohol is found in the distillation water from the unripe fruit of *Heracleum giganteum* (Gutzeit, Ann. **177**, 344), from the fruit of *H. sphondylium* (Möslinger, Ber. **9**, 998; Ann. **185**, 26) and of *Pastinaca sativa* and *Anthriscus cerefolium* (Gutzeit, *loc. cit.* 372; 382), from the oil of the leaves of *Indigofera galegoïdes* (Schimmel's Ber. April, 1896), and from the oil of storax from *Liquidambar orientalis* (v. Miller, Ann. **188**, 184). The forerunnings from the oil of *Eucalyptus globulus* contain ethyl alcohol (Bouchardat and Oliviero, Bull. Soc. [3] **9**, 429). The alcohol in these cases probably arises partly or wholly from esters by hydrolysis (Gutzeit considered the alcohol to exist in the free state in the fruit of *Heracleum*, Ann. **240**, 243).

The ethyl ester of butyric acid is contained in the oil from the unripe fruit of *Heracleum giganteum* (Gutzeit, Ann. **177**, 344). Ethyl butyrate is contained also in the oil from the fruit of *Heracleum sphondylium* (Möslinger, *loc. cit.*). Ethyl acetate is contained in the flowers of *Magnolia fuscata* (Göppert, Ann. **111**, 127); ethyl valerate probably occurs in Algerian oil of rue (Power and Lees, Trans. Ch. Soc. **81**, 1589); ethyl cinnamate in liquid storax from *Liquidambar orientalis* (v. Miller, *loc. cit.*; Tschirch and Van Itallie, Arch. Pharm. **239**, 506) and in the oil from *Kaempferia galanga* (Van Romburgh, Proc. K. Akad. Wetensch. Amsterdam, **4**, 618; Journ. Ch. Soc. **82**, I, Abst. 633).

Ethyl esters of hexoic, octoic, decoic, lauric, palmitic, and oleic acids are present in the juice from the fruit of the saw palmetto, *Sabal serrulata* (Sherman and Briggs, Pharm. Arch. **2**, 101). The oil from the root of *Kaempferia galanga* contains the ethyl ester of p-methoxycinnamic acid (Van Romburgh, Schimmel's Ber. Oct. 1900; Journ. Ch. Soc. **78**, I, Abst. 677).

Rhizocarpic acid, a product from certain lichens, is an ethyl ester of a complex acid (Hesse, Journ. pr. Ch. [2] **58**, 510). This acid has been obtained from the following species:— *Rhizocarpon geographicum* and vars. *contiguum*, *lecanorinum*, and *geronticum*, *R. viridi-atrum*, *Pleopsidium chlorophanum*, *Acarospora chlorophana*, *Raphiospora flavovirescens*, *Biatora lucida*, *Catocarpus alpicolus* = *Catocarpon chinophilum*, *Acolium tigillare*, *Gasparinia elegans*, *G. medians* (Zopf, Ann. **284**, 114; **295**, 275; **313**, 334; **321**, 37; Hesse, Ber. **30**, 362; **31**, 663; Journ. pr. Ch. [2] **57**, 446; **58**, 511; **62**, 343; see also Salkowski, Ann. **319**, 391).

An ethyl ester of vulpic acid (see under methyl alcohol [13]) = callopismic acid occurs in the lichens *Physcia medians*, *Callopisma vitellinum*, *Candelaria concolor*, and *Gyalolechia aurella* (Zopf, Ann. **284**, 123; **295**, 239; **297**, 290).

Hæmatommic acid obtained from the lichens *Hæmatomma coccineum*, *Physcia cæsia*, *Stereocaulon ramulosum*, and *Parmelia perlata*, is an ethyl ester of atranorin (Zopf, Ann. **288**, 39; 44; **295**, 280; 297; Hesse, Journ. pr. Ch. [2] **57**, 292).

Ethyl alcohol is a product of fermentation of various sugars by species of yeasts, *Saccharomyces*. The following species or forms are now recognized as alcoholic ferments:—

Saccharomyces cerevisiæ I, Hansen; *S. pastorianus* I, II, and III, Hansen; *S. logos*, Van Laer; *S. ellipsoideus* I and II, Hansen; *S. ilicis*, Grönlund; *S. aquifolii*, Grönlund; *S. pyriformis*, Marshall Ward; *S. vordermanni*, Went and Geerligs; *S. marxianus*, Hansen; *S. exiguus*, Reess and Hansen; *S. jörgensenii*, Lasché; *S. ludwigii*, Hansen; *S. octosporus*, Beyerinck; *S. pombé*, Saare and Zeidler; *S. mellacei*, Holn and Jörgensen; *S. acidi lactici*, Grotenfelt; *S. fragilis*, Jörgensen; *S. anomalus*, Hansen; *S. conglomeratus*, Reess (doubtful ferment); *S. apiculatus*,

Reess. (See for further particulars Jörgensen's 'Mikroorganismen der Gärungsindustrie,' chap. v; Klöcker's 'Gärungsorganismen, &c.'; and Lafar's 'Technical Mycology.' Vol. II.) *Saccharomyces saturnus*, Klöcker, from soil in the Himalayas, can ferment wort (Klöcker, Abst. in Journ. Fed. Inst. **8**, 523). *S. awamori*, Inui, a yeast which is concerned in the production of the Japanese drink 'awamori,' is an alcoholic ferment (Inui, Journ. Imp. Coll. Sci. Tokio, 1901, **15**; Abst. in Journ. Fed. Inst. **8**, 529).

Certain ethyl esters, such as ethyl acetate, propionate, butyrate, valerate, hexoate, heptoate, octoate, ennoate, palmitate, and oleate, are found in fusel oils and in whisky, and may be secondary products of alcoholic fermentations by yeasts and therefore of biochemical origin (Perrot, Comp. Rend. **45**, 309; Ann. **105**, 64; Rabuteau, Comp. Rend. **87**, 501; Ordonneau, *Ibid.* **102**, 217; Bell as quoted by Allen, Journ. Fed. Inst. **3**, 36; Barker, Ann. Bot. 1900, 215).

Synthetical carbohydrates, such as 'glycerose,' obtained by the oxidation of glycerol and now known to be a mixture of glyceraldehyde and dihydroxyacetone [151] (Van Deen, Jahresber. **1863**, 501; Stone, Am. Ch. Journ. **15**, 656; Fischer, Ber. **20**, 1088; Fischer and Tafel, *Ibid.* 3384; **21**, 2634; Grimaux, Comp. Rend. **104**, 1276; Bull. Soc. [2] **45**, 481; **49**, 251), dextrose [154], lævulose [155], d-mannose [156], and mannononose (Fischer and Passmore, Ber. **23**, 2237) give alcohol on fermentation by yeasts. According to Piloty (Ber. **30**, 3166) and Bertrand (Comp. Rend. **126**, 842; 984; Bull. Soc. [3] **19**, 502) dihydroxyacetone is not fermentable. According to Emmerling (Ber. **32**, 542) neither dihydroxyacetone nor glyceraldehyde are fermentable when pure.

The fermentability of sugars, natural and synthetical, by yeasts is associated with the number of the carbon atoms in the sugar, the configuration of the atoms in the molecule, and the nature of the yeast. According to Fischer (Ber. **23**, 2114) the fermentable sugars contain multiples of three carbon atoms. As regards configuration, while the three hexoses and the nonnose mentioned above are with d-galactose fermentable, the following sugars are unfermentable:—d-gulose and l-gulose (Fischer, Ber. **24**, 521; Fischer and Stahel, *Ibid.* 528; 2144); d-talose (Fischer, *loc. cit.* 3622); sorbose (Pelouze, Comp. Rend. **34**, 377; Ann. Chim. [3] **35**, 222); tagatose =l-sorbose (Lobry de Bruyn and Van Ekenstein, Rec. Tr. Ch. **16**, 257; 262; **19**, 1); glutose (*Ibid.* **16**, 257 and 274); the hexoses of the l-series, such as l-fructose (Fischer, Ber. **23**, 370), l-mannose (Fischer and Thierfelder, Ber. **27**, 2031), l-xylose (Koch, Ber. **20**, ref. 145; Thomsen, Journ. pr. Ch. **19**, 146; Stone, Ber. **23**, 3791), the pentoses, rhamnose, the synthetical heptoses and octoses (Fischer, Ber. **23**, 930; Fischer and Piloty, *Ibid.* 3102; 3827; Fischer and Morrell, Ber. **27**, 382; Fischer and Passmore, Ber. **23**, 2226; Fischer, Ann. **270**, 64; **288**, 139; Smith, Ann. **272**, 182); glucononose (Fischer, Ann. **270**, 104).

[For general summary see Fischer and Thierfelder, Ber. **27**, 2031; Fischer, Zeit. physiol. Ch. **26**, 60: for resolution of i-glucose, i-mannose, i-fructose, and i-galactose by partial fermentation with brewer's yeast see Fischer, Ber. **23**, 382; 2620; **25**, 1259.

The fermentability of twenty-one sugars and carbohydrates by various yeasts and yeast-like fungi, without reference to products, has been investigated on a microscopic scale by Lindner, Woch. Brau. **17**, 713; 733; 746; 762; Ch. Centr. 1901, **1**, 57; 404; Journ. Fed. Inst. **7**, 224: for experiments on the relative fermentability of dextrose and lævulose by Nürnberg, &c., sedimentary and other yeasts see Knecht, Centr. Bakter, II, **7**, 161; 215.]

Mannecotetrose, $C_{24}H_{42}O_{21}$, a sugar contained in 'manna,' is fermentable by yeast (Tanret. Comp. Rend. **134**, 1586; Bull. Soc. [3] **27**, 947). Three synthetical disaccharides, glucosidogalactose, galactosidoglucose (? melibiose), and galactosidogalactose, are unattacked by surface yeast, and only

the two first are fermented by sedimentary yeast (Fischer and E. F. Armstrong, Ber. **35**, 3144).

The various species of *Saccharomyces* behave differently towards different sugars, their behaviour having relationship to the enzymes contained in the yeast cell:—

S. cerevisiæ, *S. pastorianus*, and *S. ellipsoideus* ferment saccharose, maltose, and the products of their inversion, i. e. dextrose and lævulose, but not lactose; *S. ilicis* and *S. aquifolii* ferment saccharose, maltose, and dextrose; *S. pyriformis* and *S. vordermanni* ferment saccharose; *S. exiguus*, *S. marxianus*, and *S. jörgensenii* ferment saccharose and dextrose, but not maltose; *S. ludwigii* ferments dextrose and saccharose, but neither maltose nor lactose; *S. pombé* ferments dextrose and saccharose; *S. acidi lactici* and *S. fragilis* ferment lactose (summarised from Jörgensen's 'Mikroorganismen, &c.' chap. v). *S. membranæfaciens* is inactive towards most sugars (Fischer and Thierfelder, Ber. **27**, 2031). So also is *S. hansenii*. *S. hyalosporus*, *S. farinosus*, and *S. anomalus*, var. *belgicus* (all Lindner's), cannot ferment maltose, dextrose, or saccharose ('Die Gärungsorganismen, &c.,' Klöcker, p. 203). *S. ludwigii* is incapable of fermenting galactose, and may therefore be used for separating this sugar from dextrose (Thomas, Comp. Rend. **134**, 610). *S. apiculatus* ferments dextrose and mannose (Cremer, Zeit. Biol. **29**, 525), but not saccharose, lactose, maltose, or galactose (Voit, Zeit. Biol. **29**, 149; Hansen and Amthor, Zeit. physiol. Ch. **12**, 563).

S. (= *Schizosaccharomyces*) *octosporus* ferments dextrose and maltose, but not saccharose (Beyerinck, Centr. Bakter. **12**, 49; Fischer and Lindner, Ber. **28**, 984; 3034). *S. productivus*, *S. membranæfaciens*, and *S. pombé* are incapable of fermenting d-galactose under ordinary conditions, but this sugar is fermentable under suitable conditions by *S. cerevisiæ*, by *S. pastorianus* I, II, III, by *S. ellipsoideus* I, II, by *S. marxianus*, and (slowly) by the mould *Monilia candida* (Bau, Bied. Centr. **26**, 213). The yeasts appear to be capable of gradual adaptation or 'acclimatisation' towards this sugar (Dubourg, Comp. Rend. **128**, 440; Dienert, *Ibid.* 569; 617; Ann. Inst. Past. **14**, 139: *S. ludwigii* does not seem to be amenable to this treatment: for adaptation of yeasts to saccharose see also Dubourg, *loc. cit.*: for variation in chemical activity of yeasts produced by cultivation see Hansen, Zeit. ges. Brau. **25**, 41; 57; 70; 82; Journ. Fed. Inst. **7**, 299).

S. anomalus, vars. I, II, III, and IV, has been investigated by Steuber (Zeit. ges. Brau. **23**, 3; 17; 33; Journ. Fed. Inst. **6**, 123). I ferments saccharose, glucose, and fructose, but not maltose, lactose, or galactose; II ferments saccharose slowly, but not fructose, glucose, maltose, lactose, or galactose; III and IV produce a trace of alcohol from fructose, but do not ferment any of the other sugars.

According to Barker (Ann. Bot. 1900, 215) *S. anomalus* of Hansen can ferment glucose, fructose, and saccharose, but not maltose. This yeast also produces ethyl and amyl acetates. *S. bailii* of Lindner can ferment dextrose and 'invert' sugar; *S. mali duclauxi* of Kayser (found in cider) can ferment invert sugar, but neither maltose nor saccharose ('Die Gärungsorganismen, &c.,' Klöcker, p. 215). *Saccharomyces opuntiæ*, which ferments the must of Indian figs, can ferment dextrose and lævulose, but not lactose, raffinose, galactose, mannitol, or dulcitol (Ulpiani and Sarcoli, Gazz. **31**, 395). From a mixture of *S. pastorianus* II and *S. opuntiæ* sodium fluoride eliminates the latter (*Ibid.* Atti Real. Accad. [5] **11**, 173).

Milk sugar is fermentable by three yeasts from Armenian 'mazun,' by Weigmann's yeast, *Sachsia suaveolens*, and, possibly, by *Monilia variabilis* (Lindner, Ch. Centr. 1901, **1**, 56; Woch. Brau. **17**, 713). The top fermentation yeast, *S. pastorianus arborescens*, can ferment dextrose and lævulose, but not galactose nor di- and trisaccharides (Van Laer, Bull. Assoc. Belg. **16**, 177; Journ. Fed. Inst. **8**, 763).

S. (*Schizosaccharomyces*) *pombé* and *octosporus* and *S. logos* are said to be

dextrin-ferments (Jörgensen, *loc. cit.* p. 216, note; see also Marshall Ward, Journ. Fed. Inst. **4**, 355). *S. pombé*, *S. octosporus*, and *S. mellacei* are included by Lindner (*loc. cit.*) among dextrin ferments.

The pentoses from the straw of cereals which give furfural on distillation with dilute acid are said to yield alcohol on fermentation by yeast (Cross, Bevan, and Smith, Trans. Ch. Soc. **71**, 1003; Bailey and Ford, Germ. Pat. 97238 of 1896; Ch. Centr. 1898, **2**, 590). Pentoses generally, such as xylose and arabinose, are not fermentable by yeast (Stone, Ber. **23**, 3796; Stone and Tollens, Ann. **249**, 267; Tollens, Journ. Fed. Inst. **4**, 447; Schöne and Tollens, Journ. Ch. Soc. **80**, I, 367). The pentosans from jute and brewer's grains give alcohol on fermentation by pure-culture yeast from lager beer yeast (*Ibid* : also Journ. Fed. Inst. **7**, 472).

The transformation of sugar into alcohol by yeast has been found by Buchner to be brought about by the action of an enzyme-like nitrogenous compound (zymase) formed by the living cell, but capable of acting on sugar when removed from the cell. The literature relating to this discovery is given below: Buchner, Ber. **30**, 117; 1110; Buchner and Rapp, *Ibid.* 2668; Stavenhagen, *Ibid.* 2422; 2963; Neumeister, *Ibid.*; v. Manasseïn, *Ibid.* 3061; Green, Ann. Bot. **11**, 555; **12**, 491; Will, Ch. Centr. 1898, **1**, 69; Delbrück, *Ibid.* 70; Hahn, Ber. **31**, 200; Geret and Hahn, *Ibid.* 202; Buchner and Rapp, *Ibid.* 209; Schunck, *Ibid.* 309; Buchner and Rapp, *Ibid.* 1531; Will, Ch. Centr. 1898, **2**, 439; Lange, *Ibid.* 548; Abeles, Ber. **31**, 2261; Geret and Hahn, *Ibid.* 2335; Wroblewski, *Ibid.* 3218; Centr. Physiol. **12**, 697; Martin and Chapman, Proc. Physiol. Soc. June, 1898; Buchner and Rapp, Ber. **32**, 127; 2086; Wroblewski, Centr. Physiol. **13**, 284; Cremer, Ber. **32**, 2062; Albert, *Ibid.* 2372; Albert and Buchner, Ber. **33**, 266; 971; Ahrens, Zeit. angew. Ch. 1900, 483; Macfayden, Morris, and Rowland, Ber. **33**, 2764; Hahn and Geret, Ch. Centr. 1900, **2**, 641; Buchner, Ber. **33**, 3307; 3311; Albert, *Ibid.* 3775; Prior and Schulze, Zeit. angew. Ch. **14**, 208; Buchner and Rapp, Ber. **34**, 1523; Wroblewski, Bull. Acad. Sci. Cracow, 1901, 94; Journ. pr. Ch. [2] **64**, 1; R. and W. Albert, Centr. Bakter. II, **7**, 737; Buchner and Spitta, Ber. **35**, 1703; Buchner and Rapp, *Ibid.* 2376: for general summary see 'Die Zymasegärung,' by E. and H. Buchner and Martin Hahn, Munich and Berlin, 1903.

Not only the true yeasts but other related micro-fungi, and certain moulds and bacteria, are capable of producing alcohol from sugars as well as from more complex carbohydrates :—

Hansen has investigated certain species of *Torula*. Sp. III can ferment hexose, but not saccharose; Sp. IV and VI can transform saccharose, but not maltose; Sp. VII ferments dextrose, but not saccharose or maltose. Sp. I, II, and V appear to be incapable of producing alcoholic fermentation. *T. novæ carlsbergiæ* of Grönlund can invert and ferment saccharose, maltose, and dextrose. The red pigment-forming *Torula* of Kramer inverts and ferments saccharose and ferments maltose and dextrose, but not lactose (summarised from Jörgensen's 'Mikroorganismen,' &c. ch. v).

A *Torula*-like species discovered in milk by Duclaux (Ann. Inst. Past. **1**, 573) ferments lactose, which is not attacked by ordinary yeasts. '*Saccharomyces*' *lactis* of Adametz (Centr. Bakter. **5**, 1889), the non-*Saccharomyces* of Kayser (Ann. Inst. Past. **8**, 737), and Beyerinck's '*Saccharomyces*' *kephir* and *tyrocola* (Centr. Bakter. II, **6**, 44) are said to produce alcohol from lactose. *Lactomyces inflans caseigrana* from cheese (Bochiccio, Centr. Bakter. &c. **15**, 546) can ferment lactose in bouillon.

Certain species of *Mycoderma* formerly confused with *M. cerevisiæ* of Hansen produce alcohol in wort (Lasché, as quoted by Jörgensen, *loc. cit.* 4th ed. p. 263). Species of *Mycoderma* can produce small quantities of alcohol from dextrose under appropriate conditions (Beyerinck: see paper by Van Laer, Journ. Fed. Inst. **7**, 352).

The moulds *Mucor racemosus*, *M. stolonifer*, *M. circinelloïdes*, *M. spinosus*, *M. erectus*, *Exoascus alnitorquus* (Sadebeck), *Penicillium glaucum*, and *Rhizopus nigricans* are generally included among alcohol-producing fungi (Reess, 'Botan. Untersuch. über die Alkoholgärungspilze,' 1870; also J. R. Green's 'Fermentation,' p. 325 et seq.). *Mucor spinosus* and *M. circinelloïdes* ferment glucose (Gayon, Ann. Chim. [5] **14**, 258; Comp. Rend. **86**, 52; Bull. Soc. [2] **31**, 139; for earlier work on alcoholic fermentation by *Mucor racemosus* see Fitz, Ber. **6**, 48; **8**, 1540; **9**, 1352; 1354; Brefeld, Ber. **7**, 282). *Mucor mucedo*, *M. erectus*, *M. spinosus*, *M. alternans*, *M. circinelloïdes*, and *Rhizopus nigricans* cannot invert and ferment saccharose; with the exception of the latter they can all produce alcohol from maltose and they all ferment dextrose and lævulose. *Mucor alternans* ferments trehalose, but not raffinose. These moulds cannot ferment galactose directly, but only after inversion (Lafar's 'Technical Mycology,' II, 81). *M. racemosus* is the only one of these species of *Mucor* that can invert and ferment saccharose (for quantitative results see Emmerling, Ber. **30**, 454); the others ferment not only glucose, but 'invert' sugar and maltose. *M. erectus* can produce alcohol from dextrin (Hansen as quoted by Jörgensen, 'Mikroorganismen,' &c. 126). Chinese yeast contains *Mucor* (*Amylomyces*) *rouxii* (Calmette, Ann. Inst. Past. **6**, 604), and this produces alcohol in culture solutions of dextrose, d-fructose, galactose, trehalose, d-mannose, maltose, dextrin, and α-methylglucoside, but not from saccharose, lactose, xylose, arabinose, rhamnose, tagatose, raffinose, melibiose, β-methylglucoside, or inulin (Sitnikoff and Rommel, quoted by Lafar, 'Technical Mycology,' II, 89: see also ref. given below and Wehmer, Centr. Bakter. II, **6**, 353; for industrial use see Boidin and Rolants, Abst. in Journ. Fed. Inst. **3**, 445; Collette and Boidin, *Ibid.* **4**, 432; 675; **5**, 128: for behaviour of two other species of *Amylomyces* towards various carbohydrates see Sitnikoff and Rommel, Journ. Fed. Inst. **7**, 112, from Woch. Brau. **17**, 621: for technical production of alcohol by joint action of *Mucedinæ* and yeast see Lafar's 'Technical Mycology,' II, 94; also Barbet, Germ. Pat. 128173 of 1899; Ch. Centr. 1902, **1**, 444).

Chinese yeast from Cambodia contains *Mucor cambodia*, which produces alcohol in saccharine solutions (Chrzaszcz, Centr. Bakter. II, **7**, 326).

The 'koji' ferment used for preparing rice wine ('saké') in China and Japan (see also under dextrose [**154**]) can produce alcohols from sugars (not lactose). The ferment is said to contain *Eurotium* (*Aspergillus*) *oryzæ* (Liebscher, Bied. Centr. 1881, 707) yeasts, a red yeast, *Penicillium glaucum*, *Mucor stolonifer*, a *Torula*, and a white mould-fungus: the latter ferments saccharose, raffinose, dextrose, maltose, and d-fructose (all slightly), but not trehalose, rhamnose, lactose, or melezitose. The yeast (saké-yeast) ferments saccharose, maltose, d-mannose, dextrose, d-fructose, and methylglucoside (all readily); trehalose and d-galactose (less readily); and not lactose or rhamnose (Kozai, Centr. Bakter. II, **6**, 385 et seq.: see also Kellner, Mori, and Nagaoka, Zeit. physiol. Ch. **14**, 297).

The ferment used in Java for producing 'raggi' saccharifies starch by the mycelium of *Chlamydomucor oryzæ*, and alcohol is produced by the fermentation of the sugars by *Monilia javanica* and *Saccharomyces vordermanni*, the other constituents of the ferment (Went and Prinsen Geerligs, Bot. Zeit. 1895, 143; Sorel, Rev. Ch. Ind. **8**, 13; Journ. Fed. Inst. **3**, 443). The *Monilia* can ferment dextrose, lævulose, maltose, saccharose, and raffinose, but not lactose. The Javan product contains also *Mucor javanicus*, which produces alcohol from cane sugar, glucose, and lactose (Wehmer, Centr. Bakter. II, **6**, 610; Journ. Fed. Inst. **7**, 113). The *Chlamydomucor* is accompanied by a mould, *Mucor dubius* (? n. sp.; *Ibid.* Centr. Bakter. II, **7**, 313; Journ. Fed. Inst. **7**, 493).

A *Monilia* resembling *M. variabilis*, Lindner, contained among the organisms concerned in the production of the Japanese 'awamori' can produce slight fermentation in wort (Inui, Journ. Imp.

Coll. Sci. Tokio, 1901, **15**; Abst. in Journ. Fed. Inst. **8**, 529).

Monilia candida ferments dextrose, saccharose, and maltose (Hansen, Ber. Deutsch. bot. Gesell. 1884; Fischer and Lindner, Ber. **28**, 3037; Fischer, Zeit. physiol. Ch. **26**, 60 et seq.). The milk-sugar ferment *Oïdium lactis* of Fresenius can produce alcohol from lactose, glucose, and (less readily) from saccharose and maltose (Lang and Freudenreich, quoted by Jörgensen, *loc. cit.* 131; see also Jensen, Centr. Bakter. II, **8**, 248 et seq.). *Oïdium* (*Monilia*) *albicans* produces alcoholic fermentation in lævulose, glucose, and maltose, but not in lactose (Linossier and Roux, Comp. Rend. **110**, 868).

The mould *Eurotiopsis gayoni* can produce alcohol from hexoses when the mycelium is completely immersed in the solution (Laborde, Ann. Inst. Past. **11**, 1; Duclaux, Abst. in Journ. Fed. Inst. **6**, 412). According to Mazé (Comp. Rend. **128**, 1608; **134**, 191) alcohol is the first product of the assimilation of the sugar by the mould. This mould also appears to be capable of producing alcohol from lactic acid and glycerol (*Ibid.* **134**, 240; see also Ann. Inst. Past. **16**, 433). The mould *Monilia sitophila*, used in W. Java for decomposing arachis seed-cake, and found on putrefying bread, flour, &c., hydrolyses and finally ferments many carbohydrates with the production of alcohol and ethyl esters (Went, Journ. Ch. Soc. **80**, II, Abst. 412; Centr. Bakter. II, **7**, 544; 591).

Starch, dextrin, and saccharose give rise to the formation of more or less alcohol by the action of *Aspergillus oryzæ*, *Mucor alternans* of Gayon, and *Mucor* (*Amylomyces*) *rouxii* in appropriate nutrient solutions (Sanguinetti, Ann. Inst. Past. **11**, 264).

Raffinose or melitriose and melibiose can yield alcohol under the influence of appropriate ferments. The first of these sugars is only completely fermentable by energetic sedimentary beer yeasts, and is only incompletely fermented by surface yeasts (Berthelot, Comp. Rend. **109**, 548; Ann. Chim. [3] **46**, 66; [6] **19**, 500; Bull. Soc. [3] **2**, 655; Scheibler and Mittelmeier, Ber. **22**, 3118; Loiseau, Comp. Rend. **109**, 614; Bau, Ch. Zeit. **18**, 1794; Woch. Brau. **15**, 389; Andrlík, Ch. Centr. 1898, **2**, 1273: for references to species which can resolve raffinose see under lævulose [**155**]). All the races of wine yeast examined by Schukoff (Woch. Brau. **16**, 195) can only partially ferment raffinose.

Pure melibiose is neither hydrolysed nor fermented by surface yeast, but is resolved by sedimentary yeast into d-glucose and d-galactose and finally completely fermented (Bau, Woch. Brau. **16**, 397; Ch. Zeit. **21**, 186; **26**, 69; see also Gillot, Bull. Assoc. Belg. **16**, 240; Ch. Centr. 1902, **2**, 811).

Yeasts that have been 'acclimatised' by cultivation in a nitrogenous medium containing glucose and saccharose can, according to Dubourg (Comp. Rend. **128**, 440), ferment all sugars excepting lactose. The sugars experimented with comprised galactose, raffinose, and trehalose. *Mucor alternans* submitted to this treatment can ferment trehalose, d-glucose, d-maltose, d-fructose, and d-galactose, but not lactose, saccharose, or raffinose (Dubourg). These results are contested by Klöcker (Centr. Bakter. II, **6**, 241), who was unable to 'adapt' *S. marxianus* or *S. apiculatus* by the method of Dubourg. *S. apiculatus* could not be brought to invert saccharose nor *S. marxianus* to ferment maltose (see also Hansen, in Zeit. ges. Brau. **25**, as quoted above).

Trehalose is slowly fermented by surface and sedimentary yeasts of the Frohberg and Saaz types, by *S. ellipsoideus* II, *S. pastorianus* I, II, and III, by *S. logos*, and by *Monilia candida*; a milk-sugar yeast had a slight effect, and *S. pombé* and *S. apiculatus* were without action (Bau, Woch. Brau. **16**, 305; see also Kalanthar, Zeit. physiol. Ch. **26**, 88). The alcohol produced from artichoke tuber with yeast (Lévy, Comp. Rend. **116**, 1381) is probably due to the fermentation of lævulose resulting from the resolution of inulin (see under lævulose [**155**]).

Fermentation with the production of

alcohol from sugars is brought about in some cases by symbiotic associations of yeasts and bacteria. The 'képhir' ferment used for preparing an effervescent beverage from milk is sometimes considered to be of this nature. The bacterium of képhir grains is *Dispora* (*Bacillus*) *caucasica* of Kern. There are also present two species of *Streptococcus* and a yeast. The latter can produce feeble fermentation in wort, but cannot attack lactose (Kern, Bot. Zeit. 1882; Biol. Centr. 1882; Freudenreich, Centr. Bakter. II, **3**, 47; 87; 135). According to Jörgensen ('Mikroorganismen,' p. 92) a true *Saccharomyces* is present in Russian képhir grains which is capable of fermenting lactose independently of other organisms. Among the yeasts recently identified in képhir grains are *S. cartilaginosus* of Lindner and *S. fragilis* of Jörgensen.

Among the organisms which ferment milk and convert it into the alcoholic beverage 'koumiss' is a *Bacillus* which produces alcohol from milk-sugar (Schipin, Centr. Bakter. II, **6**, 775). Ethyl alcohol is among the products of fermentation of milk-sugar by lactic acid bacteria (Barthel, Centr. Bakter. II, **6**, 417). The species experimented with was possibly *Bacterium lactis acidi* of Leichmann (*Ibid.* II, **5**, 344).

The 'ginger-beer plant' consists of a symbiotic association of *Saccharomyces pyriformis* and *Bacterium vermiforme* (Marshall Ward, Phil. Trans. 1892, **183**, B, 125). A similar ferment found as a parasitic growth on the sugar-cane (Madagascar) consists of a yeast and *Bacterium*, and can ferment saccharose, maltose, d-glucose, and d-fructose (Marshall Ward and Green, Proc. Roy. Soc. **65**, 65). The industrial production of alcohol from starch by *Amylomyces rouxii* of Calmette (see above for references to process of Boidin and Collette) is regarded as a case of symbiotic association between the *Amylomyces* and the yeast ('gentil') which is subsequently added (Marbach, Abst. in Journ. Fed. Inst. **5**, 479).

Glycerol gives alcohol among the products of its fermentation by various bacteria in appropriate nutrient solutions in presence of chalk (Fitz, Ber. **9**, 1348; **10**, 266; **11**, 42; 1892; **12**, 481; **13**, 1311; **15**, 873; Morin, Bull. Soc. [2] **48**, 803). The glycerol fermenting organism obtained from hay infusion by Fitz is *Bacillus fitzianus* of Zopf, and the butyl alcohol producing organism obtained from cow-dung by this author is *B. butylicus* (see Emmerling, Ber. **30**, 451). These organisms, or bacteria associated with them, are said to give small quantities or traces of alcohol among the products of their fermentation of erythritol, mannitol, starch, dextrin, inulin, lactose, dulcitol, calcium citrate and malate (during propionic fermentation), calcium lactate (propionic fermentation), calcium glycerate, calcium tartrate, gelatine, and albumin (Fitz; erythritol, Ber. **11**, 45; 1890; **12**, 475; mannitol, **10**, 280; **11**, 1895; **15**, 875; **16**, 845; starch, **10**, 282; **11**, 44; dextrin, **10**, 282; inulin, **11**, 45; lactose, *Ibid.*; dulcitol, *Ibid.*; Ca-citrate, **11**, 1895; Ca-malate, **11**, 1896; **12**, 481; Ca-lactate, **11**, 1898; **12**, 475; **13**, 1309; Ca-glycerate, **12**, 474; **13**, 1312; **16**, 844; Ca-tartrate, **12**, 475; gelatine and albumin, **12**, 480). Bacteria from blue pus produce alcohol among other products from glycerol (Fitz, Ber. **11**, 1893). Glycerol gives alcohol among the products of its fermentation by *Pneumococcus* (Grimbert) and by *Bacillus acidi lævolactici* (Schardinger: see Emmerling's 'Die Zersetzung, &c.' p. 61).

The *Granulobacter saccharobutyricum* obtained by Beyerinck from grain (Centr. Bakter. **15**, 171) produces alcohol from glycerol (Emmerling, *loc. cit.* 453). Glycerol gives alcohol when fermented by the *Bacillus ethaceticus* of Frankland and Fox (Proc. Roy. Soc. **46**, 345). The latter produces alcohol also from mannitol, arabinose, glucose, lactose, saccharose, and calcium glycerate (Frankland and Fox, *loc. cit.*; Frankland and Lumsden, Trans. Ch. Soc. **61**, 432; F. and MacGregor, *Ibid.* 737; F. and Frew, *Ibid.* **59**, 81).

The *Bacillus butylicus* of Fitz produces alcohol (trace) also from saccharose (Ber. **15**, 876) and from glucose (Emmerling, Ber. **30**, 451). *Bacillus*

ethacetosuccinicus produces alcohol from mannitol and dulcitol (Frankland and Frew, Trans. Ch. Soc. **61**, 254).

The *Pneumococcus* of Friedländer produces small quantities of alcohol from arabinose, glucose, galactose, lactose, saccharose, maltose, and raffinose (traces), mannitol, dextrin, and creatinine (Brieger, Zeit. physiol. Ch. **8**, 306; **9**, 1; Grimbert, Comp. Rend. **121**, 698; Bull. Soc. [3] **15**, 52; 87; Ann. Inst. Past. **9**, 840; Frankland, Stanley, and Frew, Trans. Ch. Soc. **59**, 253), and from xylose (Grimbert; Bull. Soc. [3] **15**, 340).

The *Bacillus* of malignant œdema produces alcohol from lactose, saccharose, and calcium lactate in an atmosphere of hydrogen (Kerry and Fränkel, Monats. **12**, 350). Pasteur's 'butyric ferment' produces a trace of alcohol from calcium lactate (Fitz, Ber. **13**, 1310). *Bacillus boocopricus* from cowdung produces alcohol from glucose and lactose (Emmerling, Ber. **29**, 2726).

Alcohol is among the final products of (lactic) fermentation of lactose by *Bacillus acidi lactici* (Haacke, Arch. Hyg. **42**, 16; Ch. Centr. 1902, **1**, 1122; by *Bac. ac. l-lactici*, Schardinger, as quoted by Emmerling in the work referred to below) and by *Staphylococcus pyogenes aureus* (Lübbert: Emmerling, 'Die Zersetzung stickstofffreier organischer Substanzen durch Bakterien,' p. 110). *Tyrothrix claviformis* and *Actinobakter polymorphus* can produce alcohol from lactose (Duclaux, Ann. Inst. Agron. 4me Année, 1879–80, p. 103; also Gayon and Dubourg, Ann. Inst. Past. **15**, 567). The 'mannitol ferment' of Gayon and Dubourg (*loc. cit.* 527) can produce alcohol from most sugars excepting lævulose (which it converts into mannitol [51]). Alcohol is among the products of fermentation of glucose by Dunbar's and other *Vibrios* (Gosio; quoted by Emmerling, *loc. cit.* pp. 47 and 56), and of maltose by *Bacillus fervitosus* (Adametz; quoted by Emmerling, *loc. cit.* p. 59).

The *Bacillus amylozymicus* of Perdrix (Ann. Inst. Past. **5**, 287) hydrolyses and finally ferments starch with the formation of alcohol among other products. *Saccharomyces* associate themselves symbiotically with the *Bacillus* and increase the production of alcohol to 90 per cent. Alcohol is among the products of fermentation of starch by *Bacillus suaveolens* (Sclavo and Gosio, Bied. Centr. **20**, 419; Journ. Ch. Soc. **60**, Abst. 1284). Some of the organisms of putrefying cheese produce traces of alcohol from glycerol, mannitol, and sorbose in presence of chalk (Berthelot, Jahresber. **1857**, 509; Ann. Chim. [3] **50**, 350).

A l-lactic organism obtained from ripe pears can produce alcohol from mannitol and dextrose (Tate, Trans. Ch. Soc. **63**, 1263). Alcohol is formed in traces during the fermentation of dextrose and lactose, and in considerable quantity during the fermentation of mannitol by *Bacillus lactis aërogenes* (Emmerling, Ber. **33**, 2477). According to Grimbert and Legros (Comp. Rend. **130**, 1425) this *Bacillus* is identical with the *Pneumobacillus* of Friedländer, and can ferment glucose, saccharose, glycerol, mannitol, and dextrin, but not dulcitol.

Alcohol is among the products of fermentation of mucic acid (Béchamp, Bull. Soc. [3] **3**, 770). *Staphylococcus pyogenes aureus* and *Bacillus coli communis* produce alcohol (traces) from dextrose in nutrient solution in presence of calcium carbonate (Hugounenq and Doyon, Ann. Chim. [7] **15**, 145; also Lübbert as quoted by Emmerling, 'Die Zersetzung,' &c. p. 49).

Bacillus coli communis, *B. typhosus*, and allied species produce alcohol among the products of fermentation in nutrient solutions of d-glucose, lævulose, glycerol, mannitol, d-galactose, and l-arabinose in an atmosphere of nitrogen (Harden, Trans. Ch. Soc. **79**, 610). *Bacterium icteroides* ferments dextrose in a similar manner (*ibid.* Trans. Path. Soc. **52**, 115). An organism from sour milk produces alcohol from pure arabinose (Schöne and Tollens, Journ. Ch. Soc. **80**, I, 368).

Saccharobacillus pastorianus (Van Laer) produces alcohol among other products from dextrose, maltose, and saccharose

(Klöcker, 'Die Gärungsorganismen, &c.' p. 277). Alcohol is among the products of the butyric fermentation of dextrose, saccharose, and starch by the anacrobic *Amylobacter butylicum* and *A. æthylicum* (Duclaux, Ann. Inst. Past. **9**, 811), and of the fermentation of sugar in nutrient solution by a slime-forming *Bacillus* isolated from impure water (Schardinger, Centr. Bakter. II, **8**, 144; 175). Soil bacteria produce alcohol among the products of fermentation of saccharose (Dehérain and Maquenne, Comp. Rend. **97**, 803).

The sugar gelatinising *Clostridium gelatinosum* produces alcohol in nutrient solutions containing saccharose (Laxa, Zeit. Zuckerind. **26**, 122; Journ. Fed. Inst. **8**, 639).

Alcohol is formed in small quantity as a product of putrefaction of fish (Mörner, Zeit. physiol. Ch. **22**, 514). The bacteria which cause putrefaction of proteids are capable of producing alcoholic fermentation (Vitali, Ch. Centr. 1900, **1**, 141). Arabinose gives alcohol on putrefaction (Salkowski, Zeit. physiol. Ch. **30**, 478). Alcohol and ethyl acetate are formed when blood saturated with saccharose is kept for fifteen months (*Ibid.* **27**, 297). Fibrin kept for several years under chloroform water gives a cupric reducing substance which is fermentable by yeast with the production of alcohol (*Ibid.*). Rancid butter contains alcohol and ethyl esters, especially butyrate, which are probably bacterial products (Amthor, Zeit. anal. Ch. **38**, 10). Alcohol is among the products of anaerobic putrefaction of milk by *Bacillus putrificus* and by the *Bacilli* of malignant œdema and of symptomatic anthrax (Bienstock, Ch. Centr. 1901, **1**, 1209).

Alcohol is said to occur in animal tissues such as muscle, brain, and liver, and in diabetic urine (Rajewski, Pflüger's Arch. **11**, 122; Béchamp, Comp. Rend. **89**, 573; Zeit. anal. Ch. **20**, 603; Markownikoff, Ber. **9**, 1441; 1603). Ethylsulphuric acid (a salt) occurs under certain conditions in horse urine (Pfeiffer and Eber, Landw. Versuchs-Sta. **49**, 97), and in human fistula bile (Brand, Pflüger's Arch. **90**, 491).

Synthetical Processes.

[A.] From *acetylene* (see under methane [1; A]) through éthylene by reduction (Berthelot, Comp. Rend. **50**, 806; **54**, 515; **132**, 281; Wilde, Ber. **7**, 353), ethylsulphuric acid by combination of latter with sulphuric acid (Faraday, Phil. Trans. **1825**, 448; Hennell, *Ibid.* **1826**, 240; **1828**, 365; Berthelot, Ann. Chim. [3] **43**, 385), and decomposition of ethylsulphuric acid by hydrolysis (Hennell; Berthelot; see also Butleroff and Gorjainoff, Ann. **169**, 147). There is said to be some practical difficulty in reducing acetylene to ethylene (Krüger, Elektro. Zeit. **1895**, 32; Wood, Ch. News, **78**, 308).

Acetylene can be partially reduced to ethylene by passing it mixed with hydrogen over finely divided nickel heated to 300° (Sabatier and Senderens, Comp. Rend. **128**, 1173), or over finely divided copper at 130–180° (*Ibid.* **130**, 1559) or iron at 180° (*Ibid.* 1628) or platinum black at ordinary temperature (*Ibid.* **131**, 40), or by the action of heated finely divided nickel on acetylene *per se* (*Ibid.* 187). Ammoniacal chromous sulphate solution is said to reduce acetylene to ethylene (Coudert, Eng. Pat. 17159 of 1898; Journ. Soc. Ch. Ind. **17**, 1178; also Villon process, Elect. Rev. **35**, 375; Journ. Soc. Ch. Ind. **19**, 553; Berthelot, Comp. Rend. **132**, 281).

Acetylene is reduced to ethylene by the action of sodammonium (Moissan, Comp. Rend. **127**, 914). Acetylene can be reduced to ethylene and ethane electrolytically, and in sulphuric acid solution (with mercury cathode) gives rise to small quantities of alcohol (Billitzer, Sitzungsber. Wien. Akad. **110**; 'Nature,' **67**, 425).

Acetylene combines with mercuric chloride to form a compound which is decomposed on heating with aqueous hydrochloric acid with the formation of *aldehyde* [92]. The latter can be reduced to alcohol as below under H (Krüger and Pückert, Ch. Ind. **1895**, 454; see also Caro, *Ibid.* 226 and 454; Kutscheroff, Ber. **17**, 13). Acetylene

gives a trace of alcohol when oxidised by hydrogen peroxide in presence of ferrous sulphate (Cross, Bevan, and Heiberg, Ber. **33**, 2015).

Certain metallic carbides (especially uranium) give ethylene among the gases produced by interaction with water (Moissan, Bull. Soc. [3] **17**, 15; for production of ethylene, acetylene, &c., by the action of water on carbides of cerium, lanthanum, yttrium, and uranium see also Berthelot, Comp. Rend. **132**, 281; for production of ethylene by the action of water on mixed barium carbide and silicide see paper by Tucker and Moody, Journ. Soc. Ch. Ind. **20**, 971).

NOTE:—For generators of ethylene see also under methane [1; D, note].

[B.] From *methane* [1] through chloroform by chlorination (Regnault, Ann. Chim. [2] **71**, 380). Chloroform gives acetylene by passing over heated copper (Berthelot, Comp. Rend. **50**, 805) or by the action of potassium amalgam (Kletzinsky, Zeit. [2] **2**, 127; see also Fittig, *loc. cit.*).

Or from methane through methyl chloride by chlorination (Berthelot, Ann. Chim. [3] **52**, 97). Ethylene is among the products formed by passing methyl chloride through a hot tube (Perrot, Ann. **101**, 375).

Or from methyl chloride and *hydrogen cyanide* [172] through methyl cyanide (acetonitrile) and *ethylamine* [Vol. II], and then as under **FF** below.

[C.] From *heptane* [2], ethylene being among the products formed on heating the vapour to 900° (Worstall and Burwell, Am. Ch. Journ. **19**, 815).

[D.] From *methyl alcohol* [13] through ethane by the action of zinc or sodium on methyl iodide (Frankland, Journ. Ch. Soc. **2**, 173; Ann. **71**, 213; Wanklyn and Buckeisen, Ann. **116**, 329: methyl cyanide as a 'catalytic' reagent facilitates this condensation, Michael, Am. Ch. Journ. **25**, 419). Ethane gives ethyl chloride by chlorination (Schorlemmer, Comp. Rend. **58**, 703; Ann. **132**, 234; Darling, Ann. **150**, 216). The chloride gives alcohol on heating with aqueous alkali (Balard, Ann. Chim. [3] **12**, 302).

According to Glock alcohol is formed by passing a mixture of ethane and air over heated copper, asbestos, &c. (Germ. Pat. 109015 of 1899; Ch. Centr. 1900, **2**, 304; also Coquillon as quoted in Journ. Soc. Ch. Ind. **19**, 684).

Or from methyl alcohol and *potassium cyanide* [172] through methyl iodide and cyanide and *ethylamine* [Vol. II] and then as under **FF** below.

NOTE:—Many synthetical products give ethane on heating with strong aqueous hydriodic acid in sealed tubes: *acetaldehyde* [92]; *acetone* [106]; *acetic acid* [Vol. II]; *ethylamine* [Vol. II]; *styrene* [7]; tartronic acid from *tartaric* or *malonic acid* [Vol. II]; *ethylbenzene* [7; A]; *naphthalene* [12; 90]; *anthracene* [144]; *alizarin* [145] (Berthelot; for references see under methane [1; I]).

Ethylene also is reduced to ethane by passing in admixture with hydrogen over heated finely divided nickel (Sabatier and Senderens, Comp. Rend. **124**, 1358), and *acetylene* also gives ethane among other products when passed mixed with hydrogen over heated finely divided nickel, copper, iron, cobalt, or platinum (*Ibid.* Comp. Rend. **128**, 1173; 130, 1559; 1628; 131, 40; 187. Further particulars as to temperature, &c., are given above under A).

Primary alcohols, such as *methyl* [13], *isobutyl* [18], and *amyl alcohol* [22], when their vapours are passed over calcium carbide heated to 500° give acetylene, ethylene, and ethane among other products (Lefebvre, Comp. Rend. **132**, 1221).

Acetylene and ethane are produced directly by the combination of carbon and hydrogen when an electric arc passes between carbon poles in an atmosphere of hydrogen (Bone and Jerdan, Trans. Ch. Soc. **79**, 1042).

Ethane and ethylene are among the products of pyrogenic contact decomposition of *isopropyl* [16] and *isoamyl alcohol* [22] (Ipatieff, Ber. **35**, 1053; 1056). Propyl alcohol gives ethane among the products of pyrogenic contact decomposition by plumbago crucible material (Ipatieff, Ber. **35**, 1059).

[E.] From *carbon disulphide* [160], ethylene being among the products formed by passing a mixture of the vapour with hydrogen sulphide and phosphine over heated copper or a mixture of the vapour with hydrogen sulphide and carbon monoxide over heated iron (Berthelot, Comp. Rend. **43**, 236).

Or from carbon disulphide through the tetrabromide (Bolas and Groves, Journ. Ch. Soc. **23**, 161; **24**, 773; Ann. **156**, 60; **160**, 160; Höland, Ann. **240**, 238; Mouneyrat, Bu[illegible] [2] **19**, 262). The latter on treat[illegible] excess of alcoholic potash yields ethylene (Nef, Ann. **308**, 329). Or through the tetrachloride (see under methane

[1; L]), iodoform, and acetylene, &c., as under **R** below.

NOTE :—Many compounds which can be synthesised give carbon tetrabromide on treatment with bromine in the presence of alkali (from *acetone* [106], Wallach, Ann. 275, 149; from *lævulic acid* [50; D], *acetoacetic acid* [Vol. II], *dehydracetic acid* [75; D], &c. Farb. vorm. Meister, Lucius and Brüning, Germ. Pat. 76362 of 1893; Ber. 27, Ref. 930) or with a strong solution of sodium hypobromite (*acetone, glycol, glycerol, mannitol, sugars, malic* and *citric acids*, all unsaturated acids, *phenol, orcinol*, the *naphthols, anthracene derivatives*, &c. Collie, Trans. Ch. Soc. 65, 262).

[F.] *Geraniol* [36] on heating with strong alcoholic potash to 150° gives (with methylheptenone) ethyl alcohol (Tiemann, Ber. 31, 2989).

[G.] From *glycerol* [48], alcohol being among the products of the dry distillation of the calcium and sodium derivatives (Destrem, Ann. Chim. [5] 27, 20; Fernbach, Bull. Soc. [2] 34, 146).

Or glycerol can be converted into allyl alcohol by distillation with oxalic acid (Tollens, Ann. 156, 129; Tollens and Henninger, Bull. Soc. [2] 9, 394; Brühl, Ann. 200, 174; Linnemann, Ber. 7, 854; see also Bigot, Ann. Chim. [6] 22, 464). Allyl alcohol gives ethyl alcohol among the products of decomposition by heating with solid potash (Tollens, Ann. 159, 92) or with phosphorus pentoxide (Béhal, Ann. Chim. [6] 16, 360).

[H.] From *aldehyde* [92] by reduction with sodium amalgam (Wurtz, Ann. 123, 140). Or indirectly through iodoform (see under methane [1; I]) and acetylene as below under **I**.

Or from aldehyde through ethylidene chloride by the action of phosphorus pentachloride (Wurtz and Frapolli, Comp. Rend. 47, 418; Ann. 108, 223; Beilstein, Ann. 113, 110; Geuther, Ann. 105, 321). Acetylene, ethylene, and ethane are produced by the action of sodium at 200° on ethylidene chloride (Tollens, Ann. 137, 311).

Or from aldehyde through the oxime which gives nitroethane among the products of oxidation by permonosulphuric acid (Caro's reagent; Bamberger and Scheutz, Ber. 34, 2029). From nitroethane through *ethylamine* [Vol. II] and then as under **FF** below. Or the phenylhydrazone of aldehyde gives ethylamine (with aniline) by electrolytic reduction in sulphuric acid (Tafel and Pfeffermann, Ber. 35, 1510).

NOTE :—Ethane is among the products of decomposition of acetaldehyde and *propionic aldehyde* [96; 2-methylpentanal, A] at a high temperature (Tischtschenko, Ch. Centr. 1900, 1, 586, from Journ. Russ. Soc. 31, 784).

[I.] From *n-propyl alcohol* [15] through iodoform (see under methane [1; E]). The latter gives acetylene by the action of certain finely divided metals, such as silver, &c. (see under cymene [6; III]).

Or iodoform can be converted into methylene iodide by heating with iodine (Hofmann, Ann. 115, 267), with sodium ethoxide in alcohol (Butleroff, Ann. 107, 110; 111, 242), by boiling with strong aqueous hydriodic acid and phosphorus (Lieben, Zeit. 1868, 712; Baeyer, Ber. 5, 1095), or by heating with water and reduced iron (Cazeneuve, Comp. Rend. 98, 369). Methylene iodide on heating with water and copper gives ethylene among other products (Butleroff, Ann. 120, 356); also on heating with silver powder (Sudborough, Journ. Soc. Ch. Ind. 16, 408).

Or from n-propyl alcohol through n-hexane (see under n-hexyl alcohol [23]). Ethylene is among the products formed by passing a mixture of hexane and air over heated platinum (v. Stepski, Monats. 23, 773). Subsequent steps as under **A** above.

[J.] From *n-butyl alcohol* [17] through iodoform (1; F) and then as above. Or from *isobutyl* or *tertiary butyl alcohol* [18; 19] through isobutylene (see under isobutyl alcohol [18; A] and under tertiary butyl alcohol [19; B]). Ethylene is among the products of pyrogenic decomposition of isobutylene (Noyes; Beilstein, I, 115). Ethylene is among the products formed by passing the vapour of isobutyl alcohol mixed with air over heated platinum (v. Stepski, Monats. 23, 773).

NOTE :—Other generators of isobutylene given under isobutyl and tertiary butyl alcohols are: *isoamyl alcohol* [22]; *isovaleric acid* [Vol. II]; *acetic acid* [Vol. II]; *acetone* and *glycerol* [106; 48].

[K.] From *octyl alcohol* [28] through iodoform (1; G) and then as above.

[L.] From *butyric aldehyde* [94] through iodoform (1; K) and then as above.

[M.] From *acetone* [106] through chloroform or iodoform (1; J). Iodoform gives acetylene or ethylene as above. Chloroform gives acetylene by passing the vapour over heated copper (see under cymene [6; III]). Or chloroform can be converted into methylene iodide by heating with aqueous hydriodic acid at 130° (Bljuducho, Zeit. [2] 7, 91). From methylene iodide to ethylene as above under I.

Or from acetone through bromoform (Löwig, Ann. 3, 295; Dumas, Ann. Chim. [2] 56, 120; Günther, Arch. Pharm. [3] 25, 373). The latter gives ethylene by the action of alcoholic potash (Hermann, Ann. 95, 211; Long, Ann. 194, 23).

Or from acetone through *acroleïn* [101] and allyl alcohol (see under glycerol [48; E]) and then as above under G.

[N.] From *phenol* [60], ethylene being among the products of pyrogenic decomposition (Müller, Journ. pr. Ch. 58, 1). Or from phenol through chlor-*aa*-glyceric acid and chloroform (see under methane [1; M]), and then through acetylene, &c., as above under M.

[O.] From *cresol* [61; 62; 63], ethylene being among the products of pyrogenic decomposition (Müller, *loc. cit.*).

[P.] From *dextrose* [154], ethyl alcohol being produced in small quantity by the action of an alternating electric current on an aqueous solution (Berthelot, Ann. Chim. [5] 16, 450). Ethyl alcohol is among the products of reduction of dextrose by sodium amalgam (Bouchardat, Comp. Rend. 73, 1008; Ann. Chim. [4] 27, 68).

'Sugar' in alkaline solution is said to yield alcohol under the influence of light in the absence of all life (Duclaux, Ann. Inst. Past. 10, 168).

[Q.] From *hydrogen cyanide* [172] or metallic cyanides, these by interaction with red-hot magnesium giving magnesium carbide. The latter is decomposed by water with the formation of acetylene (Eidmann, Journ. pr. Ch. [2] 59, 1).

[R.] From *formic acid* [Vol. II] and *methyl alcohol* [13] through methyl formate, perchlormethyl formate, and carbon tetrachloride (see under methane [1; O]). The latter on heating with strong aqueous hydriodic acid at 130° gives iodoform (Walfisz, Bull. Soc. [3] 7, 256), from which acetylene, &c., can be obtained as above under I. Barium formate gives ethylene among the products of dry distillation (Watts' Dict. II, 484; comp. Merz and Weith, Ber. 15, 1511).

[S.] From *acetic acid* [Vol. II] through acetyl chloride or acetic anhydride and reduction with sodium amalgam (Linnemann, Ann. 148, 249; Saytzeff, Journ. pr. Ch. [2] 3, 76). Or indirectly through ethane by electrolysis (Kolbe, Ann. 69, 279; Kuenen, Proc. Physical Soc. 15, 237) and then through ethyl chloride, &c., as above under D.

Ethylene is among the products formed by dropping acetic acid on to heated zinc chloride (LeBel and Greene, Am. Ch. Journ. 2, 26), and among the products of electrolysis of an acid solution of potassium acetate (Petersen, Ch. Centr. 1897, 2, 518).

A solution of the potassium salts of acetic and *glycollic acid* [Vol. II], the acetate being at the anode, give alcohol on electrolysis (v. Miller and Hofer, Ber. 28, 2437).

Or from acetic acid through *ethylamine* [Vol. II] and then as under FF below.

[T.] From *propionic acid* [Vol. II], which gives ethane by photochemical decomposition in presence of uranium salts (Fay, Am. Ch. Journ. 18, 269). Ethyl propionate is formed by the electrolysis of an acid solution of potassium propionate (Petersen, Ch. Centr. 1897, 2, 518).

Ethyl iodide is formed by the electrolysis of sodium propionate with potassium iodide for the negative electrolyte (v. Miller and Hofer, Ber. 28, 2430). Ethylene is among the products of electrolysis of a neutral solution of potassium propionate (Bunge, Journ.

Russ. Soc. **21**, 551; Petersen, *loc. cit.*). Ethyl alcohol is among the products of electrolysis of sodium propionate in presence of sodium perchlorate (Hofer and Moest, Ann. **323**, 284).

Or from propionic acid through nitroethane or propionamide and *ethylamine* [Vol. II] and then as under **FF** below.

[**U.**] From *butyric acid* [Vol. II], which gives a small quantity of ethyl butyrate on oxidation with sulphuric acid and manganese dioxide (Veiel, Ann. **148**, 164.

[**V.**] From *lactic acid* [Vol. II], alcohol being among the products formed by heating the calcium salt with lime (Hanriot, Bull. Soc. [2] **43**, 417; **45**, 80), or by photochemical decomposition in aqueous solution (Duclaux, *Ibid.* **47**, 385). Ethylene also is among the products of distillation of calcium lactate (Gossin, *Ibid.* **43**, 49).

Or from lactic acid through iodoform by the action of iodine in presence of alkali (Lieben, Ann. Suppl. **7**, 218; 377) and then as above under **A**.

Or from lactic acid through *alanine* [Vol. II] and *ethylamine* [Vol. II] as under **GG** below.

[**W.**] From *malonic acid* [Vol. II], ethylene (small quantity) being among the products of electrolysis of the acid potassium salt (Petersen, Ch. Centr. 1897, **2**, 519).

[**X.**] From *succinic acid* [Vol. II], the acid potassium salt giving some alcohol (by reduction of aldehyde) at the kathode (Petersen, Zeit. physik. Ch. **33**, 698; Ch. Centr. 1900, **2**, 172).

Ethylene is formed also by the electrolysis of a strong solution of the sodium salt (Kekulé, Ann. **131**, 79: see also Clark and Smith, Journ. Am. Ch. Soc. **21**, 967) and of the acid potassium salt (Petersen, Ch. Centr. 1897, **2**, 519 and 1900, **2**, 171).

Also from succinic acid through the dibromo-acid, acetylenedicarboxylic acid, and acetylene (see under methane [**1**; **T**]).

[**Y.**] From *azelaïc acid* [Vol. II] through ethylene (see under methane [**1**; **V**]).

[**Z.**] From *fumaric* or *maleïc acid* [Vol. II] through acetylene by electrolysis (see under methane [**1**; **U**]), or through dibromsuccinic acid and acetylene (*Ibid.*).

[**AA.**] From *malic acid* [Vol. II] through bromoform (see under methane [**1**; **BB**]) and then as above under **M**.

[**BB.**] From *citric acid* [Vol. II] through bromoform (see under methane [**1**; **CC**]) and then as above under **M**.

[**CC.**] From *salicylic acid* [Vol. II] through trichlor-*aa*-glyceric acid and chloroform (see under methane [**1**; **W**]) and then through acetylene, &c., as above under **M**.

[**DD.**] From *gallic acid* [Vol. II] through trichlor-*aa*-glyceric acid and chloroform (see under methane [**1**; **X**]) and then as above.

[**EE.**] From *trimethylamine* [Vol. II] through methyl chloride by heating the hydrochloride of the base to 326° (Vincent, Journ. Pharm. [4] **30**, 132; Jahresber. **1878**, 1135). Subsequent steps as under **B** above.

[**FF.**] From *ethylamine* [Vol. II] by the action of nitrous acid (Linnemann, Ann. **144**, 129; Hofmann, Journ. Ch. Soc. **3**, 231).

[**GG.**] From *alanine* [Vol. II] through *ethylamine* [Vol. II] by dry distillation (Limpricht and Schwanert, Ann. **101**, 297) and then as above.

[**HH.**] *Mannitol* [**51**] gives methylene iodide among the products of the action of phosphorous iodide (Butleroff, Ann. **111**, 242). From methylene iodide through ethylene as above under **I**. Or from mannitol through n-hexane (see under n-hexyl alcohol [**23**; **B**]) and then as above under **I**.

Note:—All generators of n-hexane referred to under n-hexyl alcohol [**23**] thus become, through ethylene, generators of ethyl alcohol.

[**II.**] From *isovaleric acid* [Vol. II], ethylene and ethane being among the products of the dry distillation of the calcium salt (Dilthey, Ber. **34**, 2115).

[**JJ.**] From *n-hexyl alcohol* [**23**] through n-hexyl iodide and hexane by reduction and then as under **I** above.

[**KK.**] From *tartaric acid* [Vol. II] through pyroracemic acid (benzyl alcohol [**54**; **N**]), which gives ethyl acetate on

electrolysis in alcoholic solution in presence of acid or alkali (Rockwell, Journ. Am. Ch. Soc. **24**, 719).

[**LL.**] From *acroleïn* [**101**] through propinal and acetylene (see under cymene [**6**; XVIII]) and then as above under **A.**

15. Normal Propyl Alcohol; Ethyl Carbinol; 1-Propanol.

$CH_3 . CH_2 . CH_2 . OH$

Natural Sources.

A secondary product of alcoholic fermentation by *Saccharomyces*, being found in most fusel oils (Chancel, Comp. Rend. **37**, 410; **68**, 659; 726; Jahresber. **1853**, 503; Ann. **151**, 298; Krämer and Pinner, Ber. **3**, 75; Fittig, Zeit. [2] **4**, 44; Pierre and Puchot, Ann. **163**, 265; Comp. Rend. **66**, 302; **70**, 406; Linnemann, Ann. **160**, 195; Ekman, Ch. Zeit. **12**, 564; in old cognac fusel oil, Ordonneau, Comp. Rend. **102**, 217; Claudon and Morin, *Ibid.* **104**, 1187; **105**, 1019; in fusel oil from potato spirit, Rabuteau, Comp. Rend. **87**, 501; see also Bell as quoted by Allen in Journ. Fed. Inst. **3**, 36).

n-Propyl alcohol is among the products of fermentation of glycerol in presence of calcium carbonate and nutrient salts by *Bacillus butylicus* (Fitz, Ber. **13**, 36; 1311; Morin, Bull. Soc. [2] **48**, 803) and among the products of the lactic and butyric fermentation of sugar (Bouchardat, Comp. Rend. **78**, 1145; Meyer and Forster, Ber. **9**, 535).

The *Bacillus* of malignant œdema produces n-propyl alcohol among other products from lactic acid in an atmosphere of hydrogen (Kerry and Fränkel, Monats. **12**, 350).

Granulobacter butylicum of Beyerinck (Rec. Tr. Ch. **12**, 141) produces n-propyl and not, as formerly supposed, butyl alcohol during butyric fermentation (Emmerling, 'Die Zersetzung,' &c. p. 115, note).

n-Propyl alcohol is among the products of fermentation of starch by the anaerobic *Amylobacter butylicum* and *A. æthylicum* of Duclaux (Ann. Inst. Past. **9**, 811).

Synthetical Processes.

[**A.**] From *ethyl alcohol* [**14**] through ethyl iodide, *cyanide* [**172**] (Williamson, Phil. Mag. [4] **6**, 205; Buckton and Hofmann, Journ. Ch. Soc. **9**, 250; Rossi, Ann. **159**, 79), propylamine by reduction, and action of nitrous acid on the amine (Mendius, Ann. **121**, 133; Siersch, Ann. **144**, 137; Silva, Zeit. [2] **5**, 638; Linnemann, Ann. **161**, 44; Meyer and Forster, Ber. **9**, 535: isopropyl alcohol is simultaneously formed in this process; see under the latter [**16**; **C**]).

Or ethyl iodide and methyl iodide (from *methyl alcohol* [**13**]) can be condensed to propane by the method of Wurtz (sodium in ethereal solution; see under n-heptane [**2**; **A**]). Propane on chlorination gives n-propyl chloride (Schorlemmer, Ann. **150**, 209; **152**, 159), which can be converted into the alcohol by the usual methods.

Or from ethyl alcohol through ethylene (see under methane [**1**; **D**]), ethylene chloride, vinyl chloride, chloracetaldehyde, and (with *hydrogen cyanide* [**172**]) β-chlorlactic acid, glyceric acid, and pyrotartaric acid (see under benzyl alcohol [**54**; **A**]); n-propyl alcohol is among the products of elcctrolysis of potassium pyrotartrate (Petersen, Zeit. physik. Ch. **33**, 698; Ch. Centr. 1900, **2**, 172).

Note:—Ethyl alcohol is also a generator of chloracetaldehyde through ethyl ether or chloracetal, or through chloral (see under benzyl alcohol [**54**; **I**]).

Or from ethyl alcohol through iodoform, which by the action of sodium ethoxide gives acrylic acid (Butleroff, Ann. **114**, 204). The latter can be converted into α-chlorlactic acid (benzyl alcohol [**54**; **I**]), glyceric acid (*Ibid.*), and pyrotartaric acid (*Ibid.* **F**).

Or ethylene can be combined with phosgene (carbon oxychloride) to form β-chlorpropionyl chloride, from which the acid can be obtained by the action of water (Lippmann, Ann. **129**, 81; Henry, Comp. Rend. **100**, 114). The chloro-acid on treatment with alcoholic potash or lead oxide or sodium hydroxide

gives acrylic acid (Moureu, Ann. Chim. [7] **2**, 158; see also Schneider and Erlenmeyer, Ber. **3**, 339; Wislicenus, Ann. **166**, 2).

Or ethylene combines with hypochlorous acid to form glycolchlorhydrin (Carius, Ann. **126**, 197; Butleroff, Ann. **144**, 40: practically *glycol* from ethylene may be treated with hydrogen chloride). The chlorhydrin with *potassium cyanide* [**172**] and by hydrolysis of the nitrile gives *hydracrylic acid* (Wislicenus, Ann. **128**, 4; **167**, 346; Erlenmeyer, Ann. **191**, 268). The salts of the latter give acrylic acid on dry distillation (Beilstein, Ann. **122**, 372). From acrylic acid *via* glyceric acid and pyrotartaric acid as above.

NOTE:—By these processes all generators of ethylene become generators of n-propyl alcohol.

Or from ethyl alcohol and *trioxymethylene* [*formic aldehyde*: **91**] by the interaction of magnesium ethobromide and trioxymethylene in ethereal solution (Grignard and Tissier, Comp. Rend. **134**, 107).

[**B.**] From *isopropyl alcohol* [**16**] through isopropyl iodide, which gives propane by reduction with zinc and acid (Schorlemmer, Ann. **150**, 209). Or from isopropyl alcohol through propylene and conversion of latter into pyrotartaric nitrile (by means of *potassium cyanide* [**172**]) and pyrotartaric acid (see under dipentene [**9**; **F**]) and then as under **A**.

[**C.**] From *normal butyl alcohol* [**17**] through n-butyl iodide, n-butylene by the action of alcoholic potash on the latter (Saytzeff, Journ. pr. Ch. [2] **3**, 88; Lieben and Rossi, Ann. **158**, 164; Grabowsky and Saytzeff, Ann. **179**, 330), and secondary butyl iodide = 2-iodobutane by combining the n-butylene with hydrogen iodide (Wurtz, Ann. **152**, 23). 2-Iodobutane gives propane among other products on heating with aluminium chloride above 160° (Lothar Meyer, Ber. **27**, 2766; Kluge, Ann. **282**, 227).

[**D.**] From *tertiary butyl alcohol* [**19**] through tertiary butyl iodide, which also gives propane when heated with aluminium chloride as above (Lothar Meyer, *loc. cit.*; Kluge, *loc. cit.*).

[**E.**] From *glycerol* [**48**], which gives propane on heating in a closed vessel with strong aqueous hydriodic acid (Berthelot, Bull. Soc. [2] **7**, 60; **9**, 13; 184).

Or through allyl alcohol by distilling glycerol with oxalic acid (see under ethyl alcohol [**14**; **G**]). Allyl alcohol gives n-propyl alcohol on reduction with zinc and dilute sulphuric acid (Linnemann, Ber. **7**, 852), on heating with solid potash (Tollens, Ann. **159**, 92; Zeit. [2] **7**, 242), or by reduction with aluminium in alkaline solution (Speranski, Journ. Russ. Soc. **31**, 423).

Glycerol gives n-propyl alcohol among the products of decomposition of the sodium compound above 245° (Fernbach, Bull. Soc. [2] **34**, 146).

Or from glycerol through allyl bromide (Henry, Zeit. [2] **6**, 575; Tollens, Ann. **156**, 152; Grosheintz, Bull. Soc. [2] **30**, 98; Jacobi and Merling, Ann. **278**, 11), trimethylene bromide by combination with hydrogen bromide (Géromont, Ann. **158**, 370; Reboul, Ann. Chim. [5] **14**, 472; Erlenmeyer, Ber. **12**, 1354; Roth, Ber. **14**, 1351; Bogomolitz, Bull. Soc. [2] **30**, 23), trimethylene = cyclopropane by the action of sodium or of zinc dust on trimethylene bromide in alcohol (Freund, Monats. **3**, 626; Journ. pr. Ch. [2] **26**, 367; see also Reboul, Ann. Chim. [5] **14**, 488; Gustavson, Journ. pr. Ch. [2] **36**, 300; **50**, 381; **59**, 302; Journ. Russ. Soc. **19**, 495; Comp. Rend. **128**, 437; Wagner, Ber. **21**, 1236; Tornoë, *Ibid.* 1282; Wolkoff and Menschutkin, Ber. **31**, 3072; Journ. Russ. Soc. **32**, 118; Tanatar, Ber. **32**, 702; 1965). Trimethylene combines with strong sulphuric acid to form dipropyl sulphate (Freund), which gives n-propyl alcohol on decomposition by hot water (Gustavson; Berthelot, Ann. Chim. [7] **4**, 102). Or trimethylene combines with hydrogen iodide to form n-propyl iodide, from which the alcohol can be obtained by the usual methods (Freund).

Or from glycerol through *acroleïn* [**101**] (see also under cymene [**6**; XVIII]) and oxidation of latter to acrylic acid (Claus, Ann. Suppl. **2**, 123; also Redtenbacher, Ann. **47**, 125). From acrylic

acid through α-chlorlactic, glyceric, and pyrotartaric acids as above under **A**.

Or from glycerol and *potassium cyanide* [172] through allyl chloride and pyrotartaric nitrile and acid (dipentene [9; G]) and then as under **A** above.

[F.] *Erythritol* [50] gives 2-iodobutane on heating with aqueous hydriodic acid (De Luynes, Bull. Soc. [2] **2**, 3; Ann. **125**, 252). Subsequent steps through propane as above under **C**.

[G.] From *mannitol* [51] through secondary hexyl iodide = 2-iodohexane by heating with aqueous hydriodic acid (Wanklyn and Erlenmeyer, Jahresber. **1861**, 731; **1862**, 480; Zeit. **1861**, 606; **1862**, 641; Ann. **135**, 130; Domac, Monats. **2**, 310; Hecht, Ann. **165**, 146; **209**, 311; Uppenkamp, Ber. **8**, 55; Schorlemmer, Ann. **199**, 139: according to Combes and LeBel, Bull. Soc. [3] **7**, 551, the iodohexane thus formed is 3-iodohexane). Propane is among the products formed by heating 2-iodohexane with aluminium chloride to 225° (Lothar Meyer, Ber. **27**, 2766; Kluge, Ann. **282**, 227).

Or from mannitol through *acroleïn* and acrylic acid (see under benzyl alcohol [54; **AA** and **E**]). From the latter through α-chlorlactic acid, glyceric acid, and pyrotartaric acid as above under **A**.

[H.] From *formic aldehyde* [91] through 'oxymethylene,' which results from its polymerisation (see under formic aldehyde). Oxymethylene gives n-propyl alcohol by dissolving in strong sulphuric acid and distilling the product with water (Gustavson, Journ. pr. Ch. [2] **36**, 301).

Or oxymethylene forms a compound with *zinc ethyl* which is decomposed by water with the formation of n-propyl alcohol (Tischtschenko, Journ. Russ. Soc. **19**, 483).

[I.] From *crotonic aldehyde* [102] through crotonic acid (see under benzyl alcohol [54; **H**]). The acid combines with hydrogen bromide to form α-brombutyric acid (Naumann, Ann. **119**, 115; Wislicenus and Urech, Ann. **165**, 93; Ley, Journ. Russ. Soc. **9**, 129; Tupoleff, Ann. **171**, 249; Hemilian, Ann. **174**, 325). The latter, on distillation of the potassium salt with a solution of sodium nitrite, gives nitropropane (Auger, Bull. Soc. [3] **23**, 333), which can be reduced to propylamine and treated as above under **A**.

Or from crotonic acid, the ester of which condenses under the influence of sodium ethoxide to form dicrotonic ester, from which the acid can be obtained by hydrolysis. Dicrotonic acid gives pyrotartaric acid on oxidation by alkaline permanganate (v. Pechmann, Ber. **33**, 3323). From pyrotartaric acid as above under **A**.

[J.] From *acetic aldehyde* [92] through butyrochloral and allylene dichloride (see under benzyl alcohol [54; **H**]). The dichloride on heating with water at 180° gives acrylic acid (Pinner, Ber. **7**, 66). Subsequent steps through α-chlorlactic acid, glyceric, and pyrotartaric acids as above under **A**.

Or from acetic aldehyde through *crotonic aldehyde* [102] and crotonic acid and then as above under **I**.

Aldehyde and *hydrogen cyanide* [172] give a cyanhydrin which, by the action of phosphorus pentachloride, gives α-chlorpropionitrile, from which α-chlorpropionic acid can be obtained by hydrolysis. The acid on heating with barium hydroxide solution gives acrylic acid (Michael and Garner, Ber. **34**, 4049).

[K.] *Acetone* [106] gives propane on heating in a sealed tube with strong aqueous hydriodic acid (Berthelot, Bull. Soc. [2] **7**, 69). From propane as above under **A**. Or acetone on chlorination gives 1 : 1-dichloracetone (Fittig, Ann. **110**, 40; Borsche and Fittig, Ann. **133**, 112), which gives acrylic acid on boiling with potassium carbonate solution (Faworsky, Journ. pr. Ch. [2] **51**, 555). From acrylic acid through pyrotartaric acid as above under **A**.

Or from *acetone*, *acetic acid*, and *ethyl alcohol* through acetylacetone and methylpropyl ketone (as under n-primary amyl alcohol [20; **B**; **C**] and n-secondary amyl alcohol [21; **D**]). From the ketone through the oxime to propylamine as below under **AA**.

[L.] *Pulegone* [128] gives pyrotartaric acid among the products of its oxidation by potassium permanganate (Mar-

kownikoff, Ber. **33**, 1909). Subsequent steps as above under **A**.

[**M.**] *Menthone* [**129**] gives pyrotartaric acid as above (*Ibid.*).

[**N.**] From *propionic acid* [Vol. II] through propionic anhydride, which gives n-propyl alcohol on reduction with sodium amalgam (Linnemann, Ann. **148**, 251; **160**, 231; **161**, 18; see also Saytzeff, Zeit. [2] **6**, 105). Or ammonium propionate on dry distillation gives propionamide, which on heating with phosphorus pentoxide gives propionitrile = ethyl cyanide (Dumas, Malaguti, and Leblanc, Ann. **64**, 334; see also Aschan, Ber. **31**, 2344). The latter can be reduced to propylamine and treated as above under **A**.

Or from propionic acid through propionyl chloride, β-chlorpropionyl chloride by chlorination and β-chlorpropionic acid by hydrolysis (Michael and Garner, Ber. **34**. 4046). From the β-chloro-acid through acrylic acid to pyrotartaric acid as above under **A**.

Or from propionic acid through the αα-dibromo-acid and the αβ-dibromo-acid by transformation of the latter (see under benzyl alcohol [**54**; **O**]). From the αβ-dibromo-acid through glyceric to pyrotartaric acid (*Ibid.*) and then as above under **A**.

Or from propionic and *formic acid* [Vol. II] through propionic aldehyde by distilling a mixture of the calcium salts (Williamson, Journ. Ch. Soc. **4**, 138; Lieben and Rossi, Ann. **158**, 137; **159**, 58; 79; **165**, 109; **167**, 293; Lieben and Janecek, Ann. **187**, 126). The aldehyde gives the alcohol on reduction (Rossi, Comp. Rend. **70**, 129; Ann. **159**, 80). Propaldoxime also gives nitropropane among the products of oxidation by permonosulphuric acid (Caro's reagent; Bamberger and Scheutz, Ber. **34**, 2032). From nitropropane through propylamine as above under **I** and **A**.

Note:—Generators of propionic aldehyde are given under hexanal (2-methylpentanal [**96**; **C**, &c.]).

[**O.**] From *acetic acid* [Vol. II] and *hydrogen cyanide* [**172**] through acetyl cyanide, pyroracemic (pyruvic), and pyrotartaric acid (see under benzyl alcohol [**54**; **I**]). Then as above under **A**.

Or from acetic acid and potassium cyanide through cyanacetic acid by the interaction of chloracetic acid and the cyanide (Müller, Ann. **131**, 348; 350; Meves, Ann. **143**, 201; Fiquet, Ann. Chim. [6] **29**, 439). The sodium derivative of cyanacetic ester interacts with ethyl iodide to form α-cyanobutyric ester (Henry, Bull. Soc. [2] **48**, 656; Comp. Rend. **104**, 1618), which gives ethylmalonic acid as below under **P** and n-propyl alcohol as under **T**.

[**P.**] *Normal butyric acid* [Vol. II] gives n-propyl butyrate when the silver salt is acted upon by iodine (Simonini, Monats. **14**, 81), when the acid is oxidised by manganese dioxide and dilute sulphuric acid (Veiel, Ann. **148**, 164), or by the electrolysis of the solution of the acid potassium salt (with some isopropyl butyrate in latter process; Hamonet, Comp. Rend. **123**, 252; Petersen, Ch. Centr. 1897, **2**, 519; 1900, **2**, 172). The ester gives the alcohol by hydrolysis. The alcohol is among the products of electrolysis of sodium butyrate in presence of sodium perchlorate (Hofer and Moest, Ann. **323**, 284).

Or from butyric acid through butyramide by distilling the ammonium salt (Hofmann, Ber. **15**, 982). The amide gives n-propylamine by the action of bromine in presence of caustic potash (*Ibid.* 769). From the amine to the alcohol as above under **A**.

Butyric acid also gives propane by photochemical decomposition in the presence of uranium nitrate (Wisbar, Ann. **262**, 235).

Or butyric acid by bromination gives α-brombutyric acid (Gorup-Besanez and Klincksieck, Ann. **118**, 248; Naumann, Ann. **119**, 115; Borodin, *Ibid.* 123; Friedel and Machuca, Ann. **120**, 279; Suppl. **2**, 70; Ley, Journ. Russ. Soc. **9**, 129; Wislicenus and Urech, Ann. **165**, 93; Tupoleff, Ann. **171**, 249; Genvresse, Bull. Soc. [3] **7**, 366; Michael and Graves, Ber. **34**, 4041). From α-brombutyric acid through nitropropane and propylamine, &c., as above under **I**.

Or from *a*-brombutyric acid (ester) through crotonic acid (see under benzyl alcohol [**54**; **K**]), and then as above under **I** through dicrotonic and pyrotartaric acid, &c.

Or *a*-brombutyric acid (ester) by interaction with *potassium-mercuric cyanide* [**172**] gives *a*-cyanobutyric ester (Markownikoff, Ann. **182**, 330), and this on hydrolysis gives ethylmalonic acid (Wislicenus and Urech, Ann. **165**, 93; Tupoleff, Ann. **171**, 243; Markownikoff, *loc. cit.* 329). The latter gives n-propyl alcohol as below under **T**.

Or from butyric acid through butyrone (see under n-nonyl alcohol [**29**; **D**]), which gives dinitropropane by the action of nitric acid (Chancel, Comp. Rend. **96**, 1466; Bull. Soc. [2] **31**, 503; Ann. **52**, 296; **64**, 331; Kurtz, Ann. **161**, 208; Fileti and Ponzio, Journ. pr. Ch. [2] **55**, 193). From dinitropropane through propylamine and propaldehyde as below under **AA**.

Note:—Methylpropyl ketone from acetic and butyric acids (see under n-secondary amyl alcohol [21; **A**]) and ethylpropyl ketone from propionic and butyric acids or from zinc ethyl and butyryl chloride (Völker, Ber. **8**, 1019; Popoff, Ann. **161**, 289) also give dinitropropane on nitration (Chancel, Jahresber. **1884**, 1048; Fileti and Ponzio, *loc. cit.*). Methylpropyl ketone is also convertible into propylamine through the oxime as below under **AA**.

[**Q**.] *Isobutyric acid* [Vol. II] gives propane among the products of photochemical decomposition in presence of uranium salts (Fay, Am. Ch. Journ. **18**, 286). From propane as above under **A**.

[**R**.] From *lactic acid* [Vol. II], which gives acrylic acid among the products of the distillation of the calcium salt (Claus, Ann. **136**, 288). From acrylic acid to pyrotartaric acid, &c., as above under **A**.

Or lactic acid by the action of phosphorus pentachloride gives *a*-chlorpropionic acid (Wurtz, Ann. Chim. [3] **49**, 58; Brühl, Ber. **9**, 35). From the latter through acrylic acid by heating with barium hydroxide solution (Michael and Garner, Ber. **34**, 4050).

Or lactic acid gives pyroracemic (pyruvic) acid on oxidising the calcium salt with potassium permanganate (Beilstein and Wiegand, Ber. **17**, 840). Pyroracemic acid gives pyrotartaric acid on heating with hydrochloric acid to 100° or *per se* to 170° (Clermont, Ber. **6**, 72; Böttinger, Ber. **9**, 837; 1823; Ann. **188**, 308; De Jong, Rec. Tr. Ch. **20**, 81; **21**, 191; see also Wolff, Ann. **317**, 22).

Or lactic acid gives citraconic acid on distillation (Engelhardt, Ann. **70**, 243; 246). The latter can be converted into pyrotartaric acid (see under benzyl alcohol [**54**; **M**]).

[**S**.] *Hydracrylic acid* [Vol. II] gives acrylic acid on distillation of its salts (Beilstein, Ann. **122**, 372). Subsequent steps as above.

[**T**.] From *malonic acid* [Vol. II] and *ethyl alcohol* [**14**] through ethylmalonic acid (see under hexanal [2-methylpentanal; **96**; **G**]). The latter gives n- (with iso-) propyl alcohol on electrolysis of a solution of the potassium salt (Petersen, Zeit. physik. Ch. **33**, 698; Ch. Centr. 1900, **2**, 172).

Or from malonic acid, *aldehyde* (paraldehyde) [**92**], and *acetic acid* through crotonic acid (see under benzyl alcohol [**54**; **G**]). From crotonic acid through *a*-brombutyric acid and nitro-propane, &c., as above under **I**.

Note:—Malonic acid (ester) on treatment with chloroform and sodium ethylate gives dicarboxyglutaconic ester (Conrad and Guthzeit, Ann. **222**, 250), and this on boiling with baryta water gives (with glutaconic acid) *β*-oxyglutaric acid (Guthzeit and Bolam, Journ. pr. Ch. [2] **54**, 365), from which crotonic acid can be obtained as below under **W**.

Or from malonic ester, *methyl iodide* [**13**], and *chloracetic acid* through propanetricarboxylic acid = *a*-methyletheneyltricarboxylic acid (see under benzyl alcohol [**54**; **G**]) and pyrotartaric acid (*Ibid.*).

Malonic diethyl ester and *aldehyde* [**92**] condense when heated with acetic anhydride to form ethylidenemalonic diethyl ester (Komnenos, Ann. **218**, 157), and the latter on heating with *potassium cyanide* [**172**] in alcoholic solution gives *β*-cyanobutyric ester, which gives pyrotartaric acid on treatment with alkali (Bredt and Kallen, Ann. **293**, 350).

[**U**.] From *β-hydroxybutyric acid*

[Vol. II], which gives crotonic acid on distillation (benzyl alcohol [54; L]).

[V.] From *tartaric acid* [Vol. II] through pyrotartaric acid by heating *per se* or with hydrochloric or acetic acid (Fourcroy and Vauquelin, Ann. Chim. [1] **35**, 161; **64**, 42; Rose, Gehlen's Journ. **3**, 598; Pelouze, Ann. Chim. [2] **56**, 297; Weniselos, Ann. **15**, 148; Arppe, Ann. **66**, 73; **90**, 138; Geuther and Riemann, Zeit. [2] **5**, 318; Béchamp, *Ibid.* [2] **6**, 371; Sacc, *Ibid.* 432; Bourgoin, Ann. Chim. [5] **12**, 419). From pyrotartaric acid as above under A.

[W.] From *citric acid* [Vol. II] through citraconic, mesaconic, or itaconic acid (see under benzyl alcohol [54; M]). From these acids through pyrotartaric acid (*Ibid.*).

Note:—The following generators of citraconic acid given under benzyl alcohol [54; M] thus become generators of n-propyl alcohol through pyrotartaric acid:—*Lactic acid* (see above under R); *acetoacetic ester* and *hydrogen cyanide* through hydroxypyrotartaric acid; *isovaleric acid* through hydroxypyrotartaric acid; *propionic* and *malonic acids* through propanetricarboxylic = β-methylethenyltricarboxylic ester; *acetic* and *propionic acids*, *ethyl alcohol* and *potassium cyanide* through α methyl-β-cyanosuccinic ester; *oxalic* and *propionic acids* and *ethyl alcohol* through methyloxalacetic ester and β-methylmalic acid.

The propanetricarboxylic acid above referred to gives pyrotartaric acid directly (see under benzyl alcohol [54; G]).

Or from citric acid through acetonedicarboxylic acid (see under orcinol [75; C]), which gives β-oxyglutaric acid on reduction (v. Pechmann and Jenisch, Ber. **24**, 3250). The latter on distillation *in vacuo* gives vinylacetic acid (Fichter and Krafft, Ber. **32**, 2799; F. and Sonneborn, Ber. **35**, 938), which is readily transformed into crotonic acid by the action of mineral acids. From crotonic acid as above under I.

[X.] From *aconitic acid* [Vol. II] through itaconic acid (see under benzyl alcohol [54; X]) and then through pyrotartaric acid, &c., as above under W.

[Y.] From *succinic acid* [Vol. II] and *alcohol* [14] through succinylsuccinic ester (see under quinol [71; N]). The latter forms a dinitroso-derivative (Ebert, Ann. **229**, 55), which on long contact with water yields ethyl isonitrososuccinate = α (anti-) oximinosuccinate (*Ibid.* 65), the acid from which decomposes on heating with water with the formation of cyanacetic acid (Cramer, Ber. **24**, 1208). The latter gives α-cyanobutyric acid, ethylmalonic acid, &c., as above under O.

Or from succinic acid through the dibromo-acid by bromination (see under methane [1; T]). The dibromo-acid gives ethoxyfumaric ester on treatment with sodium ethoxide (Michael and Bucher, Ber. **29**, 1792). The ester gives oxalacetic acid by the action of hydrochloric acid (*Ibid.*) or alcoholic potash (Nef, Ann. **276**, 230). The ester of oxalacetic acid gives pyrotartaric or ethylmalonic acid as below under Z.

[Z.] From *oxalic* and *acetic acids* [Vol. II] and *alcohol* [14]. Diethyl oxalate and ethyl acetate condense by the action of sodium or sodium ethoxide with the formation of diethyl oxalacetate (Wislicenus, Ann. **246**, 315; Piutti, Gazz. **17**, 520; Drude, Ber. **30**, 952). The latter on heating with 10 per cent. sulphuric acid gives pyroracemic and through this pyrotartaric acid (Wislicenus, *loc. cit.*).

Or ethyl oxalacetate combines with hydroxylamine to form β-(syn)-oximinosuccinic ester (Cramer, Ber. **24**, 1206), the acid from which decomposes on heating with the formation of cyanacetic acid (*Ibid.*). Subsequent steps through ethylmalonic acid as above.

[AA.] From *acetoacetic ester* [Vol. II] through acetyl cyanide and pyroracemic acid (see under benzyl alcohol [54; I]). From the latter through pyrotartaric acid, &c., as above under O, &c.

Or from acetoacetic ester and *α-brompropionic ester* through β-methylacetosuccinic ester and pyrotartaric acid (benzyl alcohol [54; I]). Or from acetoacetic ester and *chloracetic ester* through acetosuccinic ester, α-methylacetosuccinic ester, and pyrotartaric acid (54; I).

Or from acetoacetic ester and *methyl iodide* through methylacetoacetic ester and mesaconic acid (54; I). From the latter through pyrotartaric acid, &c., as above under W.

Or from acetoacetic ester and *ethyl*

iodide through ethylacetoacetic ester and methyl-n-propyl ketone (see under n-secondary amyl alcohol [21; C]). The oxime of the ketone on heating to 100° with a solution of hydrogen chloride in acetic acid (with a little acetic anhydride) gives propylamine. Other acids, acetyl chloride, or phosphorus pentachloride bring about a similar decomposition (Beckmann, Ber. **20**, 2580; Hantzsch, Ber. **24**, 4018). From propylamine as above under **A**.

Or from acetoacetic ester through crotonic acid (**54**; **I**). From the latter through α-brombutyric acid and nitropropane, or through pyrotartaric acid as above under **I**.

Or acetoacetic ester on bromination under appropriate conditions gives γ-bromacetoacetic ester (Duisberg, Ber. **15**, 1379; Ann. **213**, 138; Conrad and Schmidt, Ber. **29**, 1045: see also Haller and Held, Comp. Rend. **114**, 452), and this by the action of sodium ethoxide, of alcoholic ammonia, or of sodium in ethereal solution gives succinylsuccinic ester (Wedel, Ann. **219**, 94; Duisberg, Ann. **213**, 149; Conrad and Schmidt, *loc. cit.*; Mewes, Ann. **245**, 74). From succinylsuccinic ester through ethylmalonic acid as above under **Y** and **O**.

Or dibromacetoacetic ester (see under quinol [71; O]) gives dihydroxyterephthalic diethyl ester (*Ibid.*). The latter on reduction with zinc and hydrochloric acid or with sodium amalgam gives succinylsuccinic ester (Baeyer, Ber. **19**, 432; Baeyer and Noyes, Ber. **22**, 2168).

Ethylacetoacetic ester on treatment with nitric acid gives 1:1-dinitropropane (Chancel, Jahresber. **1883**, 1079), and this when reduced in ethereal solution with aluminium amalgam gives propylamine and propionic aldehyde (Ponzio, Journ. pr. Ch. [2] **65**, 197).

[**BB.**] From *thymol* [67] through thymoquinone, *thymoquinol* [82], and dihydroxyterephthalic acid (see under quinol [71; P]), and then through succinylsuccinic acid, &c., as above.

[**CC.**] From *carvacrol* [66] through thymoquinone, &c. (quinol [71; Q]).

[**DD.**] From *malic acid* [Vol. II] through oxalacetic acid by oxidising with hydrogen peroxide and a ferrous salt at a low temperature (Fenton and Jones, Trans. Ch. Soc. **77**, 77). From oxalacetic acid through pyrotartaric or through ethylmalonic acid as above under **Z**.

[**EE.**] From *fumaric* or *maleïc acid* [Vol. II] through dibromsuccinic acid (methane [1; U]) and then through oxalacetic acid, &c., *via* ethoxyfumaric ester as above under **Y**. From oxalacetic acid through pyrotartaric or ethylmalonic acid as under **Z**.

[**FF.**] From *allyl isothiocyanate* [166] through allyl cyanide and crotonic acid (benzyl alcohol [54; J]). From crotonic acid as above under **I**.

[**GG.**] From *glycocoll* [Vol. II] and *ethyl alcohol* [14] through n-propylamine by distilling the hydrochloride of the ethyl ester with sodium carbonate (Schilling, Ann. **127**, 97; Kraut, Ann. **177**, 267; Hantzsch and Silberrad, Ber. **33**, 70; Auger, Bull. Soc. [3] **21**, 5; see also Curtius and Jay, Ber. **27**, 60; Hantzsch and Metcalf, Ber. **29**, 1684; for production of propylamine see Curtius and Goebel, Journ. pr. Ch. [2] **37**, 163). From propylamine as above under **A**.

[**HH.**] From *alanine* [Vol. II] and *methyl alcohol* [13] through acrylic acid (benzyl alcohol [54; BB]). From acrylic acid through α-chlorlactic acid, glyceric acid, and pyrotartaric acid as above under **A** (see also under benzyl alcohol [54; I and F]).

[**II.**] From *lysine* [Vol. II], pyrotartaric acid being a product of the oxidation of the base by barium permanganate (Zickgraf, Ber. **35**, 3401).

16. Isopropyl Alcohol; Dimethyl Carbinol; 2-Propanol.

$CH_3 . CH(OH) . CH_3$

Natural Source.

Said to have been found as a secondary product of fermentation in potato fusel oil (Rabuteau, Comp. Rend. **87**, 501). According to Victor Meyer and Jacobson (Lehrb. d. org. Ch. I, 161; see also Bouchardat, Ber. **7**, Ref. 657) this statement is erroneous.

Synthetical Processes.

[A.] From *acetone* [106] by reduction with sodium amalgam (the acetone should contain water) (Friedel, Ann. **124**, 327; Linnemann, Ann. **136**, 38). Acetone also gives isopropyl alcohol (with pinacone) by electrolytic reduction (Merck, Germ. Pat. 113719 of 1899; Ch. Centr. 1900, **2**, 794; Elbs and Brand, Zeit. Elektroch. **8**, 783).

Or from acetone through 2 : 2-dichlorpropane (Friedel, Ann. **112**, 236), *a*-chlorpropylene ($CH_2 : CCl . CH_3$) by the action of alcoholic potash or ammonia, *a*-chlorallyl chloride by chlorinating the chlorpropylene in the dark (Friedel and Silva, Comp. Rend. **73**, 957; **74**, 806; **75**, 81; Fittig, Ann. **135**, 359), *a*-chlorallyl alcohol by boiling with aqueous potassium carbonate (Henry, Comp. Rend. **95**, 849), and *acetyl carbinol* [43] by the action of sulphuric acid (Henry, Bull. Soc. [2] **39**, 526). Acetyl carbinol reduces to propylene glycol (W. H. Perkin, junr., Trans. Ch. Soc. **59**, 786), the latter by the action of hydrogen chloride giving propylene chlorhydrin (Oser, Ann. Suppl. **1**, 254; Morley, Ber. **13**, 1805; also Morley and Green, Trans. Ch. Soc. **47**, 133), which by the action of alcoholic potash gives propylene oxide (Oser, *loc. cit.*; Linnemann, Ann. **140**, 178; Monats. **6**, 369; Henry, Ann. Chim. [4] **27**, 261). The latter yields isopropyl alcohol on reduction by sodium amalgam (Linnemann, *loc. cit.*).

Or from acetone through acrylic and pyrotartaric acids (see under n-propyl alcohol [15; K and A]). The latter gives isopropyl alcohol among the products of electrolysis of the potassium salt (Petersen, Zeit. physik. Ch. **33**, 698; Ch. Centr. 1900, **2**, 172).

Or from acetoneoxime, which gives isopropylamine by reduction with sodium amalgam in acetic acid solution (Meyer and Warrington, Ber. **20**, 505; Goldschmidt, *Ibid.* 728) or by electrolytic reduction (Tafel and Pfeffermann, Ber. **35**, 1510).

Or from acetonephenylhydrazone, which gives isopropylamine on reduction with sodium amalgam and acetic acid (Tafel, Ber. **19**, 1926) or by electrolytic reduction (Tafel and Pfeffermann, Ber. **35**, 1207). Isopropylamine is converted into isopropyl alcohol by the action of nitrous acid (Siersch, Ann. **148**, 263; Meyer and Forster, Ber. **9**, 535).

[B.] From *normal propyl alcohol* [15] through propylene by the action of dehydrating agents (LeBel and Greene, Am. Ch. Journ. **2**, 23; Beilstein and Wiegand, Ber. **15**, 1498; Berthelot, Comp. Rend. **129**, 483; Newth, Proc. Ch. Soc. **17**, 147). Propylene combines with strong sulphuric acid, and the product gives isopropyl alcohol on hydrolysis (Berthelot, Ann. Chim. [3] **43**, 399; Ann. **94**, 78; Comp. Rend. **57**, 797; Ann. **129**, 126).

Note:—Propylene is produced from propyl alcohol to the extent of 93·3 per cent. by passing the vapour over heated plumbago crucible material (Ipatieff, Ber. **35**, 1059).

Or n-propyl alcohol can be converted into n-propyl iodide and the latter into propylene by the action of alcoholic potash (Freund, Monats. **3**, 633). Propylene combines with hydrogen iodide to form isopropyl iodide (Berthelot, Ann. **104**, 184; Erlenmeyer, Ann. **139**, 228; Butleroff, Ann. **145**, 275; Michael and Leighton, Journ. pr. Ch. [2] **60**, 447). The latter is converted into the alcohol by heating with water and lead hydroxide or with water only (Flavitzky, Ann. **175**, 380; Niederist, Ann. **186**, 391). Or propylene combines with bromine and the bromide can be converted into propylene glycol (Wurtz, Ann. Chim. [3] **55**, 438; **63**, 124; Henry, Rec. Tr. Ch. **18**, 221). From propylene glycol through propylene oxide as above under A.

Or propylene glycol by the action of hydrogen iodide gives isopropyl iodide (Wurtz, Ann. Suppl. **1**, 381), which can be converted into the alcohol as above.

Or propylene combines with chlorine to form propylene chloride, which by the action of alcoholic potash gives *a*- (with some *β*-) chlorpropylene (Cahours, Jahresber. **1850**, 496; Reboul,

Ann. Chim. [5] **14**, 462). From *a*-chlorpropylene through propylene oxide as above under **A**.

n-Propyl alcohol can also be converted into n-propyl chloride (Pierre and Puchot, Ann. **163**, 266; Ann. Chim. [4] **20**, 234; Malbot, Bull. Soc. [3] **2**, 136). The latter when chlorinated in the presence of aluminium chloride gives propylene chloride (Mouneyrat, Bull. Soc. [3] **21**, 616). Subsequent steps as above.

[**C.**] From *methyl* and *ethyl alcohols* [**13**; **14**] through propane and propyl chloride (see under n-propyl alcohol [**15**; **A**]). From propyl chloride through propylene chloride as above under **B**.

Or from ethyl alcohol through ethylene (see under methane [**1**; **D**]), ethylene bromide, and *glycol* [**45**] (Wurtz, Ann. Chim. [3] **55**, 400; Atkinson, Phil. Mag. [4] **16**, 433; Ann. **109**, 232; Debus, Ann. **110**, 316; Demole, Ann. **173**, 117; **177**, 45; Henry, Ann. Chim. [4] **27**, 250; Jeltekoff, Ber. **6**, 558; Börnstein, Ber. **9**, 480; 917; Zeller and Hüfner, Journ. pr. Ch. [2] **11**, 229; Stempnewsky, Ann. **192**, 240; Erlenmeyer, Ann. **192**, 244; Grosheintz, Bull. Soc. **31**, 293; Pribram and Handl, Monats. **2**, 673; Niederist, Ann. **196**, 354; Beilstein and Wiegand, Ber. **15**, 1368; Bouchardat, Comp. Rend. **100**, 452; Wagner, Ber. **21**, 1234; Haworth and W. H. Perkin, junr., Trans. Ch. Soc. **69**, 175; Henry, Bull. Acad. Roy. Belg. [3] **36**, 9; Rec. Tr. Ch. **18**, 221). Glycol is converted into the chlorhydrin by the action of hydrochloric acid (Wurtz, Ann. **110**, 125; Ladenburg, Ber. **16**, 1408) and into the iodhydrin by the action of potassium iodide on the chlorhydrin (Butleroff and Ossokin, Ann. **144**, 42; Demuth and Meyer, Ann. **256**, 28; Henry, Bull. Acad. Roy. Belg. [3] **18**, 182). The iodhydrin by the action of *zinc methyl* and decomposition of the product with water gives isopropyl alcohol (Butleroff and Ossokin, Ann. **145**, 257; Charon and Paix-Séailles, Comp. Rend. **130**, 1407).

Glycol chlorhydrin = chlorethyl alcohol can also be obtained directly from ethylene and hypochlorous acid (Carius, Ann. **126**, 197; Butleroff, Ann. **144**, 40).

Note :—By the above process all generators of ethylene become with methyl alcohol (for zinc methyl) generators of isopropyl alcohol.

Or from ethyl alcohol through pyrotartaric acid (see under n-propyl alcohol [**15**; **A**]). From the latter by electrolysis as above under **A**.

Or from ethyl alcohol through ethyl cyanide and propylamine and the action of nitrous acid as under n-propyl alcohol [**15**; **A**] (Linnemann and Siersch, Ann. **144**, 140; Linnemann, Ann. **150**, 370; **161**, 44; Ber. **10**, 1111; Meyer and Forster, Ber. **9**, 535; Erlenmeyer, Ber. **30**, 2961).

Also from ethyl alcohol and *bromoform* (see under methane [**1**; **D**]) or *carbon tetrachloride* (see under methane [**1**; **L**]) through propylene (see under glycerol [**48**; **D**]).

From propylene as above under **B**.

[**D.**] From *n-butyl alcohol* [**17**] through 2-iodobutane and propane (see under n-propyl alcohol [**15**; **C**]). From propane through propyl chloride and propylene chloride, &c., as above under **B**.

Or *isobutyl alcohol* [**18**] gives isobutyl chloride or bromide, which yields propylene among other products when passed over soda-lime heated above 600° (Nef, Ann. **318**, 22). Isobutylene from isobutyl alcohol also gives propylene among the products of pyrogenic decomposition (Noyes; Beilstein, 'Handbuch,' I, 115). The vapour of isobutyl alcohol yields propylene among other products when mixed with air and passed over heated platinum (v. Stepski, Monats. **23**, 773).

[**E.**] From *tertiary butyl alcohol* [**19**] through the iodide and propane (**15**; **D**). Subsequent steps as above. Or through isobutylene (see under isobutyl alcohol [**18**; **A**]) and from the latter through propylene as above under **D**.

[**F.**] From *amyl alcohols* of fusel oil [**22**], propylene being among the products formed by passing the vapour through a hot tube (Reynolds, Journ. Ch. Soc. **3**, 111; Ann. **77**, 118; Wurtz, Ann. **104**, 242). From propylene as above under **B**.

[G.] From *glycerol* [48] through propane (15; E) and then as above through propyl and propylene chlorides, &c. Or from glycerol through allyl iodide (see under isobutyl alcohol [18; D]) and propylene; or through allyl alcohol and propylene (see under acetone [106; F]). Or from glycerol through allyl bromide (15; E). The latter gives propylene on heating the alcoholic solution with zinc dust (Wolkoff and Menschutkin, Ber. 31, 3072; Journ. Russ. Soc. 30, 559). Or allyl bromide can be converted into trimethylene (15; E), and this yields propylene when heated to 600° (Tanatar, Zeit. physik. Ch. 41, 735: see also Ber. 32, 702; 1965).

Glycerol gives propylene among the products obtained by distilling it with iodine and phosphorus (Berthelot and De Luca, Ann. 92, 306; Ann. Chim. [3] 44, 350; Oppenheim, Ann. Suppl. 6, 354), or with zinc dust (Westphal, Ber. 18, 2931).

From glycerol through isopropyl iodide by distilling with iodine and phosphorus in presence of water (Erlenmeyer, Ann. 126, 305; 139, 211; Markownikoff, Ann. 138, 364; Meyer, Journ. pr. Ch. [2] 34, 98), and then as above under B.

Or from glycerol through dichlorhydrin by the action of hydrochloric acid (Berthelot, Ann. Chim. [3] 41, 297; Reboul, Ann. Suppl. 1, 222; Carius, Ann. 122, 73; Hübner and Müller, Zeit. [2] 6, 344; Watt, Ber. 5, 257; Claus, Kölver, and Nahmmacher, Ann. 168, 43; Markownikoff, Ann. 208, 358; Fauconnier and Sanson, Bull. Soc. [2] 48, 236; Fauconnier, *Ibid.* 50, 212; Bigot, Ann. Chim. [6] 22, 437). Dichlorhydrin gives isopropyl alcohol among the products of reduction by sodium amalgam (Buff, Ann. Suppl. 5, 250).

Or (indirectly) dichlorhydrin can be converted into 1 : 2 : 3-trichlorpropane (Berthelot and De Luca, Ann. Chim. [3] 48, 304; 52, 433; Fittig and Pfeffer, Ann. 135, 359), α-chlorallyl chloride ($CH_2 : CCl . CH_2Cl$) by the action of potash or triethylamine (Reboul, Ann. Suppl. 1, 229; Comp. Rend. 95, 993), α-chlorallyl alcohol by heating with aqueous potassium carbonate, and then through *acetyl carbinol*, &c., as above under A.

[H.] From *erythritol* [50] through 2-iodobutane and propane (15; F).

[I.] From *mannitol* [51] through 2-iodohexane and propane or through *acroleïn* [101], acrylic acid, &c., to pyrotartaric acid (15; G) and then as above under A.

Or from mannitol through n-hexane (see under n-hexyl alcohol [23; B] and n-propyl alcohol [15; G]). Propylene is formed among other products by passing n-hexane mixed with air over heated platinum (v. Stepski, Monats. 23, 773).

NOTE:—All generators of n-hexane given under n-hexyl alcohol [23], viz. *n-propyl alcohol* [15]; *glycerol* [48]; *suberic acid* [Vol. II]; *acetone* [106], &c., thus become generators, through propylene, of isopropyl alcohol.

[J.] *Thymol* [67] gives propylene on heating with phosphorus pentoxide (Engelhardt and Latschinoff, Zeit. [2] 5, 616). Or from thymol through thymoquinone to succinylsuccinic acid (ester) and ethylmalonic acid as under n-propyl alcohol (15; O; Y; BB). Ethylmalonic acid gives isopropyl alcohol among the products of electrolysis of the solution of the potassium salt (Petersen, Zeit. physik. Ch. 33, 698; Ch. Centr. 1900, 2, 172).

[K.] From *carvacrol* [66] through thymoquinone, &c. (15; CC), and then as above.

[L.] From *aldehyde* [92] through butyrochloral to acrylic and pyrotartaric acids (15; J). From the latter as above under A. Or from aldehyde and *methyl alcohol* by the interaction of magnesium methiodide and the aldehyde (Grignard, Ch. Centr. 1901, 2, 622).

[M.] From *acroleïn* [101] through acrylic to pyrotartaric acid (15; E).

[N.] From *crotonic aldehyde* [102] through crotonic acid to pyrotartaric acid, or through α-brombutyric acid, nitropropane, and n-propylamine (15; I). From the latter as above under C.

[O.] From *acetyl carbinol* [43] as above under A.

[P.] From *dextrose* [157], acetyl carbinol being among the products of fusion with alkali (Emmerling and Loges, Ber. **16**, 837). According to Bouchardat (Comp. Rend. **73**, 1008; Ann. Chim. [4] **27**, 68) isopropyl alcohol is among the products of reduction of dextrose by sodium amalgam.

[Q.] From *pulegone* [128] through pyrotartaric acid (**15**; **L**).

[R.] From *menthone* [129] through pyrotartaric acid (**15**; **M**).

[S.] From *acetic acid* [Vol. II], propylene being among the products formed by passing the vapour over heated zinc dust (Jahn, Ber. **13**, 2111).

Or from acetic acid and *potassium cyanide* [172] and *ethyl alcohol* [14] through pyrotartaric or ethylmalonic acid (**15**; **O**) and then as above under **A** and **J**.

[T.] From *propionic acid* [Vol. II] through the amide, nitrile, and n-propylamine (**15**; **N**) and then as above under **C**. Or from propionic acid through pyrotartaric acid (**15**; **N**).

[U.] From *butyric acid* [Vol. II], isopropyl butyrate being among the products of electrolysis of the acid potassium salt (**15**; **P**). Or from butyric acid through n-propylamine (**15**; **P**) and then as above under **C**.

Or from butyric acid through propane (**15**; **P**) and then as above under **B**. Or from butyric acid through crotonic to pyrotartaric acid (**15**; **P**) and then as above under **A**. Or from butyric acid and *ethyl alcohol* [14] (and *potassium-mercuric cyanide*) through ethylmalonic acid (**15**; **P**) and then as above under **J**.

Butyric acid gives propylene when passed over hot zinc dust (Jahn, Ber. **13**, 2115). Propylene is also among the products of electrolysis of a solution of potassium butyrate (Bunge, Journ. Russ. Soc. **21**, 552; Hamonet, Comp. Rend. **123**, 252; Petersen, Ch. Centr. 1897, **2**, 519). From propylene as above under **B**.

[V.] From *isobutyric acid* [Vol. II] through isopropylamine by the action of bromine in the presence of alkali on isobutyramide (Hofmann, Ber. **15**, 768). From the amine as above under **A** and **C**. Isopropyl isobutyrate and propylene are among the products of electrolysis of a solution of potassium isobutyrate (**15**; **P**; also under **U** above). Isopropyl alcohol is among the products of electrolysis of sodium isobutyrate in presence of sodium perchlorate (Hofer and Moest, Ann. **323**, 284).

Or from isobutyric acid through diisopropyl ketone by distillation of the calcium salt (Popoff, Ber. **6**, 1255; Münch, Ann. **180**, 327). The oxime of the ketone is transformed by acetyl chloride into isopropyl-isobutyramide, which gives isopropylamine (with isobutyric acid) on hydrolysis (Meyer and Warrington, Ber. **20**, 500).

Also from isobutyric acid through propane (**15**; **Q**).

[W.] From *isovaleric acid* [Vol. II], propylene being among the products of pyrogenic decomposition (Hofmann, Journ. Ch. Soc. **3**, 121). Propylene is among the products of the dry distillation of calcium isovalerate (Dilthey, Ber. **34**, 2115). Or from isovaleric acid through hydroxypyrotartaric, citraconic, and pyrotartaric acids (benzyl alcohol [**54**; **M**]).

[X.] From *lactic acid* [Vol. II], which gives propylene among the products of distillation of the calcium salt (Gossin, Bull. Soc. [2] **43**, 49). Or from lactic acid through acrylic or citraconic acid to pyrotartaric acid (**15**; **R**).

[Y.] From *hydracrylic acid* [Vol. II] through acrylic acid to pyrotartaric acid (**15**; **S**).

[Z.] From *β-hydroxybutyric acid* [Vol. II] through crotonic acid to nitropropane and n-propylamine (**15**; **U**) and then as above under **C**.

[AA.] From *oxalic* and *acetic* acids [Vol. II], propylene being among the products of dry distillation of a mixture of calcium oxalate and potassium acetate (Dusart, Ann. **97**, 127). Or from oxalic and acetic acids and *ethyl alcohol* [14] through pyrotartaric or through ethylmalonic acid (**15**; **Z**). Or from *oxalic* and *propionic acids* and *alcohol* [14] through β-methylmalic to citraconic and pyrotartaric acid (benzyl alcohol [**54**; **M**]).

[BB.] From *malonic acid* [Vol. II] and *ethyl alcohol* [14] through ethylmalonic acid (15 ; T). Or from malonic acid, *aldehyde* [92], and *acetic acid* through crotonic acid to nitropropane and n-propylamine (*Ibid.*). Or from malonic acid and *alcohol* [14] and *methyl iodide* [13] through propanetricarboxylic and pyrotartaric acids (*Ibid.*). Or from *malonic* and *propionic acids* through propanetricarboxylic ester, citraconic and pyrotartaric acid (benzyl alcohol [54; M]).

[CC.] From *succinic acid* [Vol. II] and *ethyl alcohol* [14] through ethylmalonic or pyrotartaric acid (15 ; Y).

[DD.] From *azelaïc acid* [Vol. II], propylene being among the products of distillation with soda-lime (Miller and Tschitschkin, Journ. Russ. Soc. 31, 414; Ann. 307, 375).

[EE.] From *acetoacetic acid* (ester) [Vol. II] through pyrotartaric acid or n-propylamine or ethylmalonic acid (15 ; AA ; and benzyl alcohol, 54 ; I).

[FF.] From *malic acid* [Vol. II] through pyrotartaric or ethylmalonic acid (15 ; DD).

[GG.] From *fumaric* or *maleïc acid* [Vol. II] through pyrotartaric or ethylmalonic acid (15 ; EE).

[HH.] From *tartaric acid* [Vol. II] through pyrotartaric acid (15 ; V).

[II.] From *citric acid* [Vol. II] through pyrotartaric acid (15 ; W).

[JJ.] From *aconitic acid* [Vol. II] through itaconic to pyrotartaric acid (15 ; X).

[KK.] From *glycocoll* [Vol. II] *ethyl ester* [14] through n-propylamine (15 ; GG) and then as above under C.

[LL.] From *alanine* [Vol. II] and *methyl alcohol* [13] through acrylic to pyrotartaric acid (15 ; HH).

[MM.] From *allyl isothiocyanate* [166] through allyl cyanide to crotonic acid (15 ; FF). From crotonic acid through nitropropane and n-propylamine or through pyrotartaric acid (15 ; I).

[NN.] *Choline* [Vol. II] gives *glycol* [45] on boiling the aqueous solution (Wurtz, Ann. Suppl. 6, 200). From glycol and *zinc methyl* as above under C.

[OO.] From *acetyl carbinol* [43] as above under A.

[PP.] From *isobutyric aldehyde* [94], which condenses under the influence of alcoholic potash to form 2 : 2 : 4-trimethylpentane-1 : 3-diol (Fossek, Monats. 4, 664 ; Brauchbar, *Ibid.* 17, 641). The latter on oxidation with potassium permanganate gives diisopropyl ketone (Lieben : Franke, Monats. 17, 92 ; 673). From the ketone through the oxime to isopropylamine as above under V.

17. Normal Butyl Alcohol ; Normal Propyl Carbinol ; 1-Butanol.

$CH_3 . CH_2 . CH_2 . CH_2 . OH$

Natural Sources.

A product of fermentation of glycerol in presence of calcium carbonate by *Bacillus butylicus* and other Schizomycetes (Fitz, Ber. 9, 1348 ; 10, 276 ; 2226 ; 11, 42 ; 13, 1311 ; Vigna, Ber. 16, 1438 ; Emmerling, Ber. 29, 2726 ; 30, 451). Butyl alcohol is formed also from mannitol (Fitz, Ber. 10, 280 ; 11, 42 ; 15, 875 ; Emmerling, Ber. 30, 452) and from saccharose by this *Bacillus* (Fitz, Ber. 15, 876), which cannot produce butyl alcohol from dextrose (Emmerling, *loc. cit.* 453).

The butyl alcohol producing *Bacillus* has been found on hay and on rotten wood and is not identical with *Granulobacter saccharobutyricum* of Beyerinck (Centr. Bakter. 15, 171), which can produce butyl alcohol from dextrose and starch, but not from glycerol (Emmerling, Ber. 30, 453).

Granulobacter polymyxa, Beyerinck (= ? *Clostridium polymyxa*, Prazmowski), gives a trace of butyl alcohol when grown anaerobically (Lafar's 'Technical Mycology, I,' 189, &c.).

Micrococcus acidi paralactici and the *Bacillus* of symptomatic anthrax when grown together in a nutrient solution containing saccharose produce butyl alcohol (Nencki ; Centr. Bakter. 11, 225 ; see also Lafar, 'Techn. Mycol.' I, 87).

Bacteria from blue pus can produce butyl alcohol from glycerol during butyric fermentation (Fitz, Ber. 11, 1893).

The species of butyric ferments com-

prised under *Clostridium butyricum* of Prazmowski (= *Bacillus amylobacter*, Van Tieghem) can produce butyl alcohol from carbohydrates (Gruber; quoted by Jörgensen, 'Mikroorganismen,' &c. p. 87).

Butyl alcohol is formed during the butyric fermentation of milk by *Bacillus butyricus* of Bodkin (Ch. Centr. 1891, **1**, 183; 1892, **1**, 484). A butyl alcohol (? normal) occurs in rancid butter, probably a bacterial product (Nagel, Am. Ch. Journ. **23**, 172).

Bacillus orthobutylicus from fermenting calcium tartrate solution ferments saccharose, lactose, maltose, glucose, galactose, mannitol, glycerol, glycogen, arabinose, inulin, and starch with the production of butyl alcohol among other products (Grimbert, Ann. Inst. Past. **7**, 353). *Amylobacter butylicum* and *A. æthylicum* of Duclaux produce small quantities of butyl alcohol during the fermentation of glycerol, glucose, saccharose, maltose, lactose, and starch (Duclaux, Ann. Inst. Past. **9**, 811).

n-Butyl alcohol has been said to be a constituent of the fusel oils of brandy (Ordonneau, Comp. Rend. **102**, 217; Claudon and Morin, *Ibid.* **104**, 1187) and potato starch spirit (Rabuteau, *Ibid.* **87**, 501: see also Allen, Journ. Fed. Inst. **3**, 33). According to Bannow (Meyer and Jacobson's 'Lehrbuch d. org. Ch.' I, 161, note) n-butyl alcohol is not a normal constituent of fusel oil. Emmerling has found n-butyl alcohol (2·5 grams from 10 kilos.) in fusel oil from grain spirit (Ber. **35**, 694).

Synthetical Processes.

[A.] From *ethyl alcohol* [14], n-butyl alcohol being among the products formed by heating barium ethylate and ethyl alcohol to 230–240° (Guerbet, Comp. Rend. **133**, 300; Bull. Soc. [3] **27**, 578).

Or from ethyl alcohol through butane from ethyl iodide (Frankland, Ann. **71**, 173; **77**, 221; Schöyen, Ann. **130**, 233; Löwig, Jahresber. **1860**, 397). From butane through n-butyl chloride by chlorination (Schöyen, *loc. cit.* 235). Butyl chloride can be converted into the alcohol by the usual methods (see under methyl alcohol [13; B]; ethyl alcohol [14; D]).

Or from ethyl and *methyl alcohols* [14; 13] and *potassium cyanide* [172]. Methyl iodide is converted into methyl cyanide (see under ethyl alcohol [14; D]), and this by the action of sodium and ethyl iodide gives n-propyl cyanide (Holtzwart, Journ. pr. Ch. [2] **39**, 233). The latter reduces to n-butylamine (Linnemann and Zotta, Ann. **162**, 3), which yields the alcohol on treatment with nitrous acid (*Ibid.*; also Victor Meyer, Ber. **10**, 130: methylethyl carbinol is the chief product by this method).

[B.] From *normal propyl alcohol* [15] through n-propyl iodide and cyanide (Schmidt, Zeit. [2] **6**, 576). From the latter through n-butylamine as above.

Or from n-propyl and *methyl alcohol* [13] through n-butane by combining the alkyls by the method of Wurtz (see under n-heptane [2; A]). From butane through butyl chloride as above.

From n-propyl alcohol and trioxymethylene (*formic aldehyde* [91]) by the interaction of magnesium propyl bromide and trioxymethylene (Grignard and Tissier, Comp. Rend. **134**, 107).

[C.] From *isoamyl alcohol* [22], isoamyl iodide giving butane when heated with aluminium chloride to 140° (Lothar Meyer, Ber. **27**, 2766).

[D.] From *glycerol* [48] through allyl iodide (see under isobutyl alcohol [18; D]), diallyl (1 : 5-hexadiene) by the action of sodium, &c., on the iodide (Berthelot and De Luca, Ann. **100**, 361; Wurtz and Leclanché, Ann. Chim. [4] **3**, 129; Linnemann, Bull. Soc. [2] **7**, 424; Ann. **140**, 180; Oppenheim, Ber. **4**, 672). Diallyl combines with hydrogen iodide to form a dihydriodide, which by the action of sodium gives β-hexylene. The latter combines with hydrogen iodide to form secondary hexyl iodide (2-iodohexane) (Wurtz, Ann. **132**, 306), and this yields butane on heating to 128° with aluminium chloride (Lothar Meyer, Ber. **26**, 2070; **27**, 2766).

[E.] From *mannitol* [51] through

secondary hexyl iodide (see under n-propyl alcohol [15 ; G]) ; from the latter as above under D.

Or secondary hexyl iodide can be converted into n-hexane (see under n-hexyl alcohol [23 ; B]). The latter on heating with aluminium chloride breaks down into pentane and the latter into butane (Friedel and Gorgeu, Comp. Rend. **127**, 590).

NOTE :—Generators of pentane (see under n-amyl alcohol [20 ; B ; C ; D]) and of hexane (see under n-hexyl alcohol [23 ; A ; B ; C ; &c.]) thus become generators of n-butyl alcohol through butane.

[F.] From *formic aldehyde* [91] and *n-propyl alcohol* [13]. Trioxymethylene (polymerisation product of the aldehyde) and zinc propyl form a compound which is decomposed by water with the formation of n-butyl alcohol (Tischtschenko, Journ. Russ. Soc. **19**, 484: see B, above).

[G.] From *acetic aldehyde* [92] through *crotonic aldehyde* [102] by condensation (Lieben, Ann. Suppl. **1**, 117 ; Bauer, Ann. **117**, 141 ; Kekulé, Ann. **162**, 92 ; Zeit. [2] **5**, 572 ; Lieben and Zeisel, Monats. **1**, 820 ; Newbury and Calkin, Am. Ch. Journ. **12**, 523 ; Orndorff and Newbury, Monats. **13**, 513 ; Lieben, *Ibid.* 519 ; Müller, Bull. Soc. [3] **6**, 796 ; Claisen, Ann. **306**, 322 ; Charon, Ann. Chim. [7] **17**, 197 ; Delépine, Comp. Rend. **133**, 876). The aldehyde is reduced by iron and acetic acid to n-butyl alcohol (with butyric aldehyde and crotonyl = butenyl alcohol) (Lieben and Zeisel, *loc. cit.* 825 ; 842).

Or from aldehyde through β-hydroxybutyric aldehyde (aldol) by condensation with acid or alkaline condensing agents (Wurtz, Comp. Rend. **74**, 1361 ; **76**, 1165 ; **92**, 1438 ; Jahresber. **1872**, 449 ; **1881**, 599 ; Michael and Kopp, Am. Ch. Journ. **5**, 185 ; Orndorff and Newbury, Monats. **13**, 516 ; Claisen, Ann. **306**, 323). Aldol gives β-butyleneglycol on reduction with sodium amalgam (Wurtz, Comp. Rend. **97**, 473 ; Demjanoff, Ber. **28**, 22). From the glycol through 1 : 3-dibrombutane and methylcyclopropane as below under P.

NOTE :—Aldol gives crotonic aldehyde on dry distillation (Wurtz, Comp. Rend. **87**, 45 ; Orndorff and Newbury, *loc. cit.*).

[H.] From *butyric aldehyde* [94] by reduction with sodium amalgam (Lieben and Rossi, Ann. **158**, 137 ; **165**, 145).

[I.] From *formic acid* [Vol. II] and *erythritol* [50], which give *crotonic aldehyde* [102] on distillation (Henninger, Ann. Chim. [6] **7**, 217), and then as above under G.

NOTE :—Other generators of crotonic aldehyde are : *aldol* (from aldehyde ; Wurtz, Jahresber. **1878**, 612 ; Newbury, Am. Ch. Journ. **5**, 112 ; Comp. Rend. **92**, 196) : *acetylene* by the successive action of sulphuric acid and water (Lagermarck and Eltekoff, Ber. **10**, 637 ; Berthelot, Comp. Rend. **128**, 336) : vinyl bromide from *ethylene bromide* by the same treatment (Zeisel, Ann. **191**, 371) : the *lactic acids* [Vol. II] by electrolysis of strong solutions of the sodium salts (v. Miller and Hofer, Ber. **27**, 468) : *β-hydroxybutyric acid* [Vol. II] by electrolysis of the sodium salt (*Ibid.* 469).

[J.] From *acetic acid* [Vol. II] and *ethyl alcohol* [14]. Ammonium acetate is converted into acetamide and acetonitrile = methyl cyanide (Dumas, Comp. Rend. **35**, 383 ; Buckton and Hofmann, Journ. Ch. Soc. **9**, 242 ; Henry, Ann. **152**, 149 ; Wallach, Ann. **184**, 21 ; Demarçay, Bull. Soc. [2] **33**, 456). From methyl cyanide and ethyl iodide through n-propyl cyanide, n-butylamine, &c., as above under A.

Or from *acetic* and *formic ethyl esters* [Vol. II ; and 14], which condense under the influence of sodium ethoxide to form formylacetic = oxymethyleneacetic ester (Wislicenus, Ber. **20**, 2930 : see also v. Pechmann, Ann. **264**, 269), which undergoes further condensation when liberated from its sodium derivative to form formylglutaconic ester (Wislicenus and Bindemann, Ann. **316**, 18). Formylglutaconic acid gives the lactone, coumalic acid, and this on heating with sulphuric acid yields *crotonic aldehyde* [102], which can be reduced as above under G.

[K.] *Propionic acid* [Vol. II] gives butane among the products of electrolysis of the potassium salt (Bunge, Journ. Russ. Soc. **21**, 551 ; Petersen, Ch. Centr. 1897, **2**, 518).

[L.] From *butyric acid* [Vol. II] through butyryl chloride, which gives the alcohol on reduction with sodium amalgam (Saytzeff, Zeit. [2] **6**, 108 ; Linnemann, Ann. **161**, 178) or with

sodium in moist ethereal solution (W. H. Perkin, junr., and Sudborough, Proc. Ch. Soc. **10**, 216).

Or from butyric acid through butyronitrile = n-propyl cyanide by distilling the ammonium salt or amide with phosphorus pentoxide (Dumas, Malaguti, and Leblanc, Comp. Rend. **25**, 442; 658; Ann. **64**, 332) or with zinc chloride (Linnemann and Zotta, Ann. **162**, 3; also Aschan, Ber. **31**, 2344). From the nitrile to n-butylamine, &c., as above under **A**.

Butyric acid gives butane by heating with hydriodic acid (Berthelot; see under methane [**1**; **I**]).

[**M.**] *Succinic acid* [Vol. II] gives butane on heating with hydriodic acid (Berthelot, *loc. cit.*).

[**N.**] *Adipic acid* [Vol. II] gives butane by distilling the calcium salt with excess of lime (Hanriot, Bull. Soc. [2] **45**, 80).

[**O.**] *Malic acid* [Vol. II] on heating with strong sulphuric acid or zinc chloride gives coumalic acid (v. Pechmann, Ann. **264**, 272). Subsequent steps through crotonic aldehyde, &c., as above under **J** and **G**. Crotonic aldehyde is among the products of electrolysis of a strong solution of sodium malate (v. Miller and Hofer, Ber. **27**, 470).

[**P.**] From *tetramethylenediamine* (*putrescine*) [Vol. II] through β-butyleneglycol by the action of nitrous acid (Demjanoff, Journ. Russ. Soc. **24**, 354), 1 : 3-dibrombutane by heating the glycol with hydrobromic acid (*Ibid.* 351), and methylcyclopropane by the action of zinc dust on the alcoholic solution of the dibrombutane (*Ibid.* Ber. **28**, 21). Methylcyclopropane gives n-butyl alcohol on treatment with strong sulphuric acid and distillation of the product with water (*Ibid.* 23).

18. Isobutyl Alcohol; Isopropyl Carbinol; 2-Methyl-1-Propanol.

$CH_3 . CH(CH_3) . CH_2 . OH$

Natural Sources.

A secondary product of alcoholic fermentation as a constituent of the fusel oils from beet molasses spirit, potato spirit, and brandy (Wurtz, Ann. Chim. [3] **42**, 129; Ann. **85**, 197; **93**, 107; Comp. Rend. **35**, 310; Chapman and Smith, Ber. **2**, 127; Krämer and Pinner, *Ibid.* 403; **3**, 77; Rabuteau, Comp. Rend. **87**, 501; Claudon and Morin, *Ibid.* **104**, 1109 and 1187; Bull. Soc. [2] **49**, 178).

Isobutyl esters of angelic and other acids occur in Roman oil of chamomile from *Anthemis nobilis* (Demarçay, Comp. Rend. **77**, 360; **80**, 1400; Fittig and Köbig, Ann. **195**, 79; 81; 92).

Isobutyl alcohol is found in traces (with the n-alcohol) among the products of the fermentation of the various carbohydrates capable of being attacked by the *Bacillus orthobutylicus* of Grimbert (Ann. Inst. Past. **7**, 353: see also under n-butyl alcohol [**17**]), the *Bacillus* isolated from fermenting calcium tartrate solution.

Synthetical Processes.

[**A.**] From *tertiary butyl alcohol* [**19**] through isobutylene by the action of alcoholic potash on the tertiary butyl iodide or by heating the alcohol with dehydrating agents (Butleroff, Ann. **144**, 19; Zeit. [2] **6**, 236: see also Lermentoff, Ann. **196**, 117). Isobutylene combines with hypochlorous acid to form chlorisobutyl alcohol, and this on reduction with sodium amalgam gives isobutyl alcohol (Butleroff, Ann. **144**, 24).

Note :—Tertiary butyl alcohol gives a butylene on heating with anhydrous oxalic acid (Cahours and Demarçay, Comp. Rend. **86**, 991).

[**B.**] From *isoamyl alcohol* [**22**], isobutylene being among the products of pyrogenic contact decomposition by passing the vapour through a hot iron tube (Ipatieff, Ber. **35**, 1053: see also Wurtz, Ann. **104**, 249; Butleroff, Ann. **145**, 277).

[**C.**] From *isovaleric acid* [Vol. II] by electrolysis of a solution of the potassium salt (Kolbe, Ann. **69**, 259). Isobutylene is among the products formed and can be treated as under **A**. Isobutylene is among the products of

the dry distillation of calcium isovalerate (Dilthey, Ber. **34**, 2115).

Also from this acid by oxidation with alkaline permanganate to β-hydroxyisovaleric acid [$(CH_3)_2 : C(OH) . CH_2 . COOH$] (v. Miller, Ann. **200**, 273), β-dimethylacrylic acid [$(CH_3)_2 : C : CH . COOH$] by distillation with dilute sulphuric acid (Neubauer, Ann. **106**, 62; v. Miller, *loc. cit.* 261), conversion into isobutylene by heating to 210–220° (Gorboff and Kessler, Bull. Soc. [2] **41**, 392), and then as under **A**.

β-Hydroxyisovaleric acid is also converted into β-dimethylacrylic acid (ethyl ester) by the action of phosphorus trichloride on ethyl β-hydroxyisovalerate (Semljanitzin and Saytzeff, Ann. **197**, 72; Ustinoff, Journ. pr. Ch. [2] **34**, 478; Bull. Soc. [2] **45**, 255). Also from isovaleric acid through the α-bromo-acid (Borodin, Ann. **119**, 122; Cahours, Ann. Suppl. **2**, 78; Fittig and Clark, Ann. **139**, 199; Ley and Popoff, Ann. **174**, 63) and the action of sodium ethylate or ammonia on α-bromisovaleric ester (Duvillier, Comp. Rend. **88**, 913; 1209; **112**, 1012; Ann. Chim. [5] **19**, 428; Bull. Soc. [3] **5**, 848): β-dimethylacrylic acid is one of the products formed and can be converted into isobutylene as above.

Ethyl β-dimethylacrylate is obtained by the action of diethylaniline or of quinoline on α-bromisovaleric ester (Weinig, Ann. **280**, 253; W. H. Perkin, junr., Trans. Ch. Soc. **69**, 1471).

[**D.**] From *acetone* [**106**] and *glycerol* [**48**] by converting the latter into allyl iodide (Berthelot and De Luca, Ann. Chim. [3] **43**, 258; Tollens, Bull. Soc. [2] **9**, 396; Claus, Ann. **131**, 59; Oppenheim, Ann. Suppl. **6**, 354; Tollens and Henninger, Ann. **156**, 156; Wagner, Ber. **9**, 1810; Kanonnikoff and Saytzeff, Ann. **185**, 191; James, Ann. **226**, 206; Béhal, Bull. Soc. [2] **47**, 875; Malbot, Ann. Chim. [6] **19**, 355 and 363), and allowing zinc to act upon a mixture of acetone and allyl iodide so as to form dimethylallyl carbinol [$CH_2 : CH . CH_2 . C(CH_3)_2 . OH$] (Saytzeff, Ann. **185**, 151 and 175); oxidation of the latter to β-hydroxyisovaleric acid (Saytzeff, Ann. **185**, 163; Schirokoff, Journ. pr. Ch. [2] **23**, 206); then to β-dimethylacrylic acid and isobutylene as under **C**.

A mixture of acetone, *malonic acid*, and *acetic anhydride* gives dimethylacrylic acid on heating (Massot, Ber. **27**, 1225). Acetone and *acetoacetic ester* condense under the influence of hydrogen chloride to form isopropylideneacetoacetic ester, and this on boiling with barium hydroxide solution yields dimethylacrylic acid (Pauly, Ber. **30**, 481).

Also from acetone and *acetic acid* by converting the latter into chloracetic ethyl ester (Willm, Ann. **102**, 109; Conrad, Ann. **188**, 218) and allowing zinc to act upon a mixture of acetone and the ester so as to form ethyl β-hydroxyisovalerate (Reformatsky, Journ. Russ. Soc. **22**, 47), which can be hydrolysed and treated as above.

The 'acetone-chloroform' referred to under tertiary butyl alcohol [**19**; **D**] gives isobutylene on boiling with alcohol and zinc dust (Jocitsch, Journ. Russ. Soc. **30**, 920; Ch. Centr. 1899, **1**, 606).

[**E.**] *Isobutyric aldehyde* [**94**] gives isobutyl alcohol (with isobutyric acid) on heating with barium hydroxide solution (Lederer, Monats. **22**, 536).

19. Tertiary Butyl Alcohol; Trimethyl Carbinol; 2-Methyl-2-Propanol.

$CH_3 . C(CH_3)(OH) . CH_3$

Natural Source.

Has been said to occur in small quantity in certain fusel oils (Rabuteau, Comp. Rend. **87**, 501; Butleroff, Ann. **144**, 34; Trommsdorf, as quoted by Meyer and Jacobson, 'Lehrb. d. org. Ch.' p. 161). It is probable, however, that the alcohol thus obtained was formed from isobutyl alcohol during the process of treatment (Meyer and Jacobson, *loc. cit.*).

Synthetical Processes.

[A.] From *acetic acid* [Vol. II] and *methyl alcohol* [13] through the compound formed by the interaction of zinc methyl and acetyl chloride and decomposition of this compound by water (Butleroff, Jahresber. **1864**, 496; Ann. **144**, 1; Wagner and Saytzeff, Ann. **175**, 361; Pawloff, Ann. **188**, 118). The same intermediate compound is formed from zinc methyl and carbonyl chloride (Butleroff, Zeit. **1863**, 484). Magnesium methyl and acetyl chloride can be used also in this synthesis (Fleck, Ann. **276**, 129). Or magnesium methiodide and methyl acetate (Grignard, Comp. Rend. **132**, 336), or magnesium methiodide and acetyl chloride (Tissier and Grignard, *Ibid.* 683).

Or from dichloracetic acid through dichloracetyl chloride (Otto and Beckurts, Ber. **14**, 1618), which, by interaction with zinc methyl and decomposition of the product with water, gives dimethylisopropyl carbinol (Bogomoletz, Ann. **209**, 82). Subsequent steps through pinacone, pinacolin, trimethylacetic acid, &c., as below under **D** and **E**.

Isobutylene is among the products formed by dropping acetic acid on to heated zinc chloride (LeBel and Greene, Am. Ch. Journ. **2**, 26).

[B.] From *isobutyl alcohol* [18] through isobutylene by heating with sulphuric acid (Lermentoff, Ann. **196**, 117; Puchot, Ann. Chim. [5] **28**, 508; Comp. Rend. **85**, 757: for use of zinc chloride as a dehydrating agent see Nevolé, Bull. Soc. [2] **24**, 122: see also Konowaloff, Ber. **13**, 2395; Bull. Soc. [2] **34**, 333, and Scheschukoff, Journ. Russ. Soc. **16**, 510: with the ordinary dehydrating agents, Konowaloff, *loc. cit.*; LeBel and Greene, Bull. Soc. [2] **29**, 306, or with heated plumbago crucible material as pyrogenic contact substance, Ipatieff, Ber. **35**, 1061, pseudobutylene is also formed: see further Faworsky and Desbout, Journ. pr. Ch. [2] **42**, 152; Ipatieff, *loc. cit.*: for production of isobutylene by passing the vapour of the alcohol mixed with air over heated platinum see v. Stepski, Monats. **23**, 773). Isobutylene is formed also by the action of alcoholic potash on isobutyl iodide (Butleroff, Ann. **144**, 19; Zeit. [2] **6**, 278: see also De Luynes, Comp. Rend. **56**, 1175; Ann. Chim. [4] **2**, 385) or chloride (Nef, Ann. **318**, 28). Isobutylene on treatment with sulphuric acid and hydrolysis gives tertiary butyl alcohol (Butleroff, Ann. **144**, 22; **180**, 246); or by combination with zinc chloride it forms a crystalline compound which yields tertiary butyl alcohol on decomposition with water (Kondakoff, Journ. Russ. Soc. **25**, 345 and 456; also Journ. pr. Ch. [2] **54**, 442). Isobutylene is converted into tertiary butyl alcohol by the action of aqueous oxalic acid (Miklaschewsky, Journ. Russ. Soc. **22**, 495). On combination with hydrogen iodide isobutylene gives tertiary butyl iodide (Butleroff, Ann. **144**, 22; Markownikoff, Zeit. [2] **6**, 29), which can be converted into the alcohol by the action of water (Scheschukoff, Bull. Soc. [2] **45**, 181; Dobbin, Trans. Ch. Soc. **37**, 238).

Isobutyl iodide on treatment with acetic acid and silver oxide gives also tertiary (with isobutyl) alcohol (Linnemann, Ann. **162**, 12; Butleroff, Ann. **168**, 143).

Isobutyl alcohol can also be converted into isobutyl chloride by the action of hydrogen chloride, and then into isobutylene by the action of aluminium chloride on isobutyl chloride (Mouneyrat, Ann. Chim. [7] **20**, 485).

Also from isobutyl alcohol through isobutylamine by the action of ammonia on the iodide or bromide (Reimer, Ber. **3**, 756; Hughes and Römer, Ber. **7**, 511) or chloride (Malbot, Bull. Soc. [2] **47**, 957; [3] **4**, 693; Comp. Rend. **104**, 63; 228) and the action of nitrous acid on isobutylamine (Linnemann, Ann. **162**, 24). Isobutylamine can also be obtained from the alcohol by heating with ammonio-zinc chloride (Merz and Gasiorowski, Ber. **17**, 623). Tertiary butyl alcohol is obtained also from isobutyl iodide through the cyanate (Brauner, Ber. **12**, 1874) and the action

of potash on the latter (Linnemann, Ann. **162**, 12).

Also from isobutyl alcohol by heating with hydrochloric acid and decomposing the tertiary chloride by heating with water, the isobutyl chloride simultaneously formed remaining undecomposed (Freund, Journ. pr. Ch. [2] **12**, 25).

Isobutyl alcohol, when converted into isobutylsulphuric acid and the barium salt of the latter heated to 130°, gives a mixture of isobutylene ($\frac{2}{3}$) and pseudobutylene ($\frac{1}{3}$) (Biron, Journ. Russ. Soc. **29**, 697).

[**C.**] From *isovaleric acid* [Vol. II] through isobutylamine by the action of bromine and potash on the amide (Hofmann, Ber. **15**, 769) and then as under **B**. Also from isovaleric acid through isobutylene (see under isobutyl alcohol [**18**; **C**]).

[**D.**] From *acetone* [**106**] and *glycerol* [**48**] through β-dimethylacrylic acid (see under isobutyl alcohol [**18**; **D**] and isobutylene as above. Or from acetone and *acetic acid* through β-hydroxyisovaleric ester and isobutylene as under isobutyl alcohol [**18**; **D**].

Also from acetone and *chloroform* [**1**; **D**] through 'acetone chloroform,' $CCl_3 . C(CH_3)_2 . OH$ (Willgerodt and Genieser, Journ. pr. Ch. [2] **37**, 364; also Willgerodt, Ber. **14**, 2451; **16**, 1585; Cameron and Holly, Journ. Physical Ch. **2**, 322), and reduction of the latter with zinc and hydrochloric acid at 100° (Willgerodt and Dürr, Journ. pr. Ch. [2] **39**, 287).

Also in small quantity from acetone and methyl iodide by the action of sodium on the moist ethereal solution (Frey, Ber. **28**, 2520). Or to the extent of 70 per cent. from acetone by interaction with magnesium methiodide (Grignard, Ch. Centr. 1901, **2**, 623).

Or from acetone through pinacone (=tetramethylethylene glycol) by the action of sodium (Fittig, Ann. **110**, 25; **114**, 54; Städeler, Ann. **111**, 277; Friedel, Ann. **124**, 329; Bull. Soc. [2] **19**, 289; Friedel and Silva, Ber. **6**, 35; 267; Jahresber. **1873**, 340; Thiele, Ber. **27**, 455), or by electrolysis (Merck, Germ. Pat. 113719 of 1899; Ch. Centr. 1900, **2**, 794), pinacolin (= dimethylbutanone) by distilling pinacone with dilute sulphuric acid (Fittig, Ann. **114**, 56: see also Vorländer, Ber. **30**, 2266), trimethylacetic = pivalic acid by the oxidation of pinacolin (Friedel and Silva, Comp. Rend. **77**, 48; Reformatzky, Ber. **23**, 1596). The acid gives trimethyl carbinol when the potassium salt is electrolysed in aqueous solution (Petersen, Zeit. physik. Ch. **33**, 698).

[**E.**] From *isobutyric acid* [Vol. II], the calcium salt of which gives pinacolin on distillation (Barbaglia and Gucci, Ber. **13**, 1572), and then as above.

Or from isobutyric acid and methyl alcohol through dimethylisopropyl carbinol, which is formed by the interaction of isobutyl chloride and zinc methyl and decomposition of the product with water (Prianischnikoff, Zeit. [2] **7**, 275). The tertiary hexyl iodide corresponding to the alcohol on treatment with alcoholic potash gives tetramethylethylene (Pawloff, Ann. **196**, 124), and the bromide of the latter on treatment with silver acetate and hydrolysis yields pinacone (*Ibid.* 126). Or the dimethylisopropyl alcohol gives tetramethylethylene on distillation with sulphuric acid (Reformatsky and Plescanossoff, Ber. **28**, 2841).

[**F.**] From *amyl alcohol* [**22**] and *methyl alcohol* [**13**] through trimethylethylene (see under acetone [**106**; **E**]), which gives tetramethylethylene on heating with lead and methyl iodide at 220–230° (Eltekoff, Journ. Russ. Soc. **14**, 380). Subsequent steps through pinacone as above. Or from fusel oil amyl alcohol through isobutylene by pyrogenic decomposition (see under isobutyl alcohol [**18**; **B**]) and then as under **B** above.

[**G.**] From *ethyl* [**14**] and *methyl alcohol* [**13**] through chloral (Liebig, Ann. **1**, 189), which by interaction with zinc methyl gives dimethylisopropyl carbinol (Rizza, Journ. Russ. Soc. **14**, 99).

[**H.**] From *propionic acid* [Vol. II] and *methyl alcohol* [**13**]. α-Brompropionic acid (Friedel and Machuca, Ann.

120, 286; Zelinsky, Ber. **20**, 2026; Michael and Graves, Ber. **34**, 4044) gives brompropionyl bromide (Kaschirsky, Journ. Russ. Soc. **13**, 81), which by interaction with zinc methyl yields dimethylisopropyl carbinol (*Ibid.* 82).

[I.] From *lactic acid* [Vol. II] and *methyl alcohol* [13]. Lactic acid reacts with hydrogen bromide to form α-brompropionic acid (Kekulé, Ann. **130**, 16). Subsequent steps as above under **H**, &c.

[J.] From *diacetyl* [113] and *methyl alcohol* [13] through pinacone by the interaction of magnesium methiodide and the former (Zelinsky, Ber. **35**, 2138). From pinacone through pivalic acid as above under **D**.

20. Normal Primary Amyl Alcohol; Normal Butyl Carbinol; 1-Pentanol.

$CH_3 . CH_2 . CH_2 . CH_2 . CH_2 . OH$

Natural Sources.

Said to occur in certain fusel oils (Wischnegradsky, Ann. **190**, 350) and among the products of fermentation of glycerol by *Bacillus butylicus* (Morin, Bull. Soc. [2] **48**, 803).

Synthetical Processes.

[A.] From *normal valeric (pentanoic) acid* [Vol. II] through the *aldehyde* [95] by distillation with a *formate* (Lieben and Rossi, Ann. **159**, 70) and reduction with sodium amalgam (*Ibid.*).

Note:—The generators of valeric aldehyde given under this compound are: *succinic acid*; *fumaric acid*; *adipic acid*; *stearic acid* (all through sebacic acid); and *n-hexoic acid*.

[B.] From *acetic acid* [Vol. II] by combining acetyl chloride with aluminium chloride, decomposing the product with water (Combes, Ann. Chim. [6], **12**, 207), and reducing the acetylacetone (2 : 4-pentanedione) thus formed to n-pentane by heating with hydriodic acid (Combes, *loc. cit.* 233). Normal pentane gives 1-chlorpentane (together with 2-chlorpentane) on chlorination (Schorlemmer, Ann. **161**, 268; Lachowicz, Ann. **220**, 191), and the corresponding alcohol is obtained by conversion into amyl acetate and hydrolysis (*Ibid.*).

Note:—Normal pentane might also be synthesised from *methyl* [13] and *n-butyl* [17] *alcohols* or from *ethyl* [14] and *n-propyl* [15] *alcohols* by acting upon mixtures of the alkyl iodides with sodium (Wurtz, Ann. Chim. [3] 44, 275: see also under heptane [2; A]).

[C.] From *acetone* [106], *acetic acid* [Vol. II], and *ethyl alcohol* [14] through acetylacetone by the action of sodium on a mixture of acetone and ethyl acetate (Claisen and Ehrhardt, Ber. **22**, 1011; Claisen, Ann. **277**, 168), reduction to pentane, &c., as under **B**.

[D.] From *pyridine* or *piperidine* [Vol. II] through n-pentane by heating with hydriodic acid to over 300° (Hofmann, Ber. **16**, 590; Spindler, Journ. Russ. Soc. **23**, 39) and then as under **B**.

[E.] From *normal hexoic acid* [Vol. II] by the action of iodine on the silver salt (Simonini, Monats. **13**, 316) and hydrolysis of the amyl hexoate formed.

Or from n-hexoic acid through n-amylamine (1-aminopentane) by the action of bromine in presence of potash on the amide of the acid (Hofmann, Ber. **15**, 770), followed by the action of nitrous acid on the amine (Gartenmeister, Ann. **233**, 253).

[F.] From *adipic acid* [Vol. II] through sebacic acid by electrolysis of potassium ethyl adipate and hydrolysis of the ester (Crum Brown and Walker, Ann. **261**, 120). Sebacic acid when distilled with lime is said to give among other products valeric aldehyde (Calvi, Ann. **91**, 110; Petersen, Ann. **103**, 184; Dale and Schorlemmer, Ann. **199**, 149), which can be treated as under **A**.

[G.] From *mannitol* [51] through n-hexane (see under n-hexyl alcohol [23; B]). The latter gives pentane on heating with aluminium chloride (Friedel and Gorgeu, Comp. Rend. **127**, 590). Subsequent steps as under **B** above.

[H.] From *glycerol* [48] through diallyl and hexane (see under n-hexyl

alcohol [23; C]) and pentane, &c., as above.

[I.] From *glutaric acid* [Vol. II] through suberic acid and hexane (see under n-hexyl alcohol [23; D]) and then as above.

NOTE:—The following generators of suberic acid referred to under n-hexyl alcohol [23] thus become generators of hexane and therefore of pentane and n-amyl alcohol: *cetyl alcohol* [33]; *myristic acid* [Vol. II]; *stearic acid* [Vol. II]; *adipic acid* [Vol. II] through sebacic acid; *azelaïc acid* [Vol. II] through ketocyclo-octane.

For aromatic generators of hexane see under n-hexyl alcohol [23; A].

[J.] From *n-butyric acid* [Vol. II] through hexane (see under n-hexyl alcohol [23; K]), pentane, &c., as above under G.

21. Methylpropyl Carbinol; Normal Secondary Amyl Alcohol; 2-Pentanol.

$CH_3 . CH_2 . CH_2 . CH(OH) . CH_3$

Natural Source.

Said to occur in fusel oil (especially Swedish) from potato starch spirit (Rabuteau, Comp. Rend. 87, 501).

Synthetical Processes.

[A.] From *acetic* and *butyric* acids [Vol. II] through methylpropyl ketone (2-pentanone) by distillation of the mixed calcium salts (Semljanitzin, Journ. pr. Ch. [2] 23, 263; Friedel, Ann. 108, 124; Grimm, Ann. 157, 251) and reduction with sodium amalgam (Friedel, Jahresber. 1869, 513; Belohoubek, Ber. 9, 924).

[B.] From *methyl alcohol* [13] and *butyric acid* [Vol. II] by the action of zinc methyl on butyryl chloride and decomposition of the product with water (Butleroff, Zeit. [2] 1, 614; Bull. Soc. [2] 5, 17) and reduction of the methylpropyl ketone thus obtained as under A.

[C.] From *ethyl alcohol* [14] by the action of zinc ethyl on chloroform (Beilstein and Rieth, Ann. 124, 245). The amylene thus formed is probably the symmetrical methylethylethylene (3-pentene), which can be converted into 2-chlor- or 2-iodopentane, &c., as under F.

Or from *ethyl alcohol* and *acetic acid* [Vol. II] through ethylacetoacetic ester by the action of sodium and ethyl iodide on acetoacetic ester (Geuther, Jahresber. 1863, 324; Frankland and Duppa, Journ. Ch. Soc. 4, 396; Wislicenus, Ann. 186, 187; Miller, Ann. 200, 281; Wedel, Ann. 219, 100), methylpropyl ketone by heating with potash or baryta (Frankland and Duppa, Ann. 138, 216), and reduction as under A. Or the ethylacetoacetic ester can be reduced by sodium amalgam to α-ethyl-β-hydroxybutyric (2-pentanol-3-methylic) acid (Waldschmidt, Ann. 188, 240), the latter decomposed by dry distillation into α-ethylcrotonic acid (*Ibid.* 245); then through the hydrobromide, 3-pentene, 2-chlorpentane, &c., as under G.

Also from acetic acid and ethyl alcohol through *acetoacetic ester* [Vol. II], the γ-chloro-derivative which is formed (with the α-derivative) on chlorination (Haller and Held, Comp. Rend. 108, 516), the γ-cyano-derivative by the action of *potassium cyanide* (*Ibid.*), acetonedicarboxylic ester, by the action of hydrogen chloride on the γ-cyano-derivative dissolved in alcohol (Haller and Held, Comp. Rend. 111, 682), dimethylacetonedicarboxylic ester, and subsequent steps as under H. Also from ethyleneacetoacetic ester (W. H. Perkin, junr., Ber. 16, 2136; 17, 1440) through acetyltrimethylenecarboxylic acid, acetyltrimethylene (ethanoyl-cyclopropane), and reduction of latter with sodium amalgam (Marshall and W. H. Perkin, junr., Trans. Ch. Soc. 59, 874).

[D.] From *acetone* [106], *acetic acid* [Vol. II], and *ethyl alcohol* [14] through acetylacetone (see under n-primary amyl alcohol [20; B and C]), ethylacetylacetone by the action of ethyl iodide on the sodium salt (Combes, Ann. Chim. [6] 12, 247), methylpropyl ketone by the action of potash (*Ibid.* 248), and reduction as under A.

Or the acetylacetone can be converted directly into 2-iodopentane by heating with hydriodic acid (Combes, Ann.

Chim. [6] **12**, 234) and the iodopentane into the alcohol by the usual methods.

[**E.**] From *propionic acid* [Vol. II] through diethyl ketone (3-pentanone) by distillation of the barium salt (Morley, Ann. **78**, 187), the dichloride by heating with phosphorus pentachloride, methylethylacetylene (3-pentine) by the action of alcoholic potash on the dichloride (Faworsky, Journ. pr. Ch. [2] **37**, 387), methylpropyl ketone by heating the acetylene derivative with water and mercuric bromide (Kutscheroff, Ber. **14**, 1542), and reduction as under **A.**

Also from propionic acid through diethyl ketone by the action of propionyl chloride on zinc ethyl (Freund and Pebal, Ann. **118**, 9) and treatment as above.

[**F.**] From *formic acid* [Vol. II] and *ethyl alcohol* [**14**] through diethyl carbinol = 3-pentanol by the action of zinc and ethyl iodide on formic ester and decomposition of the product with water (Wagner and Saytzeff, Ann. **175**, 351), diethyl ketone by oxidation of the alcohol (*Ibid.* Ann. **179**, 322), and then as under **E.**

Also by converting the diethyl carbinol into amylene = symmetrical methylethylethylene = 3-pentene by the action of alcoholic potash on the iodide (Wagner and Saytzeff, Ann. **175**, 373; **179**, 302), combining the amylene with hydrogen chloride to form 2-chlorpentane (*Ibid.* Ann. **179**, 321), and conversion into the alcohol by the usual methods (Schorlemmer, Ann. **161**, 268). Hydrogen iodide combines with the amylene to form 2-iodopentane (Wurtz, Ann. **148**, 132), which can be converted into the alcohol by the same methods.

[**G.**] From *oxalic acid* [Vol. II] and *ethyl alcohol* [**14**] through diethoxalic = hydroxydiethacetic = 3-pentanol-3-carboxylic acid by the action of zinc ethyl on oxalic ester and decomposition of the product with water (Frankland, Proc. Roy. Soc. **12**, 396; Frankland and Duppa, *Ibid.* **13**, 140; Ann. **135**, 26; Geuther, Zeit. [2] **3**, 705; Fittig, Ann. **200**, 21), diethyl ketone by the oxidation of diethoxalic acid or by heating its ester with hydrochloric acid (Chapman and Smith, Journ. Ch. Soc. **20**, 173; Geuther and Wackenroder, Zeit. [2] **3**, 709), and then as under **E.**

Or from diethoxalic ester through α-ethylcrotonic ester by the action of phosphorus trichloride (Frankland and Duppa, Journ. Ch. Soc. **18**, 133; Ann. **136**, 2; Fittig and Howe, Ann. **200**, 22: see also Geuther, Bull. Soc. [2] **10**, 34), the hydrobromide of ethylcrotonic = 2-pentene-3-carboxylic acid by the direct addition of hydrogen bromide to the acid (Fittig and Howe, *loc. cit.* 23), 3-pentene by the decomposition of the hydrobromide by cold sodium carbonate solution (Fittig, *Ibid.* 30), 2-chlor- or 2-iodo-pentane, &c., as under **F** (see also under hexoic aldehyde [2-methylpentanol; **96**; **L**]).

[**H.**] From *citric acid* [Vol. II] and *methyl alcohol* [**13**] through acetonedicarboxylic acid (3-pentanonediacid) by heating the former with sulphuric acid (v. Pechmann, Ber. **17**, 2543; Ann. **261**, 157; Peratoner and Strazzeri, Gazz. **21**, 295: see also under orcinol [**75**; **C**]), the diethyl ester, dimethylacetonedicarboxylic (2 : 4-dimethylpentanonediacid) diethyl ester by the action of sodium methylate and methyl iodide on acetonedicarboxylic ester (Dünschmann and v. Pechmann, Ann. **261**, 182), diethyl ketone by the action of hot dilute sulphuric acid on the dimethylacetonedicarboxylic ester (*Ibid.*), and then as under **E.** Citric acid gives acetonedicarboxylic acid by oxidation with potassium permanganate (Denigès, Comp. Rend. **130**, 32).

Note:—Other generators of diethyl ketone are: *sodium ethyl* and *carbon monoxide* (Wanklyn, Ann. 140, 211); *acetyl* or *propionyl chloride* acted upon by dry ferric chloride (Hamonet, Bull. Soc. [2] 50, 356 and 547); *zinc ethyl* and *nitropropane* (Bevad, Ch. Centr. 1900, 2, 944).

[**I.**] From crude (fusel oil) *amyl alcohol* [**22**] by conversion into amylene, amylene bromide, and 'valerylene' by the action of alcoholic potash (Reboul, Ann. **131**, 238; Eltekoff, Journ. Russ. Soc. **9**, 378). This 'valerylene' probably contains methylethylacetylene (3-pentine), and can be converted into methylpropyl ketone, &c., as under **E.**

Normal primary *amyl alcohol* [**20**]

can be converted into the n-amyl chloride (1-chlorpentane), and the latter on heating with acetic acid and potassium acetate to 200° gives (with amyl acetate) normal amylene (propylethylene) (Schorlemmer, Ann. **161**, 269), which combines with hydrogen iodide to form 2-iodopentane (Wurtz, Ann. **148**, 131 : see also Wagner and Saytzeff, Ann. **178**, 313; Wischnegradsky, Ann. **190**, 347), from which the alcohol can be obtained as under **F**. Normal amylene is also among the amylenes obtained from the amyl alcohols of fusel oil by the action of zinc chloride (Wischnegradsky, Journ. Russ. Soc. **9**, 192).

[**J.**] From *normal propyl alcohol* [15] and *acetic acid* [Vol. II] by the action of zinc propyl (Gladstone and Tribe, Ber. **6**, 1136; Schtscherbakoff, Bull. Soc. [2] **37**, 345) on acetyl chloride (Markownikoff, Bull. Soc. [2] **41**, 259; Wagner, Journ. Russ. Soc. **16**, 333). Ethyl alcohol is formed at the same time.

[**K.**] From *normal pentane* (see under n-amyl alcohol [**20**; **B**; **C**; **D**, &c.]) by chlorination (Schorlemmer, Ann. **161**, 268) and conversion into the alcohol by usual methods. The 1-chlorpentane formed also during chlorination can be converted into 2-pentanol through propylethylene as under **I**.

Note :—All generators of n-hexane are generators of pentane (see under n-amyl alcohol [20 ; **G**]) and therefore of 2-pentanol. The generators of hexane (see under n-hexyl alcohol [23] are: *mannitol* [51] ; *glycerol* [48] ; *glutaric acid* [Vol. II] ; *cetyl alcohol* [33] ; *myristic acid* [Vol. II] ; *stearic acid* [Vol. II] ; *adipic acid* [Vol. II] ; *n-butyric acid* [Vol. II], and aromatic compounds (see under n-hexyl alcohol [23 ; **A**]).

[**L.**] From *tartaric* and *butyric acids* [Vol. II] through pyroracemic acid (see under benzyl alcohol [**54**; **N**]), the potassium salt of which mixed with potassium butyrate gives methylpropyl ketone on electrolysis (Hofer and Uhl, Ber. **33**, 654). Subsequent steps as above under **A**.

Note :—The generators of pyroracemic acid referred to under benzyl alcohol [54] are thus, with butyric acid, generators of this amyl alcohol. These are : *ethyl alcohol* and *hydrogen cyanide* [14 ; 172] ; *acetic acid* or *acetoacetic acid* and *hydrogen cyanide* ; *citric acid* ; *propionic acid* ; *lactic acid* ; *n-* or *isopropyl alcohol* [15 ; 16].

[**M.**] From *dextrose* [154], *lævulose* [155] or *mannose* [156], and *acetic acid* [Vol. II] through lævulic acid (see under erythritol [**50**; **H**; **I**]), the potassium salt of which when electrolysed in solution with potassium acetate gives methylpropyl ketone (Hofer and Uhl, Ber. **33**, 656).

Note :—The following generators of lævulic acid referred to under erythritol [50] thus become with acetic acid generators of this amyl alcohol: *isohexoic acid* ; *malonic acid* and *glycerol* [48] ; *acetic aldehyde* [92] ; *methylheptenone* [111] ; *dimethylheptenol* [35].

The synthetical methylpropyl carbinol is inactive, but is resolved into the l-modification by *Penicillium glaucum* (LeBel, Comp. Rend. **89**, 312 ; Ber. **12**, 2163 ; Jahresber. **1879**, 492).

22. Isoamyl Alcohol; Isobutyl Carbinol; Inactive Amyl Alcohol of Fermentation; 2-Methyl-4-Butanol.

$CH_3 . CH(CH_3) . CH_2 . CH_2 . OH$

Natural Sources.

Occurs as ester of angelic and tiglic acids in Roman oil of chamomile from *Anthemis nobilis* (see under isobutyl alcohol [18]); occurs also in oil of *Eucalyptus globulus* (Bouchardat and Oliviero, Bull. Soc. [3] **9**, 429). An amyl alcohol (? this one) has been found in American oil of peppermint (Schimmel's Ber. April, 1894; Ch. Centr. 1896, **2**, 977).

Esters of amyl (probably isoamyl) alcohol occur in the oils of *Eucalyptus macrorrhyncha, E. aggregata, E. patentinervis*, &c. (Smith and Baker, Proc. Roy. Soc., N. S. Wales, July, 1898; Smith, *Ibid.* June, 1900; 'Nature,' **62**, 384; Schimmel's Ber. April, 1901; Ch. Centr. 1901, **1**, 1007).

A secondary product of alcoholic fermentation, this alcohol being the chief constituent of various fusel oils (Scheele, Crell's Ann. 1785, **1**, 61 ; Pelletan, Ann. Chim. **30**, 221 ; Berz. Jahresber. **6**, 264 ; Dumas, Ann. Chim. **56**, 314 ; Ann. **13**, 80 ; Cahours, Ann. Chim. **70**, 81 ; **75**, 193; Ann. **37**, 164 ; Dumas and Stas, Ann. Chim. **73**, 128 ; Balard, *Ibid.* [3] **12**, 294; Ann. **52**, 311 ; Pasteur, Comp. Rend. **41**, 296 ; Ann. **96**,

255; Erlenmeyer and Hell, Ann. **160**, 275; Ley, Ber. **6**, 1363; LeBel, Bull. Soc. [2] **25**, 545; Just, Ann. **220**, 148; Udránszky, Zeit. physiol. Ch. **13**, 251: for method of separation of amyl alcohols of fusel oil see Marckwald, Ber. **34**, 479; 485; **35**, 1595).

Its production during fermentation has been attributed to bacteria associated with the yeast; this alcohol is not obtained with pure cultures of elliptical yeast (Gentil, Mon. Sci. [4] **11**, II, 568; Ch. Centr. 1897, **2**, 622). *Saccharomyces anomalus* of Hansen produces amyl acetate during fermentation (Barker, Ann. Bot. 1900, 215).

An ester (amyl or isoamyl) of valeric acid is among the products of decomposition of albumin (peptone) by *Bacillus præpollens* from the intestine (Maassen, Ch. Centr. 1899, **2**, 1059). An amyl (? isoamyl) alcohol occurs as ester in rancid fat, probably as a bacterial product (Nagel, Am. Ch. Journ. **23**, 173). An amyl (? isoamyl) alcohol is among the products of hydrolysis and fermentation of starch by the *Bacillus amylozymicus* of Perdrix (Ann. Inst. Past. **5**, 287).

A 'fusel oil' (alcohols not identified) is said to occur in milk from cows fed with 'slump' (Teichert, Bied. Centr. **31**, 210; Journ. Ch. Soc. **82**, II, Abst. 348).

Synthetical Processes.

[A.] From *isovaleric aldehyde* (2-methyl-4-butanal) [95] by reduction with sodium amalgam (Friedel, Ann. **124**, 326; Balbiano, Ber. **9**, 1437 and 1692; Gazz. **6**, 229; Erlenmeyer, Ann. Suppl. **5**, 337; Wurtz, Ann. **134**, 201). Also from isovaleric aldehyde (with other products) by heating with lime (Fittig, Ann. **117**, 68).

[B.] From *isovaleric acid* [Vol. II] by conversion into the chloride and reduction of the latter with sodium in moist ethereal solution (W. H. Perkin, junr., and Sudborough, Proc. Ch. Soc. **10**, 216).

23. Normal Hexyl Alcohol; 1-Hexanol.

$CH_3 . [CH_2]_4 . CH_2 . OH$

Natural Sources.

As ester of acetic acid in oil from *Heracleum sphondylium* (Möslinger, Ber. **9**, 998; Ann. **185**, 26), and as ester of butyric acid in oil of *Heracleum giganteum* (Franchimont and Zincke, Ber. **4**, 822; Ann. **163**, 193). Hexyl alcohol (? normal) exists as ester in the ethereal oil from the root of *Aspidium filix mas* (Ehrenberg, Arch. Pharm. **231**, 345). A caproyl (? n-hexyl) alcohol occurs as ester in rancid fat, probably a bacterial product (Nagel, Am. Ch. Journ. **23**, 173). It is not certain that the alcohol from any of these sources is the normal alcohol. A hexyl alcohol occurs in fusel oil from brandy (Faget, Ann. **88**, 325; Ordonneau, Comp. Rend. **102**, 217).

Synthetical Processes.

[A.] From *normal propyl alcohol* [15] through n-hexane by the action of sodium on n-propyl iodide (Schorlemmer, Phil. Trans. **162**, 118; Ann. **161**, 277; Brühl, Ann. **200**, 183; Stohmann, Journ. pr. Ch. [2] **43**, 7; Michael, Ber. **34**, 4036), n-hexyl chloride which is formed (with secondary hexyl chloride) by chlorination (Cahours, Comp. Rend. **10**, 1241; Jahresber. **1863**, 525), and then through the acetate and hydrolysis (Cahours and Pelouze, Comp. Rend. **54**, 1245; Schorlemmer, Ann. **161**, 272).

Normal hexane is capable of being directly nitrated, and the mononitro-derivative on reduction gives *n-hexylamine* [Vol. II] (Worstall, Am. Ch. Journ. **20**, 202; **21**, 210; 218), which can be converted into the alcohol as under G.

Note :—Certain aromatic compounds such as *benzene* [6]; *styrene* [7]; *phenol* [60]; *benzoic acid* [Vol. II]; *alizarin* [145], &c., are said to give hexane among the products of reduction by strong aqueous hydriodic acid at a high temperature (Berthelot, as under methane [1; I]: see also v. Baeyer, Ann. **155**, 266; Wredin,

Ann. 187, 153; Kishner, Journ. Russ. Soc. 23, 20; 24, 451; Ann. 278, 88). The identity of this hexane has not been fully established (see under active hexyl alcohol [25; B; C, &c.]).

[B.] From *mannitol* [51] through the secondary hexyl iodide ($CH_3[CH_2]_3 \cdot CHI \cdot CH_3$; 2-iodohexane) by heating with hydriodic acid solution (Wanklyn and Erlenmeyer, Zeit. **1861**, 606; **1862**, 641; Ann. **135**, 130; Domac, Monats. **2**, 310; Hecht, Ann. **165**, 146; **209**, 311; Schorlemmer, Phil. Trans. **171**, 452), n-hexane by reduction with zinc and hydrochloric acid (LeBel and Wassermann, Comp. Rend. **100**, 1589; Jahresber. **1885**, 1211: also Schorlemmer, Phil. Trans. **162**, 118; Erlenmeyer and Wanklyn, Journ. Ch. Soc. **16**, 227; Ann. **135**, 136), and then as under **A**.

The secondary hexyl iodide is also converted into hexane by heating to 80–90° with aluminium chloride (Lothar Meyer, Ber. **27**, 2766). According to Combes and LeBel (Bull. Soc. [3] **7**, 551) the hexyl iodide obtained from mannitol is 3-iodohexane.

Mannitol gives hexane by heating with strong aqueous hydriodic acid to 280° (Berthelot, as above under **A**).

[C.] From *glycerol* [48] through allyl iodide (see under isobutyl alcohol [18; D]), diallyl (see under normal butyl alcohol [17; D]), diallyldihydriodide (2 : 5-diiodohexane) by combination with hydrogen iodide (Wurtz, Ann. Chim. [4] **3**, 129; Sorokin, Journ. pr. Ch. [2] **23**, 18), hexylene by the action of sodium on the diiodohexane (Wurtz, *loc. cit.*), recombination with hydrogen iodide to form secondary hexyl iodide (Wurtz, Ann. **132**, 306), and then through n-hexane as under **B** and **A**.

Also through diallyl by combining with sulphuric acid and distilling with water and heating the hexylene oxide thus formed with hydriodic acid so as to form secondary hexyl iodide (Jekyll, Ch. News, **22**, 221).

[D.] From *glutaric acid* [Vol. II] through suberic acid by the electrolysis of potassium ethyl glutarate (Crum Brown and Walker, Ann. **261**, 120), and hydrolysis, and then distillation of the suberic acid with baryta (Riche, Ann. Chim. [3] **59**, 432; Dale, Journ. Ch. Soc. **17**, 258; Ann. **132**, 243). Hexane is among the products (see under **A**).

NOTE:—*Myristic acid* [Vol. II], *stearic acid* [Vol. II], and *cetyl alcohol* [33] give suberic acid among the products of their oxidation by nitric acid (Noerdlinger, Ber. **19**, 1896; Laurent, Ann. Chim. [2] **66**, 157; Bromeis, Ann. **35**, 89). *Azelaïc acid* [Vol. II] gives ketocyclo-octane among the products of distillation of the calcium salt (Mayer, Ann. **275**, 364; Derlon, Ber. **31**, 1960; Müller and Tschitschkin, Ann. **307**, 375), and this gives suberic acid by oxidation (Derlon, *loc. cit.* 1962).

[E.] From *adipic acid* [Vol. II] through sebacic acid by electrolysis of potassium ethyl adipate and hydrolysis of the ester (Crum Brown and Walker, Ch. News, **66**, 91; Ann. **261**, 120), bromsebacic and hydroxysebacic acid by bromination and decomposition of the sodium salt by boiling with water, oxidation of the hydroxy-acid to suberic acid by nitric acid (Weger, Ber. **27**, 1216), and then as under **D**.

Or sebacic acid is brominated in presence of phosphorus (Auwers and Bernhardi, Ber. **24**, 2232), and the *aa*-dibromo-acid converted into the dihydroxy-acid by heating with barium hydroxide solution. The dihydroxy-acid on oxidation with lead peroxide gives octanediol, and this on oxidation with alkaline permanganate yields suberic acid (v. Baeyer, Ber. **30**, 1962).

[F.] From *normal hexoic* (*caproic*) *acid* [Vol. II] through the aldehyde by distillation of the calcium salt with *calcium formate* (Lieben and Janecek, Ann. **187**, 130) and reduction of the aldehyde by sodium amalgam (Lieben and Rossi, Ann. **133**, 178; Lieben and Janecek, Ann. **187**, 135).

[G.] From *normal heptoic* (*œnanthic*) *acid* [Vol. II] through *n-hexylamine* by the action of bromine and potash on the amide (Hofmann, Ber. **15**, 771; Frentzel, Ber. **16**, 744) and distillation of the nitrite with water (Frentzel, *loc. cit.*).

n-Hexylamine can also be obtained from n-heptoic acid and acetic acid through methyl-n-hexyl ketone (Städeler, Journ. pr. Ch. **72**, 246; Jahresber. **1857**, 359), the ketoxime by the action

of hydroxylamine, the action of phosphorus pentachloride on the ethereal solution followed by that of water, and the action of potash on the n-hexylacetamide thus formed (Hantzsch, Ber. **24**, 4021).

Also from heptoyl chloride through methylhexyl ketone by the action of *zinc methyl* (Béhal, Bull. Soc. [3] **6**, 132) and then as above.

Or from heptoic acid through the α-bromo-acid by bromination (Cahours, Ann. Suppl. **2**, 83; Hell and Schüle, Ber. **18**, 625), nitrohexane by the interaction of sodium nitrite and the sodium salt (Auger, Bull. Soc. [3] **23**, 333), and then through hexylamine as above.

[H.] From *normal butyl alcohol* [17] through n-octane by the action of sodium on the iodide (Schorlemmer, Ann. **161**, 280). On chlorination n-octane yields (among other products) secondary octyl chloride (2-chlorooctane), which is convertible into methylhexyl carbinol (2-octanol) by the usual method (Schorlemmer, Ann. **152**, 152; Pelouze and Cahours, Jahresber. **1863**, 528). The secondary alcohol gives methylhexyl ketone on oxidation (Béhal, *loc. cit.*), and this can be converted into n-hexylamine, &c., as under **G**.

Note :—Among other generators of n-octane are : *sebacic acid* (see above under **E**) by distillation with baryta (Riche, Ann. **117**, 265); *ethyl alcohol* [14] through the product of the action of zinc ethyl on titanium chloride and decomposition with water (Paternò and Peratoner, Ber. **22**, 467).

[I.] From *aldehyde* [92] through α-methylpyridine (α-picoline) by the action of aldehyde on aldehyde ammonia (Dürkopf and Schlaugk, Ber. **21**, 297), α-pipecoline by reduction (Ladenburg and Roth, Ber. **18**, 47; Ann. **247**, 62; Comp. Rend. **103**, 747; Bunzel, Ber. **22**, 1053). The latter base can be converted into the methiodide and the ammonium hydroxide base in the usual way, the latter on heating to 140° giving 'pentallylcarbindimethylamine,' $CH_2 : CH(CH_2)_4 . N(CH_3)_2$, which can again be converted into its methiodide and ammonium hydroxide base; the latter on heating to 160° gives (among other products) diallyl (Merling, Ann. **264**, 315: see also Ladenburg, Mugdan, and Brzostovicz, Ann. **279**, 344, &c.), which can be treated as under **C**.

[J.] From *pyridine* [Vol. II] through α-picoline by heating the methiodide to 300° in a sealed tube (Ladenburg and Lange, Ann. **247**, 7), and then through pipecoline, &c., as under **J**.

[K.] *Normal butyric acid* [Vol. II] gives n-hexane among the products of electrolysis of the potassium salt (Petersen, Ch. Centr. 1897, **2**, 519), and this can be converted into n-hexyl alcohol as under **A**.

[L.] From *acetone* [106] through pinacone (see under tertiary butyl alcohol [19; **D**]). The latter gives hexane on heating with strong hydriodic acid at 270° (Bouchardat, Zeit. [2] **7**, 699).

Note :—The generators of pinacone referred to under tertiary butyl alcohol [19; **E**; **F**; &c.] thus become generators of hexane. These are: *isobutyric acid* and *methyl alcohol*; *amyl* and *methyl alcohols*; *lactic acid* and *methyl alcohol*; *acetic acid* and *methyl alcohol*; *ethyl* and *methyl alcohols*; *propionic acid* and *methyl alcohol*; *diacetyl* and *methyl alcohol*.

24. Isohexyl Alcohol; 2-Methyl-5-Pentanol.

$CH_3 . CH(CH_3) . CH_2 . CH_2 . CH_2 . OH$

Natural Source.

A hexyl alcohol is said to have been found in fusel oil from brandy (Faget, Ann. **88**, 325; Ordonneau, Comp. Rend. **102**, 217). The constitution of this alcohol has not been determined, but it is probably as above.

Synthetical Processes.

[A.] From *isoamyl alcohol* [22] and *trioxymethylene* [*formic aldehyde*: **91**] by the interaction of isoamyl magnesium bromide and trioxymethylene in ethereal solution (Grignard and Tissier, Comp. Rend. **134**, 107).

[B.] From *isobutylacetic* (*4-methylpentanoic*) *acid* [Vol. II] through the aldehyde (4-methylpentanal) by distilling the calcium salt with *calcium formate* (Rossi, Ann. **133**, 178) and reduction with sodium amalgam (*Ibid.* 180).

25. Active Hexyl Alcohol; Methylethylpropyl Alcohol; 3-Methyl-5-Pentanol.

$CH_3 . CH_2 . CH(CH_3) . CH_2 . CH_2 . OH$

NATURAL SOURCE.

As ester of angelic and tiglic acids in Roman oil of chamomile from *Anthemis nobilis* (Köbig, Ann. **195**, 79; 81; 92: see also Van Romburgh, Rec. Tr. Ch. **5**, 219; **6**, 150).

SYNTHETICAL PROCESSES.

[A.] From *isopropyl alcohol* [16] through diisopropyl (2 : 3-dimethylbutane) by the action of sodium (Schorlemmer, Ann. **144**, 184), chlorination (Silva, Bull. Soc. [2] **6**, 36; **7**, 953), and conversion of the chlorhexane into the alcohol by the usual methods (*Ibid.* **6**, 147).

[B.] From *acetone* [106] through pinacone (2 : 3-dimethyl-2 : 3-butanediol) by the action of sodium (see under tertiary butyl alcohol [19; D]), diisopropyl by heating with hydriodic acid (Bouchardat, Comp. Rend. **74**, 809), and then as under **A**.

NOTE :—Generators of pinacone are summarised under normal hexyl alcohol (23; L).

[C.] *Normal heptoic (œnanthic) acid* [Vol. II] when its barium salt is heated to redness gives a hexane which is said to be diisopropyl (Riche, Ann. Chim. [3] **59**, 432).

[D.] From *glycerol* [48] through diallyl (see under normal butyl alcohol [17; D]) and action of hydriodic acid in excess on the latter at a high temperature (Berthelot, Bull. Soc. [2] **9**, 268). The hexane thus obtained is said to be diisopropyl.

[E.] From *mannitol* [51] by heating with excess of hydriodic acid (Bouchardat, Ann. Chim. [5], **6**, 124; Le Bel and Wassermann, Jahresber. **1885**, 1211). This hexane is also said to be diisopropyl.

NOTE :—The identity of Silva's alcohol with the natural product requires confirmation; it is difficult to see how an alcohol having the constitution 3-methyl-5-pentanol could be derived from diisopropyl by chlorination and hydroxylation.

26. Normal Heptyl Alcohol; 1-Heptanol.

$CH_3 . [CH_2]_5 . CH_2 . OH$

NATURAL SOURCE.

The heptyl alcohol stated to have been found in fusel oil from brandy (see under isoheptyl alcohol [27]) may be the normal alcohol, as it is said to give n-heptoic (œnanthic) acid on oxidation.

SYNTHETICAL PROCESSES.

[A.] From *n-heptane* [2] through 1-chlorheptane by chlorination and the usual method (Schorlemmer, Ann. **127**, 315; **161**, 278). n-Heptane gives 1-nitroheptane on nitration (Worstall, Am. Ch. Journ. **20**, 210; **21**, 223). The heptylamine obtained from this by reduction might give n-heptyl alcohol by the usual (nitrous acid) method.

[B.] From *œnanthol* [97] by reduction (see under n-heptane [2; D]).

27. Isoheptyl Alcohol; Isohexyl Carbinol; 2-Methyl-6-Hexanol.

$CH_3 . CH(CH_3) . [CH_2]_3 . CH_2 . OH$

NATURAL SOURCE.

Heptyl alcohol is said to have been obtained from fusel oil of brandy (Faget, Bull. Soc. **1862**, 59; Ann. **124**, 355; Ordonneau, Comp. Rend. **102**, 217). The constitution of this fermentation heptyl alcohol has not yet been satisfactorily established, and it is only placed here provisionally (see also above under n-heptyl alcohol [26]).

SYNTHETICAL PROCESSES.

[A.] From *ethyl* [14] and *isoamyl* [22] *alcohols* through isoheptane (5-methylhexane) by acting with sodium on the iodides or bromides (Wurtz, Ann. Chim. [3] **44**, 275; Grimshaw, Journ. Ch. Soc. **26**, 309; Ann. **166**,

163), isoheptyl chloride by chlorination, conversion into the alcohol by the usual method, and separation of the primary from the secondary alcohol (Grimshaw, *loc. cit.* 313).

[B.] From *isobutyl alcohol* [18], *acetic acid* [Vol. II], and *ethyl alcohol* [14] by combining isobutyl iodide with *sodio-acetoacetic ester*, decomposing the isobutylacetoacetic ester with potash, reducing the ketone (2-methyl-6-hexanone) to the secondary alcohol, converting the latter into the iodide, and reducing to isoheptane with zinc and hydrochloric acid (Purdie, Trans. Ch. Soc. **39**, 464: see also Rohn, Ann. **190**, 305). The isoheptane can then be treated as under **A**.

Note:—A heptane (possibly identical with the above) is said to be obtained from certain cyclic compounds by heating to a high temperature with strong aqueous hydriodic acid (Berthelot, Comp. Rend. **68**, 606; Bull. Soc. [2] **9**, 455). The compounds are: *toluene* [54] and the *toluidines*; *phthalic acid* (see under benzyl alcohol [54; R]) and *terephthalic acid*. The latter can be obtained by the oxidation of *cymene* [6] and *cumic aldehyde* [116] (Hofmann, Ann. **97**, 197; De la Rue and Müller, Ann. **121**, 87; Schwanert, Ann. **132**, 257; Homeyer, Arch. Pharm. [3] **5**, 326).

28. Normal Primary Octyl Alcohol; 1-Octanol.

$CH_3.[CH_2]_6.CH_2.OH$

Natural Sources.

As ester of acetic acid in oil of *Heracleum giganteum* (Franchimont and Zincke, Ann. **163**, 193); as ester of acetic, hexoic, decoic, and lauric acids in oil of *Heracleum sphondylium* (Zincke, Ann. **152**, 1; Möslinger, Ber. **9**, 998; Ann. **185**, 26). As ester of n-butyric acid in fruit of *Pastinaca sativa*, common parsnip (Renesse, Ann. **166**, 84). An octyl alcohol occurs as ester in the ethereal oil from the root of *Aspidium filix mas* (Ehrenberg, Arch. Pharm. **231**, 345).

A capryl (? n-octyl) alcohol occurs in rancid fat, probably a bacterial product (Nagel, Am. Ch. Journ. **23**, 173).

Synthetical Processes.

[A.] *Normal octane* (see under n-hexyl alcohol [23; H]) by chlorination and conversion into the primary and secondary alcohols by the usual methods gives a product which may contain an alcohol identical with the natural product, but this requires confirmation (Schorlemmer, Ann. **152**, 155).

[B.] *Sebacic acid* [Vol. II] gives octane on distillation with baryta (Riche, Ann. **117**, 265).

Notes:—Certain aromatic compounds (which can all be synthesised), such as *xylene* [62; A], *ethylbenzene* [64; A], *styrene* [7], *naphthalene* [12], *phthalic acid* [54; R], &c., according to Berthelot give octane among other products when heated with strong aqueous hydriodic acid (for references see under isoheptyl alcohol [27; B]). The constitution of the octanes thus obtained is unknown.

A secondary octyl alcohol (methylhexyl carbinol = 2-octanol) has been obtained by distilling the soap from the oil of *Curcas purgans* (Silva, Zeit. [2], **5**, 185). The alcohol has been synthesised (see under n-hexyl alcohol [23; H]), but it is doubtful whether it is at present to be regarded as a biochemical product.

29. Nonyl Alcohol; Ennyl Alcohol; Nonanol.

$C_9H_{19}.OH$

Natural Source.

A nonyl alcohol (39·4 per cent.) has been found in the oil of sweet orange (Schimmel's Ber. Oct. 1900; Ch. Centr. 1900, **2**, 969; Stephan, Journ. pr. Ch. [2] **62**, 523).

Synthetical Processes.

The constitution of the natural product is not known with certainty; it is probably the normal alcohol. The following nonyl alcohols are synthetical products:—

[A.] *Pelargonic* and *formic* [Vol. II] *acids* give the aldehyde (nonanal) on distillation of the barium salts. The aldehyde is reduced to normal nonyl alcohol by zinc dust and acetic acid (Krafft, Ber. **19**, 2221).

[B.] From *isovaleric acid* [Vol. II] and *isoamyl alcohol* [22]. Isoamyl isovalerate on treatment with sodium gives

a nonyl alcohol (Lourenço and Aguiar, Zeit. [2] 6, 404).

[C.] From *ethyl alcohol* [14] and *œnanthol* [97] by the action of zinc ethyl on the aldehyde and decomposition of the product by water. The alcohol is ethylhexyl carbinol = 3-nonanol (Wagner, Journ. Russ. Soc. 16, 306; Bull. Soc. [2] 42, 330).

Or from ethyl alcohol and œnanthol by converting the latter into *n-heptyl alcohol* [26]. A mixture of n-heptyl and ethyl alcohols gives (among other products) n-nonyl alcohol when heated with sodium to 230° (Guerbet, Comp. Rend. 135, 172; Bull. Soc. [3] 27, 1036).

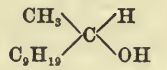
[D.] From *ethyl alcohol* [14] and *butyric acid* [Vol. II]. The latter on distillation of the calcium salt (Chancel, Ann. 52, 295; Kurtz, Ann. 161, 205; Schmidt, Ber. 5, 597), or by the action of ferric chloride on butyryl chloride and decomposition of the product with water (Hamonet, Bull. Soc. [2] 50, 358), gives dipropyl ketone=butyrone =4-heptanone. The latter on treatment with zinc and ethyl iodide yields ethyldipropyl carbinol = 4-ethyl-4-heptanol (Tschebotareff and Saytzeff, Journ. pr. Ch. [2] 33, 198).

Note:—Dipropyl ketone can also be prepared from *n-propyl alcohol* [15] and *butyric acid* by the interaction of zinc propyl and butyryl chloride (Schtscherbakoff, Journ. Russ. Soc. 13, 346). Or from *butyric acid* by heating butyric anhydride with sodium butyrate (Perkin, Trans. Ch. Soc. 49, 325) or (among other products) by the action of sodium on ethyl butyrate (Brüggemann, Ann. 246, 140). This ketone is also among the products of the action of zinc on a mixture of butyryl chloride and ethyl ether (Freund, Ann. 118, 33).

Secondary Nonyl Alcohol.

A secondary nonyl alcohol (methyl-n-heptyl carbinol) occurs partly free and partly as ester of acetic acid in Algerian oil of rue (v. Soden and Henle, Pharm. Zeit. 46, 1026; Ch. Centr. 1902, 1, 256; Ch. Drug., 60, 304; Power and Lees, Trans. Ch. Soc. 81, 1592). This alcohol has been obtained by reducing the corresponding ketone [108] (Mannich, Ber. 35, 2144; Houben, *Ibid.* 3589).

30. Secondary Hendecatyl or Hendecyl Alcohol; Methyl-n-nonyl Carbinol.



Natural Source.

Occurs partly free and partly as ester of acetic acid in Algerian oil of rue (v. Soden and Henle, Pharm. Zeit. 46, 1026; Ch. Centr. 1902, 1, 256; Ch. Drug., 60, 304; Power and Lees, Trans. Ch. Soc. 81, 1593).

Synthetical Process.

[A.] From *methylnonyl ketone* [109] by reduction with sodium amalgam (Giesecke, Zeit. [2] 6, 428; Mannich, Ber. 35, 2144; Houben, *Ibid.* 3590).

31. Normal Primary Dodecyl Alcohol; 1-Dodecanol.

$CH_3 . [CH_2]_{10} . CH_2 . OH$

Natural Sources.

Esters of this alcohol (probably stearate and palmitate of the normal alcohol) exist in *Cascara sagrada* (Dohme and Engelhardt, Journ. Am. Ch. Soc. 20, 539). Occurs also as ester (of oleic and dœglic acids) in sperm oil and in oil from the bottle-nose whale, and to a small extent in spermaceti [33] (Heintz, Ann. 84, 306; 92, 299; Allen, in Thorpe's 'Dict. of Applied Chem.' III, 20; Hammarsten's 'Lehrb. d. physiol. Chem.' 1895, p. 76).

Synthetical Process.

[A.] From *lauric acid* [Vol. II] through the aldehyde by distilling the barium salt with *barium formate* (Krafft, Ber. 13, 1414), reduction with zinc dust and acetic acid, and hydrolysis of the acetate thus formed (*Ibid.* 16, 1718).

Note:—The identity of the natural and synthetical products requires confirmation.

32. Normal Primary Tetradecyl Alcohol; 1-Tetradecanol.

$CH_3 . [CH_2]_{12} . CH_2 . OH$

Natural Source.

Occurs in small quantity as ester in spermaceti [33] (Heintz, Ann. 84, 306; 92, 299; Hammarsten's 'Lehrb. d. physiol. Chem.' 1895, p. 76).

Synthetical Process.

[A.] From *myristic acid* [Vol. II] through the aldehyde by distilling the barium salt with *barium formate* (Krafft, Ber. 13, 1415), and reduction of the aldehyde with sodium in alcoholic solution (*Ibid.* 16, 1720; 23, 2360).

Note :—The identity of the natural and synthetical products requires confirmation.

33. Cetyl Alcohol; Æthal; 1-Hexadecanol.

$CH_3 . [CH_2]_{14} . CH_2 . OH$

Natural Sources.

As ester of palmitic acid in spermaceti from the cranial cavity and blubber of the sperm whale (*Physeter macrocephalus*), from *Delphinus tursio* and *D. edentulus*. Occurs also in oil from the dolphin (*Delphinus globiceps*) and in blubber of the bottle-nose whale (*Hyperoödon rostratus* and *H. bidens*). Cetyl acetate, laurate, myristate, and stearate are present to a small extent in some kinds of spermaceti (Chevreul, 'Recherches sur les Corps Gras,' p. 171; Ann. Chim. 7, 157; Dumas and Peligot, *Ibid.* [2] 62, 4; Dumas and Stas, *Ibid.* 73, 124; Smith, *Ibid.* [3] 6, 40; Ann. 42, 247; Berthelot and Péan, Ann. Chim. [3] 58, 413; Heintz, Ann. 84, 306; 92, 299; Pogg. Ann. 87, 21; 267; 92, 429; 588; Krafft, Ber. 17, 1627). The alcohol is said to occur (as ester) in the caudal glands of certain birds (ducks and geese) (De Jonge, Zeit. physiol. Ch. 3, 225); also in the fat of ovarian cysts (Ludwig, Zeit. physiol. Ch. 23, 38; v. Zeynek, *Ibid.* 48).

Synthetical Processes.

[A.] From *adipic acid* [Vol. II] through sebacic acid (see under n-hexyl alcohol [23; E]) by distilling the barium salt of the latter (Schorlemmer, Proc. Roy. Soc. 19, 22; Ber. 3, 616).

[B.] From *palmitic acid* [Vol. II] through the aldehyde by distilling the barium salt with *barium formate* (Krafft, Ber. 13, 1416), reduction of the aldehyde with zinc dust and acetic acid, and hydrolysis of the acetate thus formed (*Ibid.* 16, 1721; 17, 1627).

34. Octadecyl Alcohol; 1-Octadecanol.

$CH_3 . [CH_2]_{16} . CH_2 . OH$

Natural Source.

An ester of this alcohol occurs in spermaceti (Heintz, Ann. 84, 306; 92, 299; Krafft, Ber. 17, 1628).

Synthetical Process.

[A.] From *stearic* and *formic acids* [Vol. II] through stearic aldehyde (Krafft, Ber. 13, 1417) and reduction of the aldehyde in the usual way (*Ibid.* 16, 1722; 17, 1627).

35. 2-6-Dimethyl-2-Heptenol-6.

$(CH_3)_2 : C : CH . CH_2 . CH_2 . C(CH_3)(OH) . CH_3$

Natural Source.

Said to occur in small quantity in oil of linaloe (Barbier, Comp. Rend. 126, 1423).

Synthetical Processes.

[A.] From *geraniol* [36] by the action of strong alcoholic potash at 150° (Barbier, *loc. cit.*).

Note :—According to Tiemann (Ber. 31, 2991) this product is methylheptenol corresponding to methylheptenone.

[B.] From *methylheptenone* [111] and *methyl alcohol* [13] by the action of

magnesium methiodide on the ketone (in ethereal solution) and decomposition of the magnesium compound by acid (Barbier, Comp. Rend. **128**, 110; Sand and Singer, Ber. **35**, 3183).

Note :—The dimethylheptenol obtained by this method is $(CH_3)_2 : C : CH . [CH_2]_2 . C(CH_3)_2 . OH$.

36. Geraniol; Lemonol; 2 : 6-Dimethyl-2 : 6-Octadienol-8.

$$(CH_3)_2 : C : CH . CH_2 . CH_2 . C(CH_3) : CH . CH_2 . OH$$

Natural Sources.

In East Indian geranium or palmarosa oil from *Andropogon schœnanthus* (Jacobsen, Ann. **157**, 232); in oil of citronella from *Andropogon nardus*, Punjaub, Ceylon, Singapore, &c. (Schimmel's Ber. Oct. 1893); in African, Spanish, French, and Réunion geranium oils from *Pelargonium odoratissimum*, *P. capitatum*, *P. radula*, &c. (Gintl, Jahresber. **1879**, 942; Bertram and Gildemeister, Journ. pr. Ch. [2] **49**, 191; Tiemann and Schmidt, Ber. **29**, 924); and in German and Turkish oils of rose from *Rosa damascena*, *R. alba*, &c. (Bertram and Gildemeister, *loc. cit.*: see also Eckart, Ber. **24**, 4205; Arch. Pharm. **229**, 355; Barbier, Comp. Rend. **117**, 177; Bull. Soc. [3] **9**, 999).

Geraniol occurs in ylang-ylang oil from *Cananga odorata* (Reychler, Bull. Soc. [3] **11**, 407; 576; 1045; **13**, 140); in French oil of lavender from *Lavandula* sp. (Schimmel's Ber. April, 1898); in oil of néroli from the flowers of the bitter orange, *Citrus bigaradia*, and in the 'orange-flower water' (Tiemann and Semmler, Ber. **26**, 2711; Hesse and Zeitschel, Journ. pr. Ch. [2] **64**, 245); in petit-grain oil from the leaves, shoots, and fruit of the same plant (Passy, Bull. Soc. [3] **17**, 519; Charabot and Pillet, *Ibid.* **21**, 74); in petit-grain oil from Paraguay (Schimmel's Ber. Oct. 1902; Ch. Centr. 1902, **2**, 1208); in lemon-grass oil from the Indian *Andropogon citratus* (Schimmel's Ber. Oct. 1894; also Oct. 1898; Ch. Centr. 1898, **2**, 985: compare Stiehl, Journ. pr. Ch. [2] **58**, 51; Tiemann, Ber. **32**, 835; Labbé, Bull. Soc. [3] **21**, 77); and in oil of linaloe from the wood of the Mexican *Bursera delpechiana* or *B. aloexylon* (Schimmel's Ber. April, 1892; Oct. 1894; Oct. 1900).

Occurs also in oil of sassafras leaves (Power and Kleber, Pharm. Rev. **14**, 103; Ch. Centr. 1897, **2**, 42); in oil of balm mint from *Melissa officinalis* (Flatau and Labbé, Comp. Rend. **126**, 1725; Bull. Soc. [3] **19**, 636); in lemon oil from *Citrus limonum*, Messina and Palermo (Umney and Swinton, Pharm. Journ. **61**, 196; 370), and in the oil from the leaves of *Verbena triphylla*, Grasse (Theulier, Rev. gén. de Chim. **5**, 324; Ch. Centr. 1902, **2**, 1208).

The oil from *Darwinia fascicularis* of Port Jackson contains geraniol and 60–65 per cent. of geranyl acetate (Baker and Smith, Journ. and Proc. Roy. Soc. of N. S. Wales, **33**, 163; Journ. Soc. Ch. Ind. **19**, 848). Certain citronella oils (Javan and Cingalese 'Lana-Batu') contain 32–38 per cent. geraniol (Schimmel's Ber. Oct. 1899; Journ. Soc. Ch. Ind. **19**, 556).

The oil from the leaves and twigs of *Eucalyptus macarthuri* contains 60 per cent. of geranyl acetate (Smith, Ch. News, **83**, 5). Geraniol is probably contained in the oil of *Eucalyptus patentinervis* (Schimmel's Ber. April, 1901; Ch. Centr. 1901, **1**, 1007). The oil from the rhizome of *Asarum canadense* contains geraniol (Power, Pharm. Rund. **6**, 101; Power and Lees, Proc. Ch. Soc. **17**, 210; Trans. **81**, 66).

Note :—The geraniol is contained in the above oils sometimes free, sometimes combined as an ester, and in some cases both free and combined. The acid most frequently combined with geranyl is acetic, but other acids, such as tiglic, valeric, &c., are sometimes present. Suggestions concerning the origin of geraniol and allied alcohols in plants have been advanced by Charabot (Ann. Chim. [7] 21, 207, &c.).

Synthetical Processes.

[A.] From *citral* [104] by reduction in alcoholic solution with sodium amalgam and acetic acid (Tiemann, Ber. **31**, 828).

[B.] *Linaloöl* [37] gives geraniol on heating with acetic anhydride or with sulphuric and acetic acids and hydrolysis of the acetate (Barbier, Comp. Rend. **116**, 1200; **117**, 122; Bouchardat, Comp. Rend. **116**, 1253; Bertram and Gildemeister, Journ. pr. Ch. [2] **49**, 192; Tiemann and Semmler, Ber. **26**, 2714; Bertram, Germ. Pat. 80711 of 1893, Ber. **28**, Ref. 582).

Note :—The product 'licarhodol' obtained by Barbier (Comp. Rend. **116**, 1200) by heating l-linaloöl with acetic anhydride and hydrolysis is said to be a mixture of geraniol and d-terpineol (Stephan, Journ. pr. Ch. [2], **58**, 109 : see also Barbier and Léser, Bull. Soc. [3] **17**, 590).

37. Linaloöl; Licareol.

$(CH_3)_2 : C : CH . CH_2 . CH_2 . C(CH_3)(OH) . CH : CH_2$

or

$CH_2 : C(CH_3) . CH_2 . CH_2 . CH_2 . C(CH_3)(OH) . CH : CH_2$

Note :—For references to constitution see paper by Harries and Schauwecker, Ber. **34**, 2981; also Barbier, Bull. Soc. [3] **25**, 687; 828. According to Barbier the first of these formulae represents myrcenol.

Natural Sources.

l-Linaloöl is contained in oil of linaloe from Guiana, probably from the wood of *Ocotea caudata* (Morin, Comp. Rend. **92**, 998; **94**, 733; Ann. Chim. [5] **25**, 427; Theulier, Rev. Gén. de Chim. **3**, 262; Bull. Soc. [3] **25**, 468; Schimmel's Ber. April, 1901), and in Mexican oil of linaloe (see above under geraniol [36] : Semmler, Ber. **24**, 207; Barbier, Comp. Rend. **114**, 674; **116**, 883; **121**, 168).

Oil of néroli (see under geraniol) contains l-linaloöl (Tiemann and Semmler, Ber. **26**, 2711; Hesse and Zeitschel, Journ. pr. Ch. [2] **64**, 245); so also does oil of bergamot from *Citrus bergamia* (Semmler and Tiemann, Ber. **25**, 1182; Bertram and Walbaum, Journ. pr. Ch. [2] **45**, 602; Charabot, Comp. Rend. **129**, 728; Fabris, Abst. in Journ. Soc. Ch. Ind. **19**, 772), mandarin oil from *Citrus madurensis* (Schimmel's Ber. Oct. 1901), oil of limette from the fruit of the Italian *Citrus limetta* (Gildemeister, Arch. Pharm. **233**, 174), and oil of lemon from *Citrus limonum* from Palermo (Umney and Swinton, Pharm. Journ. **61**, 196; 370).

Oil of petit-grain (see under geraniol) contains d- and l-linaloöl (Semmler and Tiemann, Ber. **25**, 1186; Charabot and Pillet, Bull. Soc. [3] **21**, 74 : l-linaloöl in Paraguay petit-grain oil, Schimmel's Ber. Oct. 1902; Ch. Centr. 1902, **2**, 1208).

l-Linaloöl is contained also in oil of spike lavender from *Lavandula spica* (Bouchardat and Voiry, Comp. Rend. **106**, 551; Bouchardat, *Ibid.* **117**, 53; 1094), in French lavender oil (Bertram and Walbaum, Journ. pr. Ch. [2] **45**, 590); in ylang-ylang oil (see under geraniol; Reychler, Bull. Soc. [3] **11**, 407; 576; 1045; **13**, 140); in oil of *Origanum smyrnæum* from Smyrna (Gildemeister, Arch. Pharm. **231**, 182); in oil of balm mint from *Melissa officinalis* (see under geraniol); in Russian oil of spearmint from *Mentha viridis* (Schimmel's Ber. April, 1898; Ch. Centr. 1898, **1**, 991); and in oil of thyme from *Thymus vulgaris* (Labbé, Bull. Soc. [3] **19**, 1009).

Also in lemon-grass oil (see under geraniol : Tiemann, Ber. **32**, 835); in oil of jasmine from the flowers of *Jasminum grandiflorum* with linalyl acetate (Hesse and Müller, Ber. **32**, 574; 765; Hesse, *Ibid.* 2619 : see also Erdmann, Ber. **34**, 2281, note); in German oil of rose (Walbaum and Stephan, Ber. **33**, 2304); (trace) in citronella oil (see under geraniol : Schimmel's Ber. Oct. 1899; Ch. Centr. 1899, **2**, 880); in oil of sassafras leaves (Power and Kleber, Pharm. Rev. **14**, 403; Ch. Centr. 1897, **2**, 42); in French oil of sweet basil from *Ocymum basilicum* (Dupont and Guerlain, Comp. Rend. **124**, 300; Bull. Soc. [3] **19**, 151); and probably in oil from *Eucalyptus patentinervis* (see under geraniol), and in oil from the leaves of *Darwinia taxifolia* (Baker and Smith : see under geraniol and Schimmel's Ber. Oct. 1900; Ch. Centr. 1900, **2**, 969).

Linalyl acetate is possibly contained in the oil from *Salvia sclarea* (Schim-

mel's Ber. April, 1889; Oct. 1894). l-Linaloöl is contained in Ceylon oil of cinnamon (*Ibid.* April, 1902; Walbaum and Hüthig, Journ. pr. Ch. [2] **66**, 47), and in oil of cinnamon leaf (Schimmel's Ber. Oct. 1902; Ch. Centr. 1902, **2**, 1208). Linaloöl and linalyl acetate are present in oil of *Gardenia* (Parone, Boll. Ch. Farm. **41**, 489; Ch. Centr. 1902, **2**, 703).

d-Linaloöl = coriandrol occurs in oil of coriander from the fruit of *Coriandrum sativum* (Kawalier, Ann. **84**, 351; Journ. pr. Ch. **58**, 226; Grosser, Ber. **14**, 2485; Semmler, Ber. **24**, 206; Barbier, Comp. Rend. **116**, 1460); in 'wartara' oil from the fruit of *Xanthoxylon alatum* and *X. acanthopodium* (Schimmel's Ber. April, 1900; Ch. Centr. 1900, **1**, 908); in oil of sweet (Portugal) orange from the rind of the fruit of *Citrus aurantium* (Parry, Ch. Drug. 1900, pp. 462 and 722; Stephan, Journ. pr. Ch. [2] **62**, 523); in the néroli oil from the flowers of the same plant (Theulier, Bull. Soc. [3] **27**, 278: a French néroli oil examined by Schimmel & Co. probably contained l-linaloöl; Ch. Centr. 1902, **2**, 1208), in Chinese néroli oil from *Citrus triptera* (Umney and Bennett, Pharm. Journ. [4] **15**, 146), and in oil of *Asarum canadense* (Power and Lees, Proc. Ch. Soc. **17**, 210; Trans. **81**, 63).

Inactive linaloöl and linalyl isononoate are present in oil of hops (Chapman, Proc. Ch. Soc. **19**, 72).

Note :—For remarks on general transformation and migration of linaloöl and other terpene alcoholic compounds in plants, see papers by Charabot, Bull. Soc. [3] **23**, 189; Ann. Chim. [7] **21**, 207, &c.; Charabot and Hébert, Comp. Rend. **133**, 390; Bull. Soc. [3] **25**, 884; 955). Linaloöl occurs in the above oils in some cases in the free state and in other cases combined as linalyl acetate, &c.

Synthetical Process.

[A.] *Geraniol* [**36**] by the action of hydrochloric acid gives geranyl chloride (Jacobsen, Ann. **157**, 236), and this by the action of alcoholic potash is converted partially into inactive linaloöl (Semmler and Tiemann, Ber. **31**, 832). A similar transformation is brought about by heating geraniol with water to 200° (Schimmel's Ber. April, 1898). Or sodium geranyl phthalate (from geranyl chloride and *phthalic acid* [**54**; **R**]) gives i-linaloöl on steam distillation of the neutral solution (Stephan, Journ. pr. Ch. [2] **60**, 244).

Note :—No method for resolving i-linaloöl into its optical isomerides has yet been discovered.

38. Citronellol; Rhodinol (?); 2 : 6-Dimethyl-2-Octenol-8.

$(CH_3)_2 : C : CH . CH_2 . CH_2 . CH(CH_3) . CH_2 . CH_2 . OH$

Natural Sources.

l-Citronellol occurs in Bulgarian and German oil of rose and d- and l-citronellol in Spanish, African, and Réunion oils of geranium from *Pelargonium odoratissimum*, &c. (see under geraniol: Hesse, Journ. pr. Ch. [2] **50**, 478; **53**, 238; Tiemann and Schmidt, Ber. **29**, 922; Barbier and Bouveault, Comp. Rend. **122**, 737; Walbaum and Stephan, Ber. **33**, 2306; Schimmel's Ber. May, 1901; Journ. Soc. Ch. Ind. **20**, p. 744).

Citronellol is also said to be contained in Indian geranium (palmarosa) oil (Flatau and Labbé, Comp. Rend. **126**, 1725; Bull. Soc. [3] **19**, 633: compare Schimmel's Ber. Oct. 1898, p. 67). Javan (but not Ceylon) oil of citronella contains d-citronellol (Schimmel's Ber. April, 1902).

Synthetical Processes.

[A.] From *citronellal* [**105**] by reduction with sodium amalgam and acetic acid (Dodge, Am. Ch. Journ. **11**, 463; Tiemann and Schmidt, Ber. **29**, 906).

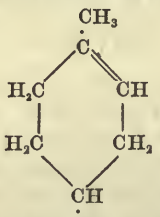
Note :—The aldehyde corresponding to the above formula of citronellol is probably not identical with l-citronellal but with the isomeric 'rhodinal' of Bouveault (Bull. Soc. [3] **23**, 458; 463: see also under citronellal [**105**]). The above synthetical process may therefore lead to the production of an alcohol isomeric with the natural l-citronellol (see also Harries and Schauwecker, Ber. **34**, 2981).

[B.] From *menthone* [**129**] through the oxime, nitrile, and aldehyde = menthocitronellal (Wallach, Ann. **277**, 154; **278**, 316; **296**, 129). The latter should be Bouveault's 'rhodinal,' and

would therefore give citronellol on reduction (Harries and Schauwecker, *loc. cit.*).

Note :—According to Bouveault citronellol and rhodinol are isomerides (see for summary Bull. Soc. [3] 23, 458; also under menthone [129]).

39. Terpineol; Terpilenol; Terpene Hydrate; Menthenol; Δ^1-8-Hydroxytetrahydrocymene; Δ^1-Terpen-8-ol.



$CH_3 . C(OH) . CH_3$

Note :—For constitutional formula see Wagner, Ber. 27, 1652.

Natural Sources.

i-Terpineol (and acetate) occurs in oil of cajeput from *Melaleuca leucadendron* and var. *minor* (Voiry, Comp. Rend. **106**, 1538; Bull. Soc. [2] **50**, 108), and in niauli oil from *Melaleuca viridifolia*, New Caledonia (Bertrand, Bull. Soc. [3] **9**, 433; Comp. Rend. **116**, 1070); in oil of Ceylon cardamom from *Elettaria cardamomum*, var. *major*, Smith (Weber, Ann. **238**, 98); and in oil of Malabar cardamom (d-terpineol) from *E. cardamomum* (Schimmel's Ber. Oct. 1897; Parry, Pharm. Journ. **9**, 105).

Oil of sweet marjoram from *Origanum majorana* contains d-terpineol (Biltz, Ber. **32**, 995). Terpineol is contained in the oil of *Lindera sericea*, the 'kuromoji' oil of Japan (Kwasnik, Arch. Pharm. **230**, 265); in the Japanese 'kesso' oil from the root of *Valeriana officinalis*, var. *angustifolia* (Bertram and Gildemeister, Arch. Pharm. **228**, 483); and in oil of fleabane from the N. American *Erigeron canadensis* (Kremers and Hunkel, Pharm. Rund. **13**, 137).

l-Terpineol is probably present in lemon-grass oil (Tiemann, Ber. **32**, 835). d-Terpineol is contained in oil of lovage from the root of *Levisticum officinale* (Schimmel's Ber. April, 1897, p. 27, and Oct. 1897, p. 9, note). The oil from Californian bay (*Umbellularia californica*) contains a mixture, 'terpinol,' of which terpineol is one of the constituents (Stillmann, Ber. **13**, 630; Wallach, Ann. **230**, 251). Oil of *Gardenia* contains terpineol (Parone, Boll. Ch. Farm. **41**, 489; Ch. Centr. 1902, **2**, 703).

The oil of the rind of the sweet orange (see under linaloöl [37]: Stephan, Journ. pr. Ch. [2] **62**, 523 and Schimmel's Ber. Oct. 1900) contains 39·4 per cent. of d-terpineol. Oil of Mexican linaloe (see under geraniol [36]: Schimmel's Ber. Oct. 1900; Ch. Centr. 1900, **2**, 970) contains terpineol. So also does mandarin oil from *Citrus madurensis* (Schimmel's Ber. Oct. 1901; Ch. Centr. 1901, **2**, 1007). Oil of spike from *Lavandula spica* may contain terpineol (Bouchardat, Comp. Rend. **117**, 53; 1094).

l-Terpineol is contained in the oil of *Asarum canadense* (Power and Lees, Proc. Ch. Soc. **17**, 210; Trans. **81**, 65). Camphor oil from *Laurus camphora* probably contains terpineol (Schimmel's Ber. Oct. 1888). d-Terpineol is present in oil of lemon (Schimmel's Ber. Oct. 1902; Ch. Centr. 1902, **2**, 1207), in French néroli oil (*Ibid.*), and in petitgrain oil from Paraguay (*Ibid.*).

Note :—No method for resolving inactive terpineol into its optical isomerides is at present known.

Synthetical Processes.

[A.] l-*Linaloöl* [37] gives d-terpineol and its acetate with geraniol on heating with acetic anhydride to 150–160° (Schimmel's Ber. April, 1898; Stephan, Journ. pr. Ch. [2] **58**, 109). The crude product thus obtained is the 'licarhodol' of Barbier (see under geraniol [36; B]).

Or linaloöl on treatment (below 20°) with acetic acid containing ½ per cent. of sulphuric acid gives 45 per cent. of its weight of d-terpineol and 10 per cent. of geraniol (Stephan, *loc. cit.*). d-Linaloöl on treatment with strong formic acid below 20° is largely converted into l-terpineol,

and l-linaloöl by the same reagent into d-terpineol (Stephan, *loc. cit.*).

Or from linaloöl through terpin hydrate (see under dipentene [**9**; **D**]), which on boiling with dilute mineral acid or with acetic acid gives terpineol among other products (Wallach, Ann. **230**, 264).

[**B.**] From *geraniol* [**36**] through terpin hydrate (see under dipentene [**9**; **C**]) and then as above (Stephan, Journ. pr. Ch. [2] **60**, 244). Geraniol is also converted by strong formic acid at ordinary temperatures into terpinyl formate in 10–12 days. Terpinyl acetate is produced in small quantity from geraniol by heating the latter to 60–70° with acetic acid containing a little sulphuric acid (Stephan, *loc. cit.*).

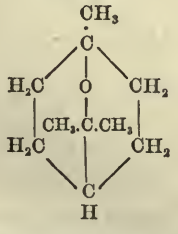
Note:—The liquid terpineol prepared on the large scale by boiling terpin hydrate with dilute acids contains a mixture of isomerides among which, together with the natural i-terpineol, is a terpineol ($\Delta^{8,9}$-terpen-1-ol) isomeric with the foregoing natural and synthetical products (Schimmel's Ber. April, 1901; Stephan and Helle, Ber. 35, 2147).

[**C.**] From *limonene* [**9**] by the action of silver or lead oxide on the hydrobromide, or by the action of acetic acid containing sulphuric acid on the hydrocarbon (Semmler, Ber. **28**, 2189). Both d- and l-limonene give terpineol by this method.

Dipentene gives terpinyl acetate on heating with glacial acetic acid to 100° (Bouchardat and Lafont, Comp. Rend. **102**, 1555).

Note:—It is not certain that the constitutional formula given above expresses the structure of all the synthetical terpineols obtained by the foregoing processes.

40. Cineole; Cajeputole; Eucalyptole.



Note:—For constitutional formula see Wallach, Ann. 291, 350.

Natural Sources.

The chief constituent of oil of wormseed from the flower heads and stalks of *Artemisia maritima* and vars. (Kraut, Jahresber. **1862**, 460; Kraut and Wahlforss, Ann. **128**, 293; Hell and Stürcke, Ber. **17**, 1970; Wallach and Brass, Ann. **225**, 291).

Occurs also in oil of *Artemisia vulgaris* (Schimmel; Gildemeister and Hoffmann, p. 891); in oil of cajeput (Wallach, *loc. cit.* 315); in niauli oil (66 per cent., Bertrand, Bull. Soc. [3] **9**, 435; Comp. Rend. **116**, 1070); in oil of *Melaleuca acuminata* (Schimmel's Ber. April, 1892); and in oil of *M. leucadendron*, var. *lancifolia* (*Ibid.*).

Cineole has been found also in oil from the leaves of *Laurus nobilis* (*Ibid.* April, 1899); in American oil of peppermint (Power and Kleber, Pharm. Rund. **12**, 157; Arch. Pharm. **232**, 639); in camphor oil from *Laurus* (*Cinnamomum*) *camphora* (Schimmel's Ber. Oct. 1888; Oct. 1902); in oil of sage from *Salvia officinalis* (Wallach, Ann. **252**, 103); in oil of spike lavender (Bouchardat and Voiry; see under linaloöl [**37**]); in oil of lavender (traces) (Schimmel's Ber. Oct. 1893), and in Portuguese oil of lavender from *Lavandula pedunculata* (*Ibid.* Oct. 1898).

Occurs also in German oil of sweet basil from *Ocymum basilicum* (Bertram and Walbaum, Arch. Pharm. **235**, 176; Schimmel's Ber. April, 1897: see also Hirschsohn as quoted by Gildemeister and Hoffmann, p. 860, note); in oil of rosemary from *Rosmarinus officinalis* (Weber, Ann. **238**, 89); in oil from the root of the 'Chinese galangal,' *Alpinia officinarum* (Schimmel's Ber. April, 1890; Schindelmeiser, Ch. Zeit. **26**, 335), and from the root of *Kaempferia rotunda* (Schimmel's Ber. April, 1894); in oil of Bengal cardamom from *Amomum* (*Elettaria*) *aromaticum* (Schimmel's Ber. April, 1897); in a Camaroon cardamom oil from (?) *Amomum danielli* (*Ibid.* Oct. 1897), and in Malabar cardamom oil from *Elettaria cardamomum* (*Ibid.* Oct. 1897; Parry, Pharm. Rev. **9**, 105).

Cineole is contained also in oil of

saffron (Hilger, Ch. Centr. 1900, **2**, 576); in the Brazilian 'carqueia' oil from *Genista tridentata* (Schimmel's Ber. April, 1896); in oil from the leaves of the Indian *Vitex trifolia* (*Ibid.* Oct. 1894); possibly in oil of pennyroyal from *Mentha pulegium* (Tétry, Bull. Soc. [3] **27**, 186); in oil of rue, probably Algerian (Power and Lees, Trans. Ch. Soc. **81**, 1590); and in oil of Russian spearmint (see under linaloöl [**37**]; Schimmel's Ber. April, 1898).

Occurs also in oil from the leaves of the Chilian *Myrtus cheken* (Weiss, Arch. Pharm. **226**, 666); in oil of myrtle from *Myrtus communis* (Jahns, Arch. Pharm. **227**, 174; Schimmel's Ber. April, 1889); in oil from *Curcuma zedoaria* (Schimmel's Ber. Oct. 1890); in oil of the W. Indian white cinnamon from the bark of *Canella alba* (Schimmel's Ber. Oct. 1890); in Japanese 'badiana' or star-anise oil from *Illicium religiosum* (Tardy, Bull. Soc. [3] **27**, 987), and also (as 'eucalyptol') in the oil from many species of *Eucalyptus* :—

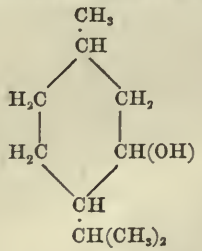
E. globulus (Jahns, Ber. **17**, 2941; Archiv. Pharm. **223**, 52); *E. oleosa* (Maiden's 'Useful Native Plants of Australia,' p. 272); *E. dumosa* (Schimmel's Ber. Oct. 1889); *E. amygdalina* (Wallach and Gildemeister, Ann. **246**, 278; Schimmel's Ber. Oct. 1889); *E. rostrata* (*Ibid.* Oct. 1891); *E. populifolia* (*Ibid.* April, 1893); *E. corymbosa* (*Ibid.*); *E. resinifera* (*Ibid.* Oct. 1898); *E. baileyana* (*Ibid.* April, 1888); *E. microcorys* (*Ibid.*); *E. risdonia* (*Ibid.* April, 1894); *E. hemiphloia* (*Ibid.* April, 1892); *E. crebra* (*Ibid.* April, 1893); *E. macrorrhyncha* (Baker and Smith, Journ. and Proc. Roy. Soc. of N. S. Wales, **32**, 104, &c.); *E. capitellata* (*Ibid.*); *E. eugenioides* (*Ibid.*); *E. obliqua* (Schimmel's Ber. Oct. 1898); *E. punctata* (Baker and Smith, *loc. cit.* **31**, 259, &c.; Schimmel's Ber. Oct. 1898); *E. loxophleba* (Parry, Pharm. Journ. **61**, 198); *E. dextropinea* and *E. lævopinea* (Baker, *loc. cit.* **27**, 414; Baker and Smith, *Ibid.* **32**, 195); *E. hæmastoma* (Schimmel's Ber. April, 1888); *E. piperita* (Baker and Smith, *loc. cit.* **31**, 195); *E. maculosa* (Baker, Proc. Linn. Soc. N. S. Wales, 1899, p. 596; Schimmel's Ber. Oct. 1900; Ch. Centr. 1900, **2**, 970); *E. bicolor* = *E. largiflorens* (Schimmel's Ber. *loc. cit.*; Journ. Soc. Ch. Ind. **19**, 1140); oil of 'red gum' of Tenterfield (? sp.; *Ibid.*); *E. smithii* and *E. camphora* (Baker, Proc. Linn. Soc. N. S. Wales, 1899, p. 292, &c.); *E. goniocalyx* (Smith, Journ. and Proc. Roy. Soc. of N. S. Wales, **33**, 86, &c.; Journ. Soc. Ch. Ind. **19**, 68); *E. intertexta* (spotted gum); *E. morrisii* (grey mallee); *E. viridis* (green, red, or brown mallee); and *E. vitræa* (white-top messmate) (Baker, *loc. cit.* 1900, p. 303, &c.; Ch. Centr. 1901, **2**, 1006); *E. melliodora* (Parry, Ch. Drug. **58**, 588); *E. pulverulenta* (Schimmel's Ber. April, 1902); *E. polybractea* (blue mallee); a little in oils from *E. angophorcides* (apple-top box), *E. intermedia* (bastard bloodwood), *E. lactea* (spotted gum), *E. ovalifolia* (red box), *E. umbra* (stringy bark or bastard white mahogany), *E. wilkinsonia* = *E. hæmastoma* var. = *E. lævopinea* var. *minor*, *E. fletcheri* (lignum vitæ or black box), and from *E. woollsiana* (mallee box) (Baker, Proc. Linn. Soc. N. S. Wales, 1900, part IV).

Synthetical Process.

[**A.**] *Terpineol* [**39**] gives cineole among other products when boiled with dilute sulphuric or phosphoric acid (Wallach, Ann. **239**, 21; **275**, 105).

Note :—No method for resolving terpineol into its optical isomerides is at present known.

41. Menthol; Terpanol; Peppermint Camphor; Methylisopropyl-hexahydrophenol.



Natural Sources.

In oil of peppermint from *Mentha piperita* (England, Germany, and

America), *M. arvensis* var. *piperascens* (Japan), and var. *glabrata* (China) (Dumas, Ann. Chim. **50**, 232; Ann. **6**, 252; Blanchet and Sell, Ann. **6**, 293; Walter, Ann. **28**, 312; **32**, 288; Kane, Phil. Mag. **16**, 418; Ann. **32**, 285; Laurent, Rev. Sci. **14**, 341; Oppenheim, Ann. **120**, 350; **130**, 176; Journ. Ch. Soc. **15**, 24). In oil of pennyroyal from *Mentha pulegium* (Tétry, Bull. Soc. [3] **27**, 186).

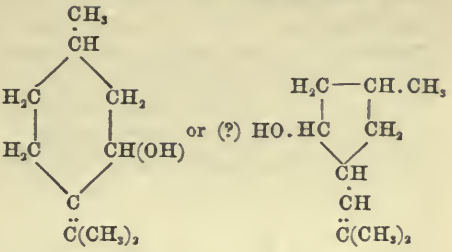
Note:—The natural product is l-menthol. For observations on the genesis of menthol compounds in *Mentha piperita* during the growth of the plant see papers by Charabot, Comp. Rend. 130, 518; 131, 806.

Synthetical Processes.

[A.] From *pulegone* [128] by reduction with sodium in ethereal solution (Beckmann and Pleissner, Ann. **262**, 32).

[B.] From *menthone* [129] as above (*Ibid.*).

42. Isopulegol.



Natural Source.

Said to occur in citronella oil (Tiemann, Ber. **32**, 825; compare Labbé, Bull. Soc. [3] **21**, 1023).

Synthetical Process.

[A.] From *citronellal* [105] by the action of acids or of acetic anhydride (Tiemann and Schmidt, Ber. **29**, 913; **30**, 27). The transformation of pure citronellal into isopulegol takes place spontaneously (Labbé, *loc. cit.*).

Note:—The foregoing cyclic alcohols are included here on account of their relationship to geraniol, linaloöl, citronellol, &c.

KETONE ALCOHOLS.

43. Acetol; Acetyl Carbinol; Pyroracemic Alcohol; Methylketol; Hydroxyacetone; Propanonol; Propanolone.

$CH_3.CO.CH_2.OH$ or $CH_3.C(OH).CH_2$ (with O)

Natural Sources.

From propylene glycol by the action of the sorbose *Bacterium* in presence of beer yeast infusion (Kling, Comp. Rend. **128**, 244; **129**, 1252). Certain varieties of *Mycoderma aceti* produce the same compound from propylene glycol (*Ibid.* **133**, 231).

Synthetical Processes.

[A.] From *normal* or *isopropyl alcohol* [15; 16] through propylene and propylene chloride and α-chlorpropylene by the action of alcoholic potash on the latter. α-Chlorpropylene by chlorination gives αβ (with ωβ) dichlorpropylene = α-chlorallyl chloride (Friedel and Silva, Comp. Rend. **73**, 957; **74**, 806; **75**, 81; Fittig, Ann. **135**, 359). The latter on boiling with potassium carbonate solution yields α-chlorallyl alcohol (Henry, Comp. Rend. **95**, 849), which, on being dissolved in sulphuric acid and on distilling the product with water, gives acetol (Henry, Bull. Soc. [2] **39**, 526).

Or from propylene through propylene chloride and 1 : 2 : 3-trichlorpropane (see under glycerol [48; A]). The latter by the action of potassium hydroxide or triethylamine gives αβ-dichlorpropylene (Reboul, Comp. Rend. **95**, 993; Ann. Suppl. **1**, 229), which can be converted into α-chlorallyl alcohol and acetol as above.

Or from propylene through the glycol and the action of bromine in presence of

sunlight on the latter (Kling, Comp. Rend. **129**, 219).

NOTE:—Generators of propylene (see under glycerol [48]) thus become generators of acetol.

[B.] From *acetone* [106] through chloracetone (Riche, Ann. **112**, 321; Mulder, Ber. **5**, 1010). The latter on heating with potassium acetate in alcoholic solution gives acetol acetate (Henry, Ber. **5**, 966), which can be hydrolysed by boiling with water and barium carbonate (W. H. Perkin, junr., Trans. Ch. Soc. **59**, 791).

Bromacetone (Sokolowsky, Journ. Russ. Soc. **8**, 330; Emmerling and Wagner, Ann. **204**, 29) on boiling with potassium carbonate solution gives acetol (E. and W. *loc. cit.* 40: compare Simoncini, Gazz. **31**, 496).

Or acetone can be converted into 2 : 2-dichlorpropane by phosphorus pentachloride (Friedel, Ann. **112**, 236), and this by alcoholic potash gives α-chlorpropylene, which can be converted into αβ-dichlorpropylene, &c., as above under **A**.

Or acetone by the action of sodium and ethyl acetate gives acetylacetone (Claisen and Ehrhardt, Ber. **22**, 1011), which by the action of sulphuryl dichloride yields chloracetylacetone (Combes, Comp. Rend. **111**, 292). The latter on heating with potassium acetate in alcoholic solution gives acetol acetate (*Ibid.*).

Or from acetone through mesityl oxide (see under aldehyde [**92**; **S**]) and trimethyltriose by oxidation of the latter with potassium permanganate. The triose decomposes readily into acetol and acetone (Harries and Pappos, Ber. **34**, 2979).

Or from acetone and *formic acid* [Vol. II] through formopyroracemic ester ($H.CO_2.CH_2.CO.CH_3$) from chloracetone and potassium formate. The ester on heating with methyl alcohol gives methyl formate and acetol (Henry, Bull. Acad. Roy. Belg. 1902, p. 445; Ch. Centr. 1902, **2**, 928).

NOTE:—Allylene by the action of fuming hydrochloric acid gives 2 : 2-dichlorpropane (Reboul, Ann. Chim. [5] 14, 453), which can be treated as above. The generators of allylene referred to under benzyl alcohol [54] thus become generators of acetol.

[C.] *Glycerol* [48] by the action of dry hydrogen chloride gives dichlorhydrin = dichlorisopropyl alcohol (see under isopropyl alcohol [**16**; **G**]), and this by the action of phosphorus pentachloride yields 1 : 2 : 3-trichlorpropane (Berthelot and De Luca, Ann. Chim. [3] **48**, 304; **52**, 433; Fittig and Pfeffer, Ann. **135**, 359), which can be treated as above under **A**.

Or from glycerol through allyl iodide, which gives 1 : 2 : 3-trichlorpropane by chlorination (Oppenheim, Bull. Soc. [2] **2**, 97).

NOTE:—*Propane* gives 1 : 2 : 3-trichlorpropane by direct chlorination, so that generators of propane thus become generators of acetol (see under glycerol [48; **A**]).

[D.] From *acetic acid* [Vol. II] through the compound formed from acetyl chloride and aluminium chloride, which compound on decomposition with water gives acetylacetone (Combes, Ann. Chim. [6] **12**, 207). The latter can be treated as above under **B**.

Or from acetic acid and *isobutyl* or *tertiary butyl alcohol* [**18**; **19**] through mesityl oxide by the condensation of isobutylene with acetyl chloride or acetic anhydride (see under acetic aldehyde [**92**; **FF**]), and then as above under **B**.

[E.] From *dextrose* [154], acetol being among the products formed by fusion with caustic potash (Emmerling and Loges, Ber. **16**, 837).

[F.] From *acetoacetic ester* [Vol. II] through mesityl oxide (see under aldehyde [**92**; **L**]), and then as above under **B**.

44. Methylacetyl Carbinol; Dimethylketol; 3-Butanol-2-one.

$CH_3.CH(OH).CO.CH_3$

Natural Source.

A product of the action of *Bacillus tartricus* (Grimbert and Ficquet, Comp. Rend. Soc. Biol. 1897, p. 962) on the ammonium or calcium salt of tartaric acid (Grimbert, Comp. Rend. **132**, 706).

Synthetical Processes.

[A.] From *diacetyl* [113] by reduction with zinc and dilute sulphuric acid (v. Pechmann and Dahl, Ber. **23**, 2421).

[B.] From *acetoacetic ester* [Vol. II] and *methyl alcohol* [13] through methylacetoacetic ester by the interaction of methyl iodide and sodio-acetoacetic ester. The methylacetoacetic ester on hydrolysis gives methylethyl ketone (Frankland and Duppa, Ann. **138**, 336; Böcking, Ann. **204**, 17), and this on chlorination yields methyl-*a*-chlorethyl ketone (Vladesco, Bull. Soc. [3] **6**, 408; 807). The latter gives methylacetyl carbinol on treatment with alcoholic sodium hydroxide (*Ibid.* 810).

[C.] From *acetic* and *propionic acids* [Vol. II] through methylethyl ketone by distilling a mixture of the calcium salts (Schramm, Ber. **16**, 1581). Subsequent steps as under **B**.

[D.] From *acetic* and *butyric acids* [Vol. II] through methylethyl ketone by distilling a mixture of the calcium salts (Grimm, Ann. **157**, 258).

Note :—Other generators of methylethyl ketone are: *zinc methyl* and *propionyl chloride* (Popoff, Ann. **145**, 289); *zinc ethyl* and *acetyl chloride* (Freund, Ann. **118**, 3) or acetic anhydride (Granichstädten and Werner, Monats. **32**, 315); *ethyl iodide* and *acetic anhydride* in presence of zinc-sodium alloy (Saytzeff, Zeit. [2] **6**, 104); **2 : 2**-*dibrombutane* by heating with water or **2 : 3**-*dibrombutane* by heating with lead oxide and water (Hölz, Ann. **250**, 234; Eltekoff, Journ. Russ. Soc. **10**, 219; Meyer and Petrenko, Ber. **25**, 3309); *crotonylene* by the action of sulphuric acid (Lwoff and Almédingen, Bull. Soc. [2] **37**, 493); *secondary butyl alcohol* (methylethyl carbinol) by passing the vapour over a heated platinum spiral (Trillat, Comp. Rend. **132**, 1495), or by oxidation (Kanonnikoff and Saytzeff, Ann. **175**, 377).

Methylethyl ketone is also obtained from the generators of pseudobutylene, the latter giving with hypochlorous acid a chlorhydrin which yields the ketone on heating with water (Krassuski, Journ. Russ. Soc. **34**, 287). Generators of pseudobutylene are: *n-propyl alcohol* [15] through hexane; *n-butyl alcohol* [17]; *secondary butyl alcohol*, from the n-alcohol through n-butylene and the secondary iodide; *isobutyl alcohol* [18]; *methyl alcohol* [13] and *glycerol* [48]; *aldehyde* [92]; *angelic* and *tiglic acids* [Vol. II]; *isovaleric acid* [Vol. II]; *isoamyl alcohol* [22]. For references see under secondary butyl isothiocyanate [165; **A**; **B**; **C**; **D**, &c.].

POLYHYDRIC ALCOHOLS.

45. Ethylene Glycol; Ethanediol.

$CH_2(OH).CH_2(OH)$

Natural Source.

Said to be a product of oxidation of glycerol by a micro-organism found in wine (Rensch, Pharm. Zeit. **39**, 864).

Synthetical Processes.

[A.] From *ethyl alcohol* [14] through ethylene (see under isopropyl alcohol [16; **C**]).

Note :—All generators of ethylene are thus generators of glycol (see under methane [1; **D**], and under ethyl alcohol [14; **A**; **C**; **E**; **J**; **N**; **O**; **T**; **W**; **X**; **Y**, &c.]).

[B.] From *choline* [Vol. II] by boiling the aqueous solution (Wurtz, Ann. Suppl. **6**, 200).

46. Trimethylene Glycol; Normal Propylene Glycol; 1 : 3-Propanediol.

$CH_2(OH).CH_2.CH_2(OH)$

Natural Sources.

A product of the bacterial fermentation of glycerol in presence of chalk (Freund, Monats. **2**, 638; Fitz, Ber. **15**, 876). Fitz's organism was probably *Bacillus butylicus* (see under n-butyl alcohol [17]). Propylene glycol occurs as a product of hydrolysis of the fats used for soap manufacture (Noyes and Watkins, Journ. Am. Ch. Soc. **17**, 890).

Synthetical Processes.

[A.] From *glycerol* [48] through allyl bromide (n-propyl alcohol [15; **E**]), trimethylene bromide by combination

with hydrogen bromide (Géromont, Ann. **158**, 370; Reboul, Ann. Chim. [5] **14**, 472; Lermontoff, Ann. **182**, 358; Erlenmeyer, Ber. **12**, 1354; Ann. **197**, 184; Roth, Ber. **14**, 1351; Bogomolitz, Bull. Soc. [2] **30**, 23) and conversion into the glycol by the action of moist silver oxide, or by forming the diacetate and hydrolysing (Reboul, *loc. cit.* 491; Beilstein and Wiegand, Ber. **15**, 1497; Zander, Ann. **214**, 178; Niederist, Monats. **3**, 839). The hydrolysis is best effected by barium or calcium hydroxide (Henry, Bull. Acad. Roy. Belg. [3] **36**, 9).

Or from glycerol through allyl alcohol (ethyl alcohol [**14**; **G**]), the monochlorhydrin by combination with hypochlorous acid, and reduction with sodium amalgam (Henry, Rec. Tr. Ch. **16**, 208).

47. Isobutylene Glycol; 2-Methyl-2 : 3-Propanediol.

$CH_3 . C(CH_3)(OH) . CH_2 . OH$

Natural Source.

Among the products of fermentation of saccharose by *Saccharomyces ellipsoideus* (Claudon and Morin, Comp. Rend. **104**, 1109; Bull. Soc. [2] **49**, 178; Henninger and Sanson, Comp. Rend. **106**, 208).

Synthetical Processes.

[**A.**] From *isobutyl alcohol* [**18**] through isobutylene (tertiary butyl alcohol [**19**; **B**]), the bromide (2-methyl-2 : 3-dibrompropane) by combination with bromine (Linnemann, Ann. **162**, 36), and decomposition of the bromide by heating with potassium carbonate solution (Nevolé, Bull. Soc. [2] **27**, 63; Comp. Rend. **83**, 65; 146).

Isobutylene bromide can also be obtained from isobutyl alcohol by heating isobutyl chloride or bromide with bromine in the presence of iron (Meyer and Müller, Journ. pr. Ch. **46**, 161; Herzfelder, Ber. **27**, 1260). The glycol can be prepared also direct[1] iso- butyl alcohol by the action o[illegible]s) hydrochloric acid (Lwoff, Bull. Soc. [2] **43**, 112).

Isobutylene gives this glycol by oxidation with potassium permanganate (Wagner, Ber. **21**, 1232). Isobutylene bromide is also converted into the glycol by heating with water and lead oxide to 50° (Krassusky, Journ. Russ. Soc. **33**, 791).

[**B.**] From *tertiary butyl alcohol* [**19**] through isobutylene (see under isobutyl alcohol [**18**; **A**]), and then as under **A** above. Or by conversion into tertiary butyl chloride or bromide and then into isobutylene bromide by heating with bromine and iron (Herzfelder, *loc. cit.* 1261: see also Meyer and Müller, Journ. pr. Ch. **46**, 161).

Also from tertiary butyl alcohol through isobutylene bromide by the action of bromine (Étard, Comp. Rend. **114**, 753), and then as under **A**.

Note:—All generators of isobutylene given under isobutyl [18] and tertiary butyl alcohol [19] are generators of this glycol. These are: *isoamyl alcohol* [18; B]; *isovaleric acid* [18; C]; *acetone* and *glycerol* or *acetic acid via* β-dimethyl-acrylic acid [18; C], &c.

48. Glycerol; 1 : 2 : 3-Propanetriol.

$CH_2(OH) . CH(OH) . CH_2(OH)$

Natural Sources.

Widely distributed in vegetable and animal kingdoms, glyceryl esters of acids of the fatty and other series being found in most saponifiable fats and fixed oils (Scheele, 1779, Crell's Ch. Journ. **4**, 190; Crell's Ch. Ann. **1**, 99; Chevreul, 'Recherches sur les Corps Gras'; Pelouze, Ann. **19**, 210; **20**, 46; Comp. Rend. **21**, 718: for list of oils and fats see A. H. Allen's tables in Thorpe's 'Dictionary of Applied Chemistry,' III, 28–34).

Glyceryl esters occur also in certain waxes, such as Japan wax from *Rhus succedanea* and other species, the wax from species of *Balanophora* (Java), myrtle-berry wax from *Myrica cerifera* (N. America), and other species of [illegible]*a* found in N. and S. America, [illegible]nia, and the Cape of Good Hope.

Note :—For further information on distribution of esters of glycerol see under the respective fatty acids in Vol. II of this work. For synthesis of esters see paper by Scheij, Rec. Tr. Ch. **18**, 169; Ch. Centr. 1899, 2, 20.

Glycerol is formed as a secondary product of the alcoholic fermentation of sugars by Saccharomycetes (Pasteur, Comp. Rend. **46**, 857; **47**, 224), and also of dextrose, lævulose, and maltose by *Oïdium albicans* (Linossier and Roux, Comp. Rend. **110**, 355 and 868). According to Udránszky (Zeit. physiol. Ch. **13**, 549) glycerol can be formed by yeast independently of alcoholic fermentation.

Glycerol is formed from cane-sugar by fermentation with the mould *Mucor racemosus* (Emmerling, Ber. **30**, 454).

The quantity of glycerol produced from various sugars during alcoholic fermentation appears to be inversely proportional to the activity of the yeast (Laborde, Comp. Rend. **129**, 344: this paper discusses the various conditions determining the fluctuation in the quantity of glycerol).

The glycerol found in fermented liquids may in part arise from the action of an oleolytic enzyme present in yeast on the fats of the yeast itself (Delbrück, Abst. in Journ. Fed. Inst. **8**, 243).

Glycerol is among the products of fermentation by the mould-fungus *Eurotiopis gayoni* (Duclaux, Journ. Fed. Inst. **6**, 412).

Mycoderma vini I can produce glycerol (1·5 per cent. in fourteen weeks) in a nutrient solution containing alcohol and malic acid (Seifert, as quoted by Klöcker, 'Die Gärungsorganismen, &c.' p. 242).

According to Schultz *Mycoderma vini* can transform 7 per cent. of alcohol into glycerol in appropriate solution (Van Laer, Journ. Fed. Inst. **7**, 351). Species of *Mycoderma* grown in nutrient solutions containing saccharose and maltose produce traces of glycerol (*Ibid.*).

The mannitol ferment of Gayon and Dubourg can produce glycerol from most sugars (Ann. Inst. Pasteur, **15**, 527).

Glycerol is found in the gastric juice (? hydrolysis of fats; Nencki and Sieber, Zeit. physiol. Ch. **32**, 291).

Synthetical Processes.

[**A.**] From *normal* [**15**] or *isopropyl alcohol* [**16**] through propylene (see under isopropyl alcohol [**16**; **B**]: also LeBel and Greene, Am. Ch. Journ. **2**, 23; Beilstein and Wiegand, Ber. **15**, 1498; Friedel and Silva, Jahresber. **1873**, 322; Mouneyrat, Bull. Soc. [3] **21**, 616: for pyrogenic contact production of propylene from isopropyl alcohol see Ipatieff, Ber. **35**, 1056), propylene chloride by combination with chlorine, 1 : 2 : 3-trichlorpropane (trichlorhydrin) by heating with iodine chloride (Friedel and Silva, Zeit. [2] **7**, 683), and the action of water at 180° on the trichlorpropane (*Ibid.* Comp. Rend. **74**, 805; **76**, 1594; Bull. Soc. [2] **20**, 98). Also from propylene through propylene bromide, 1 : 2 : 3-tribrompropane (tribromhydrin) by heating the latter with bromine in the presence of iron (Kronstein, Ber. **24**, 4246), triacetin by the action of silver acetate, and hydrolysis (Wurtz, Ann. **102**, 340).

According to Schorlemmer propylene chloride and 1 : 2 : 3-trichlorpropane can be obtained by the direct chlorination of propane (Proc. Roy. Soc. **17**, 372; Ann. **150**, 214; **152**, 159), so that generators of the latter (see under n-propyl alcohol [**15**; **A**; **B**; **C**; **D**, &c.]) become generators of glycerol.

According to Mouneyrat tribromhydrin is among the products of the action of bromine on propylene bromide in presence of aluminium bromide (Bull. Soc. [3] **19**, 805).

The following synthetical products are generators of propylene, and therefore of glycerol by the above methods:—

[**B.**] *Amyl alcohols* of fusel oil [**22**] by passing the vapour through a hot tube (Reynolds, Journ. Ch. Soc. **3**, 111; Ann. **77**, 118; Wurtz, Ann. **104**, 242), or by pyrogenic contact decomposition (Ipatieff, Ber. **35**, 1053).

[**C**] *and oxalic acids* [Vol. II] by [illegible] a mixture of calcium oxalate

and potassium acetate (Dusart, Ann. **97**, 127). Also among the products obtained by passing the vapour of acetic acid over heated zinc dust (Jahn, Ber. **13**, 2111).

[**D.**] *Ethyl alcohol* [**14**] by the interaction of zinc ethyl and *carbon tetrachloride* [methane; **1**; **L**; **O**, &c.] (Beilstein and Rieth, Ann. **124**, 242), or of bromoform and zinc ethyl (Beilstein and Alexejeff, Jahresber. **1864**, 470).

Also from dichloracetal (Lieben, Ann. **104**, 114; Jacobsen, Ber. **4**, 217; Pinner, Ber. **5**, 148; Krey, Jahresber. **1876**, 474) by the action of zinc ethyl (Paternò, Comp. Rend. **77**, 458).

[**E.**] *Acetone* [**106**] through 2 : 2-dichlorpropane by the action of phosphorus pentachloride (Friedel, Ann. **112**, 236) and the action of sodium at 130–150° (Friedel and Ladenburg, Zeit. [2] **4**, 48). Also from 2 : 2-dibrompropane by the same process (Reboul, Ann. Chim. [5] **14**, 488).

Acetone combines with bromine to form an unstable dibromide (Linnemann, Ann. **125**, 307) which gives *acroleïn* [**101**] on distillation (*Ibid.* 310); or, by the action of iodine trichloride on acetone, diiodacetone is formed (Simpson, Journ. pr. Ch. **102**, 380), and this yields *acroleïn* on treatment with silver cyanide (*Ibid.*). Acroleïn when reduced with zinc and hydrochloric acid gives allyl alcohol (Linnemann, Ann. Suppl. **3**, 260), and the latter yields glycerol by oxidation with potassium permanganate (Wagner, Ber. **21**, 1237).

Or allyl alcohol can be converted into allyl iodide (Tollens, Bull. Soc. [2] **9**, 396), or allyl carbonimide (Cahours and Hofmann, Phil. Trans. 1857, p. 555) and allylamine (*Ibid.* Ann. **102**, 301). The latter on acetylation and bromination gives acetyl-$\beta\gamma$-dibrompropylamine and the dibrompropylamine by hydrolysis, γ-amino-$\alpha\beta$-propyleneglycol by heating the latter with water, and glycerol by the action of nitrous acid (Chiari, Monats. **19**, 571).

[**F.**] *Butyric* and *isobutyric* [Vol. II] *acids*; propylene is among the products of electrolysis of the potassium salts (Bunge, Journ. Russ. Soc. **21**, 552; Hamonet, Comp. Rend. **123**, 252; Petersen, Ch. Centr. 1897, **2**, 519). Propylene is also among the products formed by passing butyric acid vapour over heated zinc dust (Jahn, Ber. **13**, 2115).

[**G.**] *Isovaleric acid* [Vol. II]; propylene is among the products (ethylene, butylene, &c.) formed by passing the vapour through a hot tube (Hofmann, Journ. Ch. Soc. **3**, 121); also among the products of dry distillation of calcium isovalerate (Dilthey, Ber. **34**, 2115).

[**H.**] *Lactic acid* [Vol. II]; propylene is among the products (ethylene, &c.) formed by distilling calcium lactate (Gossin, Bull. Soc. [2] **43**, 49).

[**I.**] *Azelaïc acid* [Vol. II]; propylene is among the products of distillation with soda-lime (Miller and Tschitschkin, Journ. Russ. Soc. **31**, 414; Ann. **307**, 375).

[**J.**] *Thymol* [**67**] gives propylene on heating with phosphorus pentoxide (Engelhardt and Latschinoff, Zeit. [2] **5**, 616).

[**K.**] From *acetic acid* [Vol. II] and *ethyl alcohol* [**14**] through ethoxychloracetoacetic ester by the action of sodium on ethylchloracetate in ethereal solution and decomposition of the product by dilute hydrochloric acid (Fittig and Erlenbach, Ann. **269**, 15). The ester on heating with dilute hydrochloric acid gives symmetrical dichloracetone = 1 : 3-dichlorpropanone (*Ibid.* 18), and this yields diiodacetone on heating with potassium iodide solution (Völker, Ann. **192**, 89). Diiodacetone can be converted into acroleïn, &c., as under **E**.

Or acetic acid can be converted into chloracetic acid and nitromethane by distilling potassium chloracetate with potassium nitrite (Preibisch, Journ. pr. Ch. [2] **8**, 316). Nitromethane gives glycerol as below under **L**.

[**L.**] From *methyl alcohol* [**13**] and *formic aldehyde* [**91**] by converting the alcohol into methyl iodide and nitromethane by the action of silver nitrite (Bewad, Journ. Russ. Soc. **24**, 126; Meyer, Ann. **171**, 32); the sodium or barium compound of nitromethane gives bromnitromethane by the action of bromine (Tscherniak, Ber. **7**, 916; Ann. **180**, 128; Ber. **30**, 2588), and this condenses

with formic aldehyde (2 mols.) to give trimethylenebromnitroglycol, which by reduction yields trimethyleneaminoglycol, and the latter by the action of nitrous acid is converted into glycerol (Henry, Rec. Tr. Ch. **16**, 250; Bull. Acad. Roy. Belg. **30**, 25).

Or nitromethane and formic aldehyde may be combined so as to form 'nitroisobutylglycerol,' $(CH_2 . OH)_3 C . NO_2$ (Henry, *loc. cit.*; Piloty and Ruff, Ber. **30**, 1656), from which the corresponding hydroxylamine derivative can be obtained and converted by oxidation with mercuric oxide into the oxime of dihydroxyacetone. Bromine converts the latter into *dihydroxyacetone* [151], and this by reduction with sodium amalgam in presence of aluminium sulphate gives glycerol (Piloty, Ber. **30**, 3161).

NOTE:—Methyl alcohol gives nitromethane also by the interaction of dimethyl sulphate and a nitrite (Kaufler and Pomeranz, Monats. **22**, 492).

[M.] *Citric acid* [Vol. II] by the action of sulphuric acid gives acetonedicarboxylic acid (v. Pechmann, Ber. **17**, 2543; Ann. **261**, 157: see also Peratoner and Strazzeri, Gazz. **21**, 295, and under orcinol [75; C]), which by the action of sodium nitrite yields diisonitrosoacetone (v. Pechmann and Wehsarg, Ber. **19**, 2465). The latter on reduction gives diaminoacetone (Gabriel, Ber. **27**, 1043; Kalischer, Ber. **28**, 1519), which by the action of nitrous acid is converted into dihydroxyacetone (*Ibid.* 1521), and this can be reduced to glycerol as under **L** above.

[N.] *Hippuric acid* [Vol. II] when its ethyl ester is heated with dry sodium ethoxide gives with another product 'dibenzaminodioxytetrol' (Rügheimer, Ber. **21**, 3325), which on heating with sulphuric and acetic acids and water yields diaminoacetone (*Ibid.* 3328). The latter can be converted into dihydroxyacetone and glycerol as above. The other product, 'α-oxy-β-benzamino-β-oxypyrroline,' also gives diaminoacetone by the same method (*Ibid.* **22**, 1955).

[O.] From *mannitol* [51], which gives *acroleïn* [101] among the products of oxidation by sulphuric acid and manganese dioxide (Backhaus, Jahresber. **1860**, 522). Subsequent steps through allyl alcohol, &c., as above under **E**. Or through n-hexane and propylene (as under isopropyl alcohol [16; I]).

NOTE:—All generators of n-hexane (see under n-hexyl alcohol [23; A, &c.]) thus become generators of glycerol.

[P.] *Uric acid* [Vol. II] gives glycerol among the products of reduction by heating with aqueous hydriodic acid (Strecker, Zeit. [2] **4**, 215).

[Q.] From *isobutyl alcohol* [18] through isobutyl chloride or bromide. The haloids give propylene among other products when passed over lime heated above 600° (Nef, Ann. **318**, 22).

Or from isobutyl or *tertiary butyl alcohol* [19] through isobutylene and propylene (see under isopropyl alcohol [16; D; E]). Isobutyl alcohol gives propylene and isobutylene among the products of partial combustion by air in contact with heated platinum (v. Stepski, Monats. **23**, 773).

49. Glycerophosphoric Acid.

$CH_2(OH) . CH(OH) . CH_2 . O . P . O(OH)_2$

Natural Sources.

Has been found in small quantity in human urine, in certain (animal) gallstones, in the juices of the spleen and other organs and tissues. In all cases it is probably a product of decomposition of lecithin (Sotnitschewsky, Zeit. physiol. Ch. **4**, 214; Robin, Arch. Pharm. **2**, 532; Ch. Centr. **1888**, 186; Lépine, Eymonnet, and Aubert, Comp. Rend. **98**, 238; in leucæmic blood, Salamon and Kossel as quoted by Hammarsten, 'Lehrb. d. physiol. Ch.' 1895, p. 152).

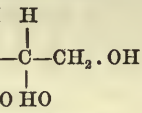
Lecithin, a complex substance related to natural fats and obtained from many animal and vegetable sources, is a choline ester of palmito-stearo-glycerophosphoric acid.

Synthetical Process.

[A.] From *glycerol* [48] by heating with metaphosphoric acid or phosphoric anhydride (Pelouze, Journ. pr. Chem.

36, 257; Comp. Rend. 21, 720; Portes and Brunier, Bull. Soc. [3] 13, 96; Imber and Belugou, *Ibid.* 21, 935: for technical production, Guédras, Monit. Sci. 13, 577; Ch. Centr. 1899, 2, 626).

50. Erythritol; Erythroglucin; Erythromannite; Phycite; 1 : 2 : 3 : 4-Butanetetrol.



(Inactive modification).

Natural Sources.

Occurs in the free state in *Protococcus vulgaris* (Lamy, Ann. Chim. [3] 35, 138; 51, 232; Comp. Rend. 36, 655) and as an ester of a complex acid (orcellic acid) in erythrin and β-erythrin, which are found in the lichens *Roccella tinctoria*, *R. montagnei*, and *R. fuciformis*. (For distribution of erythrin = erythric acid in lichens see also under orcinol [75]: for β-erythrin see β-orcinol [77].) Hesse (Journ. pr. Ch. [2] 57, 258) regards erythrin as a condensation product of erythritol and lecanoric acid.

Erythritol has been found in the alga *Trentepohlia jolithus* (Bamberger and Landsiedl, Monats. 21, 571).

Synthetical Processes.

[A.] From *acetylene* and *ethylene* (see under methane [1; A; D, &c.]). When these gases are passed through a hot tube a hydrocarbon is formed which is apparently identical with erythrene or pyrrolylene (divinyl; 1 : 3-butadiëne; $CH_2 : CH . CH : CH_2$) (Berthelot, Ann. Chim. [4] 9, 466), and this can be converted into an unstable dibromide by bromination in chloroform solution at −21°, then into a stable isomeric dibromide which, with silver acetate, forms a diacetin. The latter is again brominated, the dibromdiacetin converted into a tetracetin by further treatment with silver acetate, and the product hydrolysed (Griner, Comp. Rend. 116, 723; Bull. Soc. [3] 9, 218). When the unstable dibromide is heated to 100° there is formed, with the stable dibromide above referred to, another dibromide which, on oxidation with permanganate, gives the dibromhydrin of natural erythritol from which the latter can be obtained through the diacetin and hydrolysis, or by heating the dibromhydrin with potassium hydroxide and then hydrating the dihydroxybutane thus obtained by heating with water (Griner, Comp. Rend. 117, 553; Bull. Soc. [3] 9, 218; also Thiele, Ann. 308, 333; Maquenne and Bertrand, Comp. Rend. 132, 1565).

Or the acetylene and ethylene could be indirectly converted into erythrene through pyrrole as under C, this last compound being formed among other products when a mixture of acetylene, ethylene, and ammonia are passed through a hot tube (Dewar, Proc. Roy. Soc. 26, 65).

[B.] From *amyl alcohol* [22]. Erythrene is said to be among the products formed by passing the vapour through a hot tube (Caventou, Ann. 127, 93), or by pyrogenic decomposition by passing the vapour over heated iron (Ipatieff, Ber. 35, 1053).

[C.] From *succinic acid* [Vol. II] and *methyl alcohol* [13] through succinimide (D'Arcet, Ann. Chim. [2] 58, 294; Fehling, Ann. 49, 198; Laurent and Gerhardt, Comp. Rend. d. Travaux de Chim. 1849, 108; Menschutkin, Ann. 162, 165; 187; 182, 93; Bogert and Eccles, Journ. Am. Ch. Soc. 24, 20), *pyrrole* [Vol. II] by distilling succinimide with zinc dust (Bell, Ber. 13, 877). N-methylpyrrole ($C_4H_4 . N . CH_3$) by the action of methyl iodide on potassium pyrrole (Ciamician and Dennstedt, Ber. 17, 2951), dihydromethylpyrrole (methylpyrroline) by reduction with zinc dust and acetic acid (Ciamician and Magnaghi, Ber. 18, 725: see also Knorr and Rabe, Ber. 34, 3491; Ciamician, *Ibid.* 3952), tetrahydromethylpyrrole (N-methylpyrrolidine) by further reduction with hydriodic acid and phosphorus (C. and M. *Ibid.* 2080), the methiodide by addition of methyl iodide, dimethylpyrrolidine ($C_4H_7 .$

$N[CH_3]_2$) by distilling the methiodide with potassium hydroxide, and dimethylpyrrolidine-methiodide (trimethylpyrrolidine iodide; $C_4H_7 . N[CH_3]_3I$) by addition of methyl iodide. The latter compound on distillation with caustic alkali gives (among other products) pyrrolylene or erythrene, which can be treated as under **A** (Ciamician and Magnaghi, Ber. **18**, 2081; **19**, 569; Gazz. **15**, 504).

Or the succinimide can be converted into dichlormaleïnimide by the action of chlorine at 160° (Ciamician and Silber, Ber. **16**, 2393), perchlorpyrrole chloride by the action of phosphorus pentachloride, reduction to tetrachlorpyrrole with zinc dust and acetic acid, conversion into tetraiodopyrrole by heating with potassium iodide solution, and reduction to pyrrole with zinc dust in alkaline solution (*Ibid.* **17**, 554; **19**, 3027), and then through N-methylpyrrole, &c., as above.

Also from succinic acid through methylsuccinimide by distilling the *methylamine* [Vol. II] salt (Menschutkin, Ann. **182**, 92), conversion into N-methylpyrrole by distilling with zinc dust, and then as above.

Or indirectly from succinic acid through lævulic acid by heating with acetic anhydride (Fittig, Ber. **30**, 2148). From lævulic acid through N-methylpyrrole, &c., as below under **D**.

Or succinic acid is converted into the anhydride by heating with acetyl chloride, the anhydride into monosodium ethyl ester by treatment with *sodium ethoxide* in alcoholic solution, and the ester into succinoyl-ester chloride (carbethoxypropionyl chloride) by the action of phosphorus trichloride. The chloride on treatment with *zinc methyl* in benzene solution and decomposition of the product with water gives ethyl lævulate, from which the acid can be obtained by hydrolysis (Blaise, Bull. Soc. [3] **21**, 641; 647). From lævulic acid as below under **D**.

Succinic ester and methylethyl ketone (from *acetic* and *propionic acids*) condense under the influence of sodium ethoxide to form γ-ethylidene-γ-methylpyrotartaric acid ($CH_3 . CH : C[CH_3] . CH[COOH] . CH_2 . COOH$), which gives lævulic acid on oxidation with potassium permanganate (Stobbe, Strigel, and Meyer, Ann. **321**, 105).

[**D.**] From *ethyl alcohol* [**14**] and *acetic acid* [Vol. II] by converting the latter into chloracetic ethyl ester (Willm, Ann. Chim. [3] **49**, 97; Ann. **102**, 109; Conrad, Ann. **188**, 218), and then into acetylsuccinic ester by the interaction of chloracetic ester and sodio-acetoacetic ester (Conrad, *loc. cit.*; Rach, Ann. **234**, 36). Acetylsuccinic ester on boiling with dilute hydrochloric acid is converted into β-acetylpropionic or lævulic (4-pentanonic) acid (Conrad, Ann. **188**, 222; Ber. **11**, 2177), the oxime of which (γ-isonitrosovaleric acid) is formed by the action of hydroxylamine on the ketonic acid (Müller, Ber. **16**, 1618; Rischbieth, Ber. **20**, 2670). The oxime on heating with sulphuric acid forms methylsuccinamic acid (Bredt and Böddinghaus, Ann. **251**, 319), and the latter on heating gives methylsuccinimide (*Ibid.* 320), from which N-methylpyrrole can be obtained by heating with zinc dust as under **C**.

Or sodio-acetoacetic ester and ethylene bromide interact to form bromethylacetoacetic ester, which on heating with dilute hydrochloric acid gives acetylpropyl alcohol. The latter gives lævulic acid on oxidation with chromic acid mixture (Lipp, Ber. **22**, 1197).

Divinyl is among the products formed by passing the vapour of ethyl alcohol over aluminium powder heated to 580–680° (Ipatieff, Journ. pr. Ch. [2] **67**, 420).

[**E.**] From *isohexoic acid* [Vol. II] by long boiling with dilute nitric acid, which gives the anhydride of α-methylhydroxyglutaric acid = 2 : 2-methylpentanoldiacid (Bredt, Ber. **14**, 1781). This anhydride on heating with sulphuric acid gives lævulic acid (Tollens and Block, Ber. **19**, 707), which can be treated as under **D**.

The anhydride can also be obtained from *isohexoic* (*isobutylacetic*) *acid* through the anhydride of γ-hydroxyisohexoic acid by oxidising the former acid with potassium permanganate (Bredt,

Ann. 208, 59) and boiling the γ-hydroxy-isohexoic anhydride with dilute nitric acid (*Ibid.* 62).

[F.] From *malonic acid* [Vol. II] and *glycerol* [48] through allylmalonic acid by the action of allyl iodide on sodio-malonic ester and hydrolysis (Conrad and Bischoff, Ann. 204, 168), allylacetic acid by heating allylmalonic acid (*Ibid.* 170), and γδ-dibromvaleric acid by the addition of bromine (Messerschmidt, Ann. 208, 100). The dibromo-acid on boiling with water gives (with much dihydroxyvaleric acid) lævulic acid (Fittig and Urban, Ann. 268, 64), which can be treated as under D.

Or from malonic acid, glycerol, and *methylamine* [Vol. II] (with ethyl alcohol as accessory) through ethylbrompropyl malonate by the action of trimethylene bromide (see under propylene glycol [46; A]) on sodio-malonic ester. Ethylbrompropyl malonate on bromination gives ethyl-αδ-dibrompropyl malonate, and this on treatment with methylamine yields a methylamide which on hydrolysis gives among other products N-methylpyrollidine-2-carboxylic = hygric acid (Willstätter, Ber. 33, 1160; W. and Ettlinger, Ber. 35, 620). The latter on dry distillation yields N-methylpyrollidine (Liebermann and Cybulski, Ber. 28, 582), which can be treated as above under C.

Malonic acid and *acroleïn* [101] from glycerol condense in presence of pyridine to form β-vinylacrylic acid, and this is reduced by sodium amalgam to allylacetic acid (Doebner, Ber. 35, 1136: according to Thiele and Jehl, Ber. 35, 2320, the acid thus formed is βγ-pentenoic acid).

[G.] From *acetic acid* [Vol. II], *glycerol* [48], and *ethyl alcohol* [14] through allylacetoacetic ester by the action of allyl iodide on sodio-acetoacetic ester (Zeidler, Ann. 187, 33), allylacetic ester by the action of sodium ethoxide (*Ibid.* 39), allylacetic acid by hydrolysis, and then as under F.

Or allylacetoacetic ester can be hydrolysed to allylacetone (Zeidler, Ann. 187, 35; Conrad, Ann. 192, 153; Merling, Ann. 264, 323), which gives lævulic acid on oxidation with potassium permanganate (v. Braun and Stechele, Ber. 33, 1472).

Or glycerol can be converted into trimethylene bromide (see under propylene glycol [46; A]) and the latter condensed with sodio-acetoacetic ester to form brombutylmethyl ketone (Lipp, Ber. 18, 3278). The latter on decomposition by alkali gives allylacetone (v. Braun and Stechele, *loc. cit.* 1473), which can be oxidised to lævulic acid as above.

Or from acetic acid or ethyl acetate and *acetone* [106] through acetylacetone (see under n-primary amyl alcohol [20; B; C]). The latter by the action of ethyl chloracetate on the sodium derivative gives ββ-diacetylpropionic ethyl ester (March, Comp. Rend. 130, 1192), and this on treatment with strong caustic soda solution yields lævulic acid (*Ibid.* 132, 697).

Or sodio-acetylacetone and *ethyl-α-brompropionate* (see under aldehyde [92; E]) interact to form ββ-diacetyl-α-methylpropionic ethyl ester, which is decomposed by alkali as above into lævulic acid and ester (March, *loc. cit.* 134, 179: see also Ann. Chim. [7] 26, 295).

Also from *glycerol* through allylamine by the interaction of allyl iodide and silver cyanate, and decomposition of the allyl cyanate with alkali (Cahours and Hofmann, Phil. Trans. 1857, 555; Ann. 102, 301). Allylamine by the action of *ethyl iodide* gives ethylallylamine (Rinne, Ann. 168, 261), and the vapour of the latter yields (among other products), when passed over heated lead oxide, pyrrole (Königs, Ber. 12, 2344), which can be treated as under C.

Or from glycerol through allyl alcohol, allyl chloride (Tollens, Ann. 156, 154; Eltekoff, Journ. Russ. Soc. 14, 394), and trimethylene-chlorobromide = 1 : 3-chlorbrompropane (Reboul, Ann. Chim. [5] 14, 487). The latter by the action of *potassium cyanide* gives γ-chlorbutyronitrile (Henry, Bull. Soc. [2] 45, 341; Gabriel, Ber. 23, 1771), and the chlornitrile by interaction with sodium phenolate yields γ-phenoxybutyronitrile (Gabriel, Ber. 24, 3231), which by reduction with sodium in

alcohol gives δ-phenoxybutylamine, and the latter on heating with strong hydrochloric acid at 180–185° δ-chlorbutylamine (*Ibid.* 3232). On distilling the amine with potash solution pyrrolidine is formed (*Ibid.* 3234; Schlinck, Ber. **32**, 1025) and the latter might be methylated and treated as above under **C**.

Or from glycerol through allyl alcohol (see under ethyl alcohol [**14**; **G**]), which probably gives divinyl among the products of pyrogenic contact decomposition (Ipatieff, Ber. **35**, 1054).

[**H.**] From *lævulose* [**155**] through lævulic acid by boiling with dilute sulphuric acid (Grote and Tollens, Ann. **175**, 181) and subsequent treatment as under **D**.

[**I.**] *Mannose* [**156**] gives lævulic acid when its phenylhydrazone is heated with hydrochloric acid (Fischer and Hirschberger, Ber. **22**, 370).

[**J.**] From *dextrose* [**154**] through saccharic acid by oxidation with nitric acid or bromine (Trommsdorff, Ann. **8**, 36; Guérin-Varry, Ann. Chim. [2] **49**, 280; **52**, 318; **65**, 332; Herzfeld, Ann. **220**, 352; Tollens, Ann. **249**, 218). Ammonium saccharate gives pyrrole on distillation (Bell and Lapper, Ber. **10**, 1962), and this can be converted into dimethylpyrrolidine, &c., as under **C**.

Or from dextrose through *gluconic acid* [Vol. II], d-arabinose, and *d-erythrose* (see under latter [**152**; **D**]). The latter gives i-erythritol on reduction with sodium amalgam (Ruff, Ber. **32**, 3677).

[**K.**] From *diethylamine* [Vol. II]. Pyrrole is formed when the vapour is passed through a hot tube (Bell, Ber. **10**, 1868), and can be treated as under **C**.

[**L.**] From *glutamic acid* [Vol. II] by converting the acid into pyroglutamic acid by heating to 190°, the latter on further heating giving pyrrole (Haitinger, Monats. **3**, 228).

[**M.**] From *piperidine* [Vol. II] through dimethylpiperidine by heating the hydrochloride with methyl alcohol at 250° and decomposition of the ammonium chloride derivative by silver oxide, &c. (Ladenburg, Ber. **16**, 2057; Ladenburg, Mugdan, and Brzostovicz, Ann. **279**, 344). Dimethylpiperidine hydrochloride when treated with hydrogen chloride at 220° is converted into dimethylpyrrolidine (Ladenburg, Mugdan, and Brzostovicz, *loc. cit.*: also Merling, Ann. **264**, 310), which can be converted into erythrene as under **C**, &c.

[**N.**] *Dimethylheptenol* [**35**] gives lævulic acid among the products of its oxidation by chromic acid mixture (Barbier, Comp. Rend. **126**, 1424).

[**O.**] From *crotonic aldehyde* [**102**] and *hydrogen cyanide* [**172**]. The cyanhydrin of crotonic aldehyde hydrolyses to α-hydroxypentenoic acid [CH_3 . CH : CH . CH(OH) . COOH], and this on heating with dilute hydrochloric acid undergoes (isomeric) transformation into lævulic acid (Fittig, Ber. **29**, 2582: see also Lobry de Bruyn, Bull. Soc. [2] **42**, 159; Fittig, Ann. **299**, 1).

[**P.**] From *furfural* [**126**] through pyromucic acid by oxidation (Schwanert, Ann. **114**, 63; **116**, 257; Volhard, Ann. **261**, 379). The acid on heating with lime and ammonio-zinc chloride gives pyrrole (Canzoneri and Oliveri, Gazz. **16**, 487). From pyrrole to erythrene as above under **C**.

[**Q.**] *Methylheptenone* [**111**] on oxidation with potassium permanganate gives a ketone glycol which, on further oxidation with chromic and sulphuric acid, yields (with acetone) lævulic acid (Tiemann and Semmler, Ber. **28**, 2128).

[**R.**] From *d-erythrose* [**152**] by reduction as above under **J**.

[**S.**] *Azelaïc acid* [Vol. II] gives erythrene among the products of its distillation with soda-lime (Miller and Tschitschkin, Journ. Russ. Soc. **31**, 414; Ann. **307**, 375).

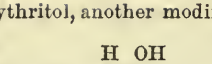
[**T.**] From *gluconic acid* [Vol. II] through d-arabinose and d-erythrose as above under **J**.

[**U.**] From *pyrrole* [Vol. II] and *methyl alcohol* [**13**] as above under **C**.

[**V.**] *Isopropyl alcohol* [**16**] gives divinyl (erythrene) among the products of pyrogenic contact decomposition (Ipatieff, Ber. **35**, 1056).

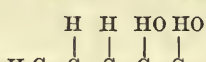
Note:—The biochemical product, d-erythrulose [**152**], obtained from i-erythritol by the action of the sorbose *Bacterium*, gives with the

above i-erythritol, another modification, d-erythritol :—



on reduction (Bertrand, Comp. Rend. 130, 1472). A partial synthesis of l-erythritol starting from l-xylose has been effected by Maquenne (Comp. Rend. 130, 1402).

51. Mannitol; 1:2:3:4:5:6-Hexanehexol.



(Dextro-modification).

Natural Sources.

Mannitol is widely distributed throughout the vegetable kingdom. Occurs in 'manna,' the thickened sap of the manna ash, *Fraxinus ornus* = *Ornus europæa* and *O. rotundifolia* (Proust, Ann. Chim. **57**, 143; Tanret, Bull. Soc. [3] **27**, 947); in Australian manna from *Myoporum platycarpum* (Flückiger, Ch. Zeit. **18**, 185); in root of monkshood, *Aconitum napellus* (Smith, Jahresber. **1850**, 535); in celery, *Apium graveolens* (Payen, Ann. **12**, 60; Monteverde, Ann. Agronom. **19**, 444), parsley (Monteverde, *loc. cit.*), and pomegranate root (Boutron-Charlard and Guillemette, Journ. Pharm. **21**, 169); in leaves and twigs of lilac, *Syringa vulgaris* (Roussin, Jahresber. **1851**, 550; Ludwig, *Ibid.* **1857**, 503: see also Monteverde, *loc. cit.*); in bark of *Canella alba* (Meyer and Reiche, Ann. **47**, 234; Petroz and Robiquet, Journ. Pharm. **8**, 198), and of ash, *Fraxinus excelsior* (Rochleder and Schwarz, Ann. **87**, 186).

Mannitol exists also in the sap of Coniferæ such as *Pinus* and *Abies*, &c. (Kachler, Monats. **7**, 410); in coffee berries (Boussingault, Comp. Rend. **91**, 639) and berries of *Ephedra distachya* (Meunier, Ann. Chim. [6] **22**, 412); in fruit of cherry laurel, *Prunus laurocerasus* (Vincent and Delachanal, Comp. Rend. **114**, 486); in olives (De Luca, Jahresber. **1861**, 740; **1862**, 505; Bull. Soc. **1863**, 372); in pine-apple (Lindet, *Ibid.* [2] **40**, 65), and in the fruit of *Cactus opuntia* (Berthelot, Ann. Chim. [3] **46**, 66). The 'manna' of olives is an exudation resulting from a bacterial disease of the cambium layer and contains 52 per cent. of mannitol (Trabut and Schweinfurth, Comp. Rend. **132**, 225: see also Battandier, Journ. Pharm. [6] **13**, 177).

Mannitol occurs in the cambium layer of larch, *Larix europæa*, and other Coniferæ; in the water dropwort, *Œnanthe crocata*; in *Meum athamanticum*; *Polypodium vulgare*; *Scorzonera hispanica*; *Triticum repens*; root-bark of *Punica granatum*; in leaves of privet, *Ligustrum vulgare*; in fruit of *Laurus persea*, and in leaves of the cocoanut palm, *Cocos nucifera* (Watts's Dict. Morley and Muir, III, 189).

Mannitol occurs also in the tubercles of *Cyclamen europæum* (De Luca, Comp. Rend. **47**, 295; **87**, 297; Bull. Soc. [2] **32**, 417). The mannitol complex appears to be contained in cyclamin, the glucoside occurring in this and other species of *Cyclamen* and in Primulaceæ.

Mannitol has been found in certain Scrophulariaceæ (272 species) of the genera *Rhinanthus* and *Euphrasia* and in some Orobancheaceæ, Oleaceæ, and Umbelliferæ (Monteverde, Ann. Agronom. **19**, 444; Journ. Ch. Soc. **66**, II, abst. 25); in leaves and bark of *Genipa brasiliensis* (Kwasnik, Ch. Zeit. **16**, 109); in leaves and bark of *Basanacantha spinosa*, var. *ferox* (Grützner and Pecholt, Arch. Pharm. **233**, 1); in leaves of *Catha edulis* (Beitler, *Ibid.* **239**, 17); in sap of the sea buckthorn, *Hippophaë rhamnoides* (Erdmann, Ber. **32**, 3353).

A true manna found on *Andropogon annulatus* contains 58 per cent. mannitol (Baker and Smith, Journ. and Proc. Roy. Soc. N. S. Wales, **30**, 291). The lichens *Physcia* (*Xanthoria*) *parietina* and *Callopisma vitellinum* contain mannitol (Zopf, Ann. **300**, 354; for the former Zopf quotes Lilienthal).

Mannitol occurs in algæ and fungi:—*Laminaria saccharina* (Stenhouse, Ann. **51**, 349; *Russula integra* (= *Agaricus integer*) to the extent of 20 per cent. (Thörner, Ber. **12**, 1635); *Lactarius*

pallidus, *L. pyrogallus*, *L. vellevreus*, *L. turpis*, *L. piperatus*, *L. controversus*, &c. (Bourquelot, Comp. Rend. **108**, 568); *Boletus* and *Amanita* sp., *Pholiota radicosa*, *Hypholoma fasciculare* (*Ibid.* **111**, 578); *Elaphomyces granulatus* (Bissinger, Arch. Pharm. [3] **21**, 321); also in ergotised rye (Pelouze and Liebig, Comp. Rend. **3**, 418; Ann. Chim. [2] **63**, 113: for occurrence of mannitol in algæ, fungi, &c., see also Braconnot, Ann. Chim. [1] **79**, 265; **80**, 272; **87**, 237; Vauquelin, *Ibid.* **85**, 5; Knop and Schnedermann, Ann. **49**, 293; Journ. pr. Ch. **32**, 411; Döpping and Schlossberger, Ann. **52**, 117; Müntz, Comp. Rend. **76**, 649; **79**, 1182; **82**, 210; Ann. Chim. [5] **8**, 56; Ferry, Ch. Centr. 1889, **1**, 541; 1891, **1**, 220).

The alcoholic extract of *Agaricus campestris* contains mannitol (Zega, Ch. Zeit. **24**, 285).

The mould *Penicillium glaucum* can under certain conditions produce mannitol as a product of metabolism (Müntz; see Klöcker's 'Gärungsorganismen, &c.' p. 229).

Mannitol is formed during the lactic fermentation of sugar (Liebig, Jahresber. **1847-48**, 466; Strecker, Ann. **92**, 80; Pasteur, Jahresber. **1857**, 511; Dragendorff, *Ibid.* **1879**, 854; Arch. Pharm. [3] **15**, 47), and also during the viscous or mucous fermentation of sugar (Pasteur, Jahresber. **1861**, 728; Bull. Soc. **1861**, 30; Journ. Pharm. [3] **39**, 433). The sugar in wine is converted into mannitol during the degeneration known as 'bittering' (Basile, Staz. Sper. Agrar. **26**, 451; Gayon and Dubourg, Ann. Inst. Past. **8**, 1894; Laborde, Comp. Rend. **126**, 1223). This mannitol fermentation is an anaerobic process (Peglion, Centr. Bakter. II, **4**, 73) and the ferment can produce mannitol from lævulose only (Gayon and Dubourg, *loc. cit.* **15**, 527).

Reducing micro-organisms generally may give rise to mannitol during the fermentation of sugars, especially under anaerobic conditions. Thus, many fermented liquors from various fruits, &c., may contain mannitol (Vauquelin and Fourcroy, Ann. Chim. [1] **65**, 161; Pelouze, *Ibid.* [2] **47**, 409; Berthelot, Comp. Rend. **41**, 392; Ann. Chim. [3] **46**, 66; Scheibler, Ber. **6**, 612; Guibourt, Ann. Chim. [2] **16**, 371; Marcano, Comp. Rend. **108**, 955; Carles, *Ibid.* **112**, 811; Blarez, Journ. Pharm. [5] **27**, 260; Roos, Ch. Centr. 1893, **1**, 1098; Malbot, Bull. Soc. [3] **11**, 87; 176; 413; Jandrier, Comp. Rend. **117**, 498).

Mannitol has been found in beet-sugar molasses (Margueritte; quoted by Maquenne, 'Les Sucres, &c.' p. 131: also Scheibler, *Ibid.*; and v. Lippmann, Ber. **25**, 3216). The mannitol is produced in this case from sugar by *Leuconostoc mesenterioides* (Greig-Smith and Steel, Journ. Soc. Ch. Ind. **21**, 1386). *Bacillus gummosus* produces mannitol from sugar (Happ; quoted by Emmerling, 'Die Zersetzung, &c.' p. 91).

Mannitol has been found in the urine of dogs after giving morphia or after feeding with rye bread (Jaffé, Zeit. physiol. Ch. **7**, 297). The mannitol in the last case may have been derived directly from the bread.

Synthetical Processes.

[A.] *Formic aldehyde* [**91**] in contact with lime water or a mixture of magnesia, magnesium sulphate, and lead gives a syrupy mixture containing *a*-acrose = i-fructose (Loew, Journ. pr. Ch. [2] **33**, 321, **34**, 51; Fischer, Ber. **21**, 989; Fischer and Passmore, Ber. **22**, 359; Loew, *ibid.* 475: see also Butleroff, Ann. **120**, 295; Tollens, Ber. **15**, 1629; **16**, 1917; Wehmer and Tollens, Ber. **19**, 707 and 2135). On treatment with phenylhydrazine the *a*-acrosazone is obtained (Fischer), and this by the action of strong hydrochloric acid furnishes the corresponding *a*-acrosone (Fischer and Tafel, Ber. **22**, 98). The latter by reduction with zinc dust and acetic acid gives i-fructose which, by reduction with sodium amalgam, is converted into i-mannitol = *a*-acritol (Fischer and Tafel, Ber. **22**, 100); the i-mannitol by oxidation with dilute nitric acid gives i-mannose (Fischer, Ber. **23**, 390), and by further oxidation with bromine i-mannonic acid. The

latter by fractional crystallisation of the morphine or strychnine salt is resolved into d- and l-mannonic acids. The d-acid on reduction with sodium amalgam in acid solution gives *d-mannose* [156], and by further reduction of the latter with sodium amalgam in alkaline solution d-mannitol (Fischer and Hirschberger, Ber. **21**, 1808: see also Ber. **23**, 2133).

[B.] *Glycerol* [48] when heated with dehydrating agents, such as acid potassium sulphate, yields *acroleïn* [101] (Redtenbacher, Ann. **47**, 120; Aronstein, Ann. Supp. **3**, 180; Van Romburgh, Bull. Soc. [2] **36**, 550; Griner, Ann. Chim. [6] **26**, 367; Wohl and Neuberg, Ber. **32**, 1352), which combines with bromine to form acroleïn bromide = 2 : 3-dibrompropionic aldehyde (Aronstein, *loc. cit.* 185; Henry, Ber. **7**, 1112; Linnemann and Penl, Ber. **8**, 1097). The latter on treatment with baryta water gives a product from which the osazone of *α*-acrose can be isolated (Fischer and Tafel, Ber. **20**, 1092; 2566) and converted into mannitol as under **A**.

Glycerol can also be directly oxidised by means of bromine in presence of sodium carbonate solution (Fischer and Tafel, Ber. **20**, 3385), the 'glycerose' thus obtained giving rise by the action of alkali to a mixture of sugars from which *α*-acrose can be isolated and treated as above.

Note:—According to Neuberg (Ber. **35**, 2632) acrose partly consists of d-fructose. Glycerose is a mixture of dihydroxyacetone and glyceric aldehyde, the former predominating (see under dihydroxyacetone [151; D]).

[C.] *Acetone* [106] gives a dibromide (C_3H_6O . Br_2) by the action of bromine, this compound on distillation giving acroleïn (Linnemann, Ann. **125**, 310), which can be converted into *α*-acrose, &c., as under **B**.

[D.] From *dextrose* [154] by reduction with sodium amalgam (Dewar, Phil. Mag. **4**, 39; Adrian Brown, Trans. Ch. Soc. **51**, 642; Bouchardat, Bull. Soc. [2] **16**, 38). The yield is small.

[E.] From *lævulose* [155] by reduction with sodium amalgam (Krusemann, Ber. **9**, 1465; Fischer, Ber. **23**, 3684). The yield is 30–40 per cent. of the lævulose, about 50 per cent. of sorbitol being formed simultaneously.

[F.] From *mannose* [156] through lævulose (see under sorbitol [52; C]), and then as above under **E**.

[G.] From *tartaric acid* [Vol. II] through dihydroxymaleïc acid by oxidation with hydrogen peroxide in presence of ferrous salts. The acid referred to decomposes in aqueous solution with the formation of glycollic aldehyde, and the latter, on heating *in vacuo* at 100°, polymerises to a mixture of *α*- and *β*-acrose (Fenton, Trans. Ch. Soc. **65**, 899; **67**, 48; 774; **69**, 546; **71**, 375; Jackson, *Ibid.* **77**, 129). The polymerisation of the aldehyde takes place in presence of dilute caustic soda at 0° (Jackson, *loc. cit.*).

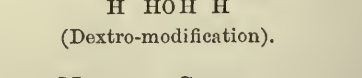
[H.] From *acetal* [93] through glycollic aldehyde (see under furfural [126; F]), and then as above.

[I.] From *ethyl alcohol* [14] through glycollic aldehyde (see under furfural [126; G]), and then as above.

[J.] From *choline* [Vol. II] through glycollic aldehyde (see under furfural [126; H]), and then as above.

[K.] *Gluconic acid* [Vol. II] has been said to give mannitol on reduction with sodium amalgam in acid solution (v. Wachtel; Tollens, 'Kohlenhydrate,' II, 282; Fischer, Ber. **23**, 930: see also Herzfeld, Ann. **220**, 335).

52. Sorbitol; Hexanehexol.



(Dextro-modification).

Natural Sources.

In berries of mountain-ash (Boussingault, Ann. Chim. [4] **26**, 376; Hitzemann and Tollens, Ber. **22**, 1048); in apples, pears, medlars, plums, and cherries (Vincent and Delachanal, Comp. Rend. **108**, 354; **109**, 676; **114**, 486; Bull. Soc. [2] **34**, 218), and in beet-sugar molasses (v. Lippmann, Ber. **25**, 3216).

Sorbitol is converted into sorbose, the hexose (ketose) from mountain-ash berries, by the action of a *Bacterium* (Bertrand, Comp. Rend. **122**, 900; **126**, 653). The sorbose *Bacterium* of Bertrand is, as suspected by this author, *B. xylinum* of A. J. Brown (Emmerling, Ber. **32**, 541).

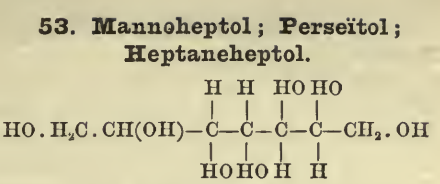
Synthetical Processes.

[A.] From *dextrose* [154] by reduction with sodium amalgam (Meunier, Comp. Rend. **111**, 49). Mannitol is formed to some extent [51; D].

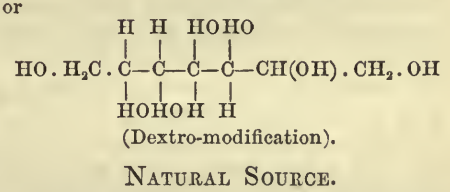
[B.] From *lævulose* [155] by reduction with sodium amalgam (Fischer, Ber. **23**, 3684: see also under mannitol [51; E]).

[C.] *Mannose* [156] with phenylhydrazine in excess gives glucosazone (Fischer, Ber. **20**, 821; Fischer and Hirschberger, Ber. **21**, 1805; **22**, 365; 1155; Reiss, *Ibid.* 609), and this on heating with fuming hydrochloric acid yields the osone (Fischer, Ber. **21**, 2631; **22**, 88; **23**, 2120). The latter on reduction with zinc and acetic acid gives *lævulose* [155] (Fischer, Ber. **23**, 2121), which can be reduced to sorbitol as above under **B**.

53. Mannoheptol; Perseïtol; Heptaneheptol.



or



(Dextro-modification).

Natural Source.

In fruit, seeds, and leaves of *Laurus persea* (Avequin, 1831; Melsens, Ann. Chim. [2] **72**, 109; Müntz and Marcano, Comp. Rend. **99**, 38; Ann. Chim. [6] **3**, 279; Maquenne, Comp. Rend. **107**, 583; Ann. Chim. [6] **19**, 5).

Synthetical Process.

[A.] From *formic aldehyde* [91] or *glycerol* [48] through *d-mannose* as under mannitol [51; A]. The d-mannose forms a cyanhydrin by the action of *hydrogen cyanide* [172], which hydrolyses to d-mannoheptonic acid (Fischer and Hirschberger, Ber. **22**, 370; Fischer and Passmore, Ber. **23**, 2226). The anhydride (lactone) of this acid reduces to d-mannoheptol by the action of sodium amalgam (Fischer, Ber. **23**, 936; Fischer and Passmore, *ibid.* 2231).

AROMATIC ALCOHOLS AND PHENOLS.

54. Benzyl Alcohol; Phenylcarbinol; Phenemethylol.

Natural Sources.

Occurs as benzoate in Peru balsam from *Myroxylon* (*Toluifera*) *pereiræ*, San Salvador; as cinnamic ester in this balsam and in liquid storax from *Liquidambar orientalis*. As benzoate and cinnamate in tolu balsam from *Myroxylon toluiferum*, New Granada, Venezuela, Brazil, and Ecuador (Scharling, Ann. **97**, 168; Kraut, Ann. **107**, 208; **109**, 255; **152**, 129; Strecker, Jahresber. **1868**, 566; Laubenheimer, Ann. **164**, 289; Busse, Ber. **9**, 830; Erdmann, Pharm. Journ. **65**, 387; Journ. Soc. Ch. Ind. **19**, 1140).

The alcohol is said to occur in small quantity in the free state in Peru balsam (Kraut, Ann. **152**, 129: compare Thoms, Arch. Pharm. **237**, 271). Benzyl alcohol has been found in the volatile oil of the cherry laurel, *Prunus*

laurocerasus (Tilden, Pharm. Journ. [3] **5**, 761).

Benzyl acetate is the chief constituent of the ethereal oil of jasmine from *Jasminum grandiflorum* (Hesse and Müller, Ber. **32**, 565; 765; Hesse, *Ibid.* 2611; **33**, 1585; **34**, 291; 2916: see also E. Erdmann, Ber. **34**, 2281). The free alcohol occurs also in this oil (Hesse and Müller, *loc. cit.*, 765; Hesse, *Ibid.* 2619; Ch. Ind. **25**, 1).

The lower boiling fraction of the oil of cassia flowers from *Acacia farnesiana* probably contains benzyl alcohol (Schimmel's Ber. April, 1901). The alcohol has been found in considerable quantity in the distillation water from ylang-ylang essence (v. Soden and Rojahn, Ber. **34**, 2809). It is contained in this last oil probably as benzyl salicylate and benzoate (Schimmel's Ber. Oct. 1901). The chief constituent of the oil of *Gardenia* is benzyl acetate (Parone, Boll. Chim. Farm. **41**, 489; Ch. Centr. 1902, **2**, 703).

Synthetical Processes.

[**A.**] From *acetylene* through *benzene* (see under cymene [**6**; **A**]). Benzene can be converted into toluene by treating brombenzene and *methyl iodide* with sodium (Fittig and Tollens, Ann. **131**, 303), or by passing methyl chloride into benzene containing aluminium chloride (Friedel and Crafts, Ann. Chim. [6] **1**, 460; **11**, 264). Toluene gives benzyl alcohol among the products of its oxidation by manganese dioxide and sulphuric acid (Weiler, Ber. **33**, 464), and benzyl acetate by oxidation with chromic acid or potassium permanganate in acetic acid solution (Boedtker, Bull. Soc. [3] **25**, 843).

Toluene is converted into benzyl chloride by passing chlorine into the boiling liquid (Cannizzaro, Ann. Chim. [3] **45**, 468; Beilstein and Geitner, Ann. **139**, 337: see also Lauth and Grimaux, Bull. Soc. [2] **7**, 105), or at ordinary temperatures by chlorinating in sunlight (Schramm, Ber. **18**, 608). Benzyl chloride can be converted into benzyl alcohol by treatment with potassium acetate and subsequent hydrolysis (Cannizzaro, Ann. **96**, 246; Seelig, Journ. pr. Ch. [2] **39**, 167), by heating with a solution of potassium carbonate (Meunier, Bull. Soc. [2] **38**, 159), with water and lead hydroxide (Lauth and Grimaux, Ann. **143**, 81), or with water only (Niederist, Ann. **196**, 353). Benzyl acetate is formed by the interaction of benzyl chloride and lead acetate (Bodroux, Bull. Soc. [3] **21**, 288).

Also from acetylene through ethylene (see under ethyl alcohol [**14**; **A**]), ethylene chloride, vinyl chloride by alcoholic potash (Regnault, Ann. **14**, 28), and chloracetaldehyde by the action of mercuric oxide on vinyl chloride (Glinsky, Zeit. [2] **3**, 678; **4**, 617; **6**, 647). The aldehyde by treatment with *hydrogen cyanide* [**172**] and hydrochloric acid gives β-chlorlactic acid (*Ibid.* [2] **6**, 515; Frank, Ann. **206**, 344), which is converted by silver oxide into glyceric acid (Frank, *loc. cit.* 348). The latter gives pyrotartaric acid as under **F**, citrabrompyrotartaric acid and allylene as under **N**, mesitylene, uvitic acid, and toluene as under **D**.

Note:—All generators of ethylene thus become generators of toluene and of benzyl alcohol.

[**B.**] *Benzoic aldehyde* [**114**] on treatment with caustic alkali gives benzyl alcohol and benzoic acid (Cannizzaro, Ann. **88**, 129; Meyer, Ber. **14**, 2394; Kohn and Trantom, Trans. Ch. Soc. **75**, 1155; Raikoff and Raschtanoff, Ch. Centr. 1902, **1**, 1212), or benzyl alcohol by reduction with sodium amalgam (Friedel, Jahresber. **1862**, 263; Bull. Soc. **1862**, 18). Also from benzoic aldehyde through toluene by heating with hydriodic acid (Berthelot, Jahresber. **1867**, 346), and then as under **A**.

Or benzaldoxime or hydrazone gives benzylamine on reduction with sodium amalgam and acetic acid, or by electrolysis (Goldschmidt, Ber. **19**, 3232; Tafel, *Ibid.* 1928; Tafel and Pfeffermann, Ber. **35**, 1510). Benzylamine may be converted into benzyl alcohol by the action of nitrous acid (see Curtius, Ber. **17**, 958).

Note:—For generators of benzylamine see also under benzyl mustard oil [**169**].

[C.] *Benzoic acid* [Vol. II] gives benzyl alcohol on reduction with sodium amalgam (Herrmann, Ann. **132**, 76; **133**, 335).

Benzoyl chloride by reduction with sodium amalgam in presence of hydrogen chloride, or by reduction with sodium amalgam alone in moist ethereal solution, gives benzyl alcohol (Lippmann, Zeit. [2] **1**, 700; Bull. Soc. [2] **4**, 249; W. H. Perkin, junr., and Sudborough, Proc. Ch. Soc. **10**, 216).

The following synthetical products are generators of toluene, and therefore of benzyl alcohol under **A**:—

Generators of Toluene through Mesitylene and Uvitic Acid.

[D.] *Acetone* [103] on treatment with sulphuric acid condenses to mesitylene (Kane, Phil. Trans. **44**, 474; Hofmann, Journ. Ch. Soc. **2**, 104; Cahours, Comp. Rend. **24**, 255; Varenne, Bull. Soc. [2] **40**, 266; Fittig and Brückner, Ann. **147**, 42; Orndorff and Young, Am. Ch. Journ. **15**, 249; Meyer and Molz, Ber. **29**, 2831; Lucas, *ibid.* 2884; Küster and Stallberg, Ann. **278**, 210; Noyes, Am. Ch. Journ. **20**, 807). Mesitylene on oxidation with nitric acid gives uvitic acid (Fittig and v. Furtenbach, Zeit. [2] **4**, 1; Ann. **147**, 295), and the latter on distillation with soda-lime yields toluene (Baeyer, Zeit. [2] **4**, 119).

[E.] *Normal* and *isopropyl alcohols* [15; 16] through propylene (see under glycerol [48; A]), propylene bromide, allylene by the action of alcoholic potash on the latter (Markownikoff, Ann. **118**, 332: see also Valentin, Ber. **28**, 2664), mesitylene by the action of sulphuric acid on allylene (Schrohe, Ber. **8**, 17; Michael, Journ. pr. Ch. [2] **60**, 441), and then as under **D**.

Or indirectly through propylene bromide and cyanide, pyrotartaric acid by hydrolysis of the latter (Simpson, Ann. **121**, 161), and then through citrabrompyrotartaric acid as under **N** and allylene as under **M**.

Propylene also forms a compound with mercuric sulphate in acid solution which readily decomposes with the formation of *acroleïn* [101] (Denigès, Comp. Rend. **126**, 1145). The latter oxidises readily to acrylic acid, which can be converted into α-chlorlactic acid, glyceric acid, pyrotartaric or pyroracemic acid, allylene, &c. (see under **F**, **I**, **M**).

Note:—All the generators of propylene referred to under glycerol [48; B; C; D; E; F; G, &c.] can be regarded as sources of allylene as above.

[F.] *Glycerol* [48] gives rise to allyl alcohol or iodide (see under ethyl alcohol [14; G] and under isobutyl alcohol [18; D]), either of which can be converted into allyl chloride (Oppenheim, Ann. **140**, 205; Tollens, Ann. **156**, 154; Eltekoff, Journ. Russ. Soc. **14**, 394). The latter on heating with strong aqueous hydrochloric acid at 100° gives propylene chloride (Reboul, Ann. Chim. [5] **14**, 453), which by the action of alcoholic potash yields a mixture of α- and β-chlorpropylene (*Ibid.*, *loc. cit.* 462), the latter on further treatment with alcoholic potash giving allylene (Friedel, Ann. **134**, 262), which can be converted into mesitylene and toluene as under **E** and **D**.

Or the allyl iodide can be converted into allyl cyanide by the action of *potassium cyanide* [172] (Claus, Ann. **131**, 58; Rinne and Tollens, Ann. **159**, 106), and then into α-crotonic acid by heating with potash solution (Will and Körner, Ann. **125**, 273). The crotonic acid can be converted into allylene as under **G**.

Or the allyl iodide can be converted into pyrotartaric (methylsuccinic) acid by heating with alcoholic potassium cyanide and decomposition of the product with potash (Claus, Ann. **191**, 37; Ber. **5**, 612; Euler, Ber. **28**, 2952). The pyrotartaric acid can be converted into citrabrompyrotartaric acid and then into allylene as under **N**.

Glycerol on oxidation with nitric acid (Debus, Phil. Mag. [4] **15**, 195; Ann. **106**, 79; Sokoloff, *Ibid.* 95; Mulder, Ber. **9**, 1902; Beilstein, Ann. **120**, 226), with bromine and water (Barth, Ann. **124**, 341) or mercuric oxide in presence of barium hydroxide (Börnstein, Ber. **18**, 3357) gives glyceric acid which on dry distillation yields, among other products, pyrotartaric acid (Mol-

denhauer, Ann. 131, 337; 339; Böttinger, Ann. 196, 92), which can be treated as above. Glyceric acid also gives among the products of its distillation (with acid potassium sulphate) pyroracemic acid (Moldenhauer, Ann. 131, 337; Böttinger, Ann. 196, 92), which can be converted into uvitic acid, &c., as under I. (For preparation of glyceric acid from glycerol by oxidising with nitric acid in presence of red lead see Zinno, Ch. Centr. 1898, 1, 26; also Wöhlk, Journ. pr. Ch. [2] 61, 200: by alkaline silver chloride, Cazeneuve, Bull. Soc. [3] 15, 763.)

Or from glycerol through epichlorhydrin by the action of hydrochloric acid (Berthelot, Ann. 92, 302; Ann. Chim. [3] 41, 299; Hübner and Müller, Zeit. [2] 6, 344; Watt, Ber. 5, 257; Reboul, Ann. Suppl. 1, 221; Tollens and Münder, Zeit. [2] 7, 252; Prevost, Journ. pr. Ch. [2] 12, 160; Claus, Ber. 10, 557; Cloëz, Ann. Chim. [6] 9, 145). Epichlorhydrin condenses with *hydrogen cyanide* [172] to form a nitrile which gives crotonic acid on reduction with hydriodic acid (Lespieau, Comp. Rend. 127, 965; 129, 224).

Or from glycerol through *acroleïn* [101] (see under mannitol [51; B]), acrylic acid (Wöhlk, Journ. pr. Ch. [2] 61, 200), α-chlorlactic, glyceric, pyrotartaric acids, and allylene as above under E. Or from acroleïn through β-chlorpropionic aldehyde and acid and acrylic acid (Geuther and Cartmell, Ann. 112, 3; Krestownikoff, Jahresber. 1880, 696; Wöhlk, *loc. cit.*).

Or from glycerol through allyl alcohol (see under ethyl alcohol [14; G]), αβ-dibrompropyl alcohol, αβ-dibrompropionic acid and acrylic acid (Bülmann and Wöhlk, Journ. pr. Ch. [2] 61, 199; 215), and then as above. Or from αβ-dibrompropionic acid to glyceric acid as under O below. Or from allyl alcohol through glyoxal (172; BB), and, by means of *hydrogen cyanide* [172], the nitrile of pyroracemic acid as below under H.

[G.] *Malonic acid* [Vol. II], *paraldehyde* (by polymerisation of *acetaldehyde* [92]), and glacial *acetic acid* [Vol. II] when heated to 100° give α-crotonic (2-butenoic) acid (Komnenos, Ann. 218, 149). The latter combines with hypochlorous acid to form α-chlor-β-hydroxybutyric acid (Erlenmeyer and Müller, Ber. 15, 49; Melikoff, Ann. 234, 198). This acid on heating with strong aqueous hydrochloric acid at 100° gives αβ-dichlorbutyric acid (Melikoff, *loc. cit.* 201), which, by heating with excess of aqueous alkali, yields α-chlorisopropylene (Wislicenus, Ann. 248, 297). The latter on heating with alcoholic potash gives allylene which can be treated as above.

Or crotonic acid (ester) is condensed by sodium ethoxide to form dicrotonic ester from which the acid can be obtained by hydrolysis. Dicrotonic acid gives on oxidation with alkaline permanganate methylsuccinic = pyrotartaric acid (v. Pechmann, Ber. 33, 3323), which can be converted into allylene, &c., as under N below.

Or malonic acid (ester) can be converted into methylmalonic ester by sodium and *methyl iodide*. The sodium derivative of methylmalonic ester interacts with ethyl chloracetate to form a propanetricarboxylic ester, the acid (= α-methylethenyltricarboxylic acid) from which gives pyrotartaric acid on hydrolysis (Bischoff and Kuhlberg, Ber. 23, 635).

Or from diethyl malonate, aldehyde, and acetic anhydride through ethylidenemalonic ester, β-cyanobutyric acid, and pyrotartaric acid (see under n-propyl alcohol [15; T]).

[H.] *Acetic aldehyde* [92] by the action of chlorine gives butyrochloral = 2 : 2 : 3-trichlorbutanal (Krämer and Pinner, Ber. 3, 383; Pinner, Ann. 179, 26), which, by oxidation with nitric acid, yields ααβ-trichlorbutyric acid (Krämer and Pinner, *loc. cit.* 389; Judson, Ber. 3, 785; Garzarolli, Ann. 182, 181). The latter on reduction with zinc and water (Sarnoff, Ann. 164, 93) gives α-chlorcrotonic acid, which, by heating with aqueous hydrochloric acid, yields αβ-dichlorbutyric acid (Merlikoff, Ann. 234, 201). The latter can be converted into allylene, &c., as under G.

ααβ-Trichlorbutyric acid also decomposes on heating the aqueous solution

of the sodium salt with the formation of *aa*-dichlorpropylene; the latter on heating with alcoholic potash at 150° gives allylene (Valentin, Ber. **28**, 2661). Butyrochloral also on treatment with caustic alkali gives an allylene dichloride which yields allylene by the action of sodium (Krämer and Pinner, Ann. **158**, 47; Pinner, Ann. **179**, 44; Ber. **8**, 898; **14**, 1081). The *aaβ*-trichlorbutyric acid also gives the same allylene dichloride when the silver salt is boiled with water (*Ibid.*).

Or *aaβ*-trichlorbutyric acid by the action of caustic potash gives *aβ*-dichlorcrotonic acid (Garzarolli, Ber. **9**, 1209) which, on heating with zinc and water, yields tetrolic acid (Szenic and Taggesell, Ber. **28**, 1671). The latter decomposes at 210° with the formation of allylene (see below under **I**).

Or the acetic aldehyde can be converted into *crotonic aldehyde* [**102**] (see under normal butyl alcohol [**17**; **G**]) and the latter oxidised to *a*-crotonic acid (Kekulé, Ber. **3**, 604; Zeit. [2] **6**, 705), which can be converted into allylene, &c., as under **G**.

Note:—Other generators of *crotonic aldehyde* [102] are given under that compound, viz. *malic acid, acetylene, formic* and *acetic esters.*

Or acetic aldehyde and *hydrogen cyanide* [**172**] give a cyanhydrin which by the action of phosphorus pentachloride yields a chlorcyanhydrin, and this by hydrolysis *a*-chlorpropionic acid (Michael and Garner, Ber. **34**, 4049). The latter on heating with barium hydroxide gives acrylic acid (*Ibid.* 4050). From the latter through *a*-chlorlactic acid, glyceric acid, &c., as above under **E**, **F**, &c.

Or from the aldehyde through glyoxal (see under hydrogen cyanide [**172**; **O**]): the latter combines with hydrogen cyanide to form pyroracemic nitrile, from which the acid can be obtained and treated as under **I** below.

[**I.**] From *ethyl alcohol* [**14**] and *acetic acid* through *acetoacetic ester* [Vol. II], which gives *a*-crotonic acid by reduction with sodium amalgam (Beilstein and Wiegand, Ber. **18**, 482). The acid can be converted into allylene as under **G**.

Ethyl alcohol on treatment with iodine in the presence of alkali gives iodoform, which by the action of sodium ethylate yields acrylic acid (Butleroff, Ann. **114**, 204). The latter combines with hypochlorous acid to form *a*-chlorlactic acid (Melikoff, Ber. **12**, 2227), which by treatment with silver oxide gives glyceric acid (*Ibid.* **13**, 272): from the latter pyrotartaric acid, citrabrompyrotartaric acid, allylene, &c., can be obtained as under **F** and **M**.

Ethyl ether (from ethyl alcohol) on chlorination gives dichlorether (D'Arcet, Ann. **28**, 82; Malaguti, Ann. Chim. [2] **70**, 338; [3] **16**, 5; 19; Regnault, *Ibid.* [2] **71**, 392; Lieben, Ann. **111**, 121; **123**, 130; **133**, 287; **141**, 236; **146**, 180; **150**, 87; Abeljanz, Ann. **164**, 197), which by the action of strong sulphuric acid yields chloracetaldehyde (Jacobsen, Ber. **4**, 216). The latter can be converted into *β*-chlorlactic acid, glyceric acid, &c., as under **A**.

Or ethyl alcohol can be converted into chloracetal by chlorination (Lieben, Ann. **104**, 114), and the latter into chloracetaldehyde by heating with acetic acid, dilute sulphuric, or dry oxalic acid (Natterer, Monats. **3**, 446). The chloracetaldehyde is treated as above.

Or ethyl alcohol can be converted into chloral by chlorination, into chloral cyanhydrin (Hagemann, Ber. **5**, 151; Pinner and Bischoff, Ann. **179**, 77; Pinner, Ber. **17**, 1997), trichlorlactic acid by hydrolysis (Pinner and Bischoff, *loc. cit.* 179; Pinner, *loc. cit.*), dichloracetaldehyde by heating the sodium salt with water (Reisse, Ann. **257**, 331), dichlorlactic acid by forming the cyanhydrin of dichloracetaldehyde and hydrolysing (Grimaux and Adam, Ber. **10**, 903; Bull. Soc. [2] **34**, 29), chloracetaldehyde by heating sodium dichlorlactate with water (Reisse, Ann. **257**, 335), and then as above.

Or ethyl alcohol can be converted into ethyl cyanide (propionitrile: see under normal propyl alcohol [**15**; **A**]), *aa*-dichlorpropionic acid by chlorination of the nitrile and hydrolysis (Otto, Ann. **132**, 181; Beckurts and Otto, Ber. **9**, 1877), pyroracemic (propanonic) acid by heating dichlorpropionic ester with water or the acid with water and silver

oxide (B. and O., Ber. **10**, 264; **18**, 228). Pyroracemic acid gives pyrotartaric acid among other products by heating to 100° with hydrochloric acid or to 170° *per se* (De Clermont, Ber. **6**, 72; Böttinger, Ber. **9**, 837; 1823; Ann. **188**, 308; De Jong, Rec. Tr. Ch. **20**, 81; **21**, 191: see also Wolff, Ann. **317**, 22). Pyrotartaric acid can be converted into allylene, mesitylene, &c., as above.

Or (more directly) pyroracemic acid gives uvitic acid, among other products, on boiling with baryta water (Finckh, Ann. **122**, 184; Böttinger, Ann. **172**, 241; 253; **188**, 313; **208**, 129; Wolff and Heipp, Ann. **305**, 125; 152), which acid can be converted into toluene, &c., as under **D**.

Or uvitic acid may be synthesised by heating a mixture of pyroracemic acid and *acetic aldehyde* [**92**] with baryta water (Doebner, Ber. **23**, 2377).

Acetic and pyroracemic acids are also generators of toluene through phthalide-dicarboxylic acid (see under cymene [**6**; IX]).

Acetic acid can be converted into acetyl cyanide by the interaction of acetyl chloride and *silver cyanide* (Hübner, Ann. **120**, 334; **124**, 315); the cyanide on hydrolysis gives pyroracemic acid (Claisen and Shadwell, Ber. **11**, 620; 1563), which yields uvitic acid, &c., as above.

Acetoacetic ester by the action of nitrous acid gives isonitrosoacetone (Meyer and Züblin, Ber. **11**, 695; Ceresole, Ber. **15**, 1328), which, by the action of acetyl chloride, yields acetyl cyanide (Claisen and Manasse, Ber. **20**, 2196). The latter can be converted into pyroracemic acid as above.

Acetoacetic ester by the interaction of the sodium derivative and *α-brom-propionic ester* (Friedel and Machuca, Ann. **120**, 286; Comp. Rend. **53**, 408; Bischoff, Ann. **206**, 319; Zelinsky, Ber. **20**, 2026) gives β-methylacetosuccinic ester (Conrad, Ann. **188**, 226; Bischoff, *loc. cit.* 320): the latter on treatment with alcoholic potash yields pyrotartaric acid (Conrad, *loc. cit.* 227).

Or by the interaction of chloracetic ester and sodio-acetoacetic ester aceto-succinic ester is formed (Conrad, *loc. cit.* 218; Rach, Ann. **234**, 36), which by the action of sodium and *methyl iodide* gives α-methylacetosuccinic ester (Kressner, Ann. **192**, 135): the latter on treatment with alcoholic potash also yields pyrotartaric acid (*Ibid.* 138).

Or the α- and β-methylacetosuccinic esters on heating with hydrochloric acid give β-acetylbutyric and β-acetylisobutyric acids respectively (Bischoff, Ann. **206**, 319 and 331). Both these acids on oxidation with dilute nitric acid yield pyrotartaric acid (*Ibid.* 337) with other products.

Acetoacetic ester also by the action of methyl iodide on its sodium derivative gives methylacetoacetic ester, which by the successive action of bromine and alcoholic potash yields mesaconic acid (Demarçay, Ann. Chim. [5] **20**, 473; Gorboff, Journ. Russ. Soc. **19**, 605; Cloëz, Bull. Soc. [2] **3**, 598 and 602; Wolf, Ann. **260**, 89; Ssemenoff, Journ. Russ. Soc. **23**, 430; **30**, 1009; Conrad, Ber. **32**, 1005). Potassium mesaconate solution gives allylene on electrolysis (Aarland, Journ. pr. Ch. [2] **7**, 142).

Acetoacetic ester by the action of phosphorus pentachloride gives a mixture of β-chlor-α- and β-crotonic acids (Frölich, Zeit. [2] **5**, 270; Geuther, *ibid.* [2] **7**, 237; Autenrieth, Ann. **259**, 359; Fittig, Ann. **268**, 13). Both these acids by the action of potassium hydroxide give tetrolic (2-butinic) acid (Geuther, *loc. cit.* 245; Friedrich, Ann. **219**, 319, 342; Kahlbaum, Ber. **12**, 2338; Fittig and Clutterbuck, Ann. **268**, 96: see also Desgrez, Bull. Soc. [3] **11**, 391). Tetrolic acid is decomposed at 210° into carbon dioxide and allylene.

[**J.**] *Allyl isothiocyanate* [**166**] by the action of zinc dust is converted into allyl cyanide (Schwarz, Ber. **15**, 2508), which can be converted into α-crotonic acid, allylene, &c., as under **F**. Water also in contact with allyl isothiocyanate gives allyl cyanide (Will and Körner, Ann. **125**, 272).

[**K.**] From *normal butyric acid* [Vol. II] through the α-bromo-acid (see under n-propyl alcohol [**15**; **P**]), which gives crotonic acid when the ethyl ester is

treated with alcoholic potash or barium hydroxide solution (Hell and Lauber, Ber. **7**, 560; Michael and Graves, Ber. **34**, 4041: compare also Duvillier, Ann. Chim. [5] **17**, 532; Michael, Journ. pr. Ch. [2] **35**, 92; **38**, 12; Erlenmeyer and Marx as quoted by Michael and Graves, *loc. cit.* 4040). The sodium salt of α-brombutyric acid also gives crotonic acid on distillation (Bischoff and Walden, Ann. **279**, 101).

Butyryl chloride on chlorination also gives α- (with β and γ) chlorbutyryl chloride. The corresponding α-chloro-acid gives crotonic acid (with α-hydroxy-butyric acid) on treatment with barium hydroxide solution (Michael and Garner, Ber. **34**, 4051).

[L.] *β-Hydroxybutyric acid* [Vol. II] gives crotonic acid on distillation (Wislicenus, Zeit. [2] **5**, 325; Araki, Zeit. physik. Ch. **18**, 1). Or the acid (sodium salt) gives *crotonic aldehyde* [**102**] on electrolysis (v. Miller and Hofer, Ber. **27**, 468). From the aldehyde through crotonic acid, &c., as under **H**.

[M.] *Citric acid* [Vol. II] gives citraconic anhydride on distillation (Lassaigne, Ann. Chim. [2] **21**, 100; Robiquet, *Ibid.* **75**, 78; Liebig, Ann. **26**, 119; 152; Gottlieb, Ann. **77**, 265; Baup, Ann. Chim. [3] **33**, 192; Wilm, Ann. **141**, 28; Kämmerer, Ann. **170**, 191), which combines readily with water to form citraconic acid. The latter is also obtained by heating citric acid with hydriodic acid (Kämmerer, Ann. **139**, 269). Potassium citraconate gives on electrolysis in aqueous solution allylene (Aarland, Journ. pr. Ch. [2] **7**, 142) among other products, and this can be converted into mesitylene, &c., as under **E**.

Or the citraconic anhydride can be converted into citrabrompyrotartaric acid by the action of hydrogen bromide (Fittig, Ann. **188**, 77), the silver salt of the acid giving allylene on heating with water at 130° (Bourgoin, Bull. Soc. [2] **28**, 459).

Mesaconic acid, the isomeride of citraconic acid produced from the latter by heating with aqueous acids or alkalis or by the action of bromine (Gottlieb, Ann. **77**, 268; Kekulé, Ann. Suppl. **2**, 94; Fittig, Ann. **188**, 77; 80; Delisle, Ann. **269**, 82; Swarts, Jahresber. **1873**, 579; Fittig and Langworthy, Ann. **304**, 145), also gives allylene on electrolysis of a solution of the potassium salt (Aarland, Journ. pr. Ch. [2] **7**, 142).

Citraconic acid also by boiling with alkali gives (with mesaconic acid) itaconic acid. The three isomerides, citraconic, mesaconic, and itaconic acids, all give pyrotartaric acid on reduction by sodium amalgam, preferably in acid solution (Kekulé, Ann. Suppl. **1**, 338; Suppl. **2**, 95: also Fittig and Langworthy, *loc. cit.*). The latter can be treated as under **N**. Citraconic and mesaconic acids give pyroracemic (pyruvic) acid on oxidation (Fittig and Köhl, Ann. **305**, 41). The latter can be converted into uvitic acid, &c., as under **I** above. Conversely pyroracemic and *malonic acid* combine when heated in acetic acid solution to form itaconic acid and some citraconic acid (Garzarolli-Thurnlach, Monats. **20**, 467).

Note:—Other synthetical products which are generators of citraconic acid are:—*Lactic acid* [Vol. II] by distillation (Engelhardt, Ann. 70, 243; 246).

Acetic acid [Vol. II], *alcohol* [14], and *hydrogen cyanide* [172], by the action of the latter on *aceto-acetic ester* (Morris, Journ. Ch. Soc. 37, 7; Demarçay, Bull. Soc. [2] 27, 120), hydroxypyrotartaric acid by boiling the product with dilute hydrochloric acid and dry distillation of the former, which thus gives citraconic anhydride (Demarçay, Comp. Rend. 82, 1337; Ber. 9, 962).

Isovaleric acid [Vol. II], which by oxidation with nitric acid gives hydroxypyrotartaric acid (Bredt, Ber. **14**, 1782; **15**, 2318) and citraconic anhydride as before. [The hydroxypyrotartaric acid formed is the β-acid = citramalic = 2-methyl-2-butanoldiacid; for preparation from acetoacetic ester and potassium cyanide see also Michael, Journ. pr. Ch. [2] **46**, 287.]

Propionic and *malonic acids* [Vol. II] by the action of α-brompropionic ester (Friedel and Machuca, Ann. **120**, 286) on sodio-malonic ester, which gives propanetricarboxylic triethyl (β-methylethenyltricarboxylic) ester (Bischoff, Ann. 214, 53), the chloro-derivative of the latter (*Ibid.* Ber. **23**, 1934) giving citraconic (and mesaconic) acid on heating with hydrochloric acid (*Ibid.*). [This propanetricarboxylic acid obtained from the ester by hydrolysis gives pyrotartaric acid on heating with hydrochloric acid or *per se*.]

Acetic and *propionic acids* [Vol. II], *alcohol* [14], and *potassium cyanide* [172] through α-methyl-β-cyanosuccinic ester by the action of α-brom-propionic ester on sodio-cyanacetic ester (Barthe, Ann. Chim. [6] 27, 277), and decomposition with alcoholic hydrogen chloride (*Ibid.* 281).

Oxalic and *propionic acids* [Vol. II] and *alcohol* [14] through methyloxalacetic ester by the action of sodium ethoxide followed by that of ethyl propionate on oxalic diethyl ester (Arnold, Ann. 246, 329). Methyloxalacetic ester gives β-methylmalic (2-methyl-3-butanoldicarboxylic) acid on reduction with sodium amalgam (Wislicenus, Ber. 25, 199), and this acid gives citraconic anhydride and mesaconic acid on distillation.

[N.] *Tartaric acid* [Vol. II] through pyrotartaric (methylsuccinic) acid (see under normal propyl alcohol [15; V]), citrabrompyrotartaric acid by the action of bromine and phosphorus (Auwers and Imhäuser, Ber. 24, 2236), and then through allylene, &c., as under M.

Racemic acid also gives pyrotartaric acid on distillation (references as under normal propyl alcohol [15; V]).

Both tartaric and racemic acids give pyroracemic acid among the products of their distillation (Berzelius, Pogg. Ann. 36, 1; Ann. 13, 61; Völckel, Ann. 89, 65; Wislicenus, Ann. 126, 225). Tartaric acid gives pyroracemic acid by heating to 180° with hydrochloric acid (Geuther and Riemann, Zeit. [2] 5, 318), to 40° with strong sulphuric acid (Bouchardat, Comp. Rend. 89, 99), or by dry distillation *per se*, or mixed with sand, or with acid potassium sulphate at 220° (Clewing, Journ. pr. Ch. [2] 17, 243; Erlenmeyer, Ber. 14, 320; Döbner, Ann. 242, 269; Seissl, Ann. 249, 297; Erdmann, Zeit. f. Naturwissenschaften, 71, 385). Pyroracemic acid is produced in aqueous solutions of tartaric acid by photochemical action (Otto, Ber. 27, 838; 1264). Pyroracemic acid can be converted into uvitic acid, &c., as under I. (For conversion of acetic and pyroracemic acids into toluene *via* phthalidedicarboxylic acid see under cymene [6; IX].)

[O.] *Propionic acid* [Vol. II] on bromination gives αα-dibrompropionic acid (Friedel and Machuca, Comp. Rend. 54, 220; Philippi and Tollens, Ann. 171, 315; Epstein, Comp. Rend. 124, 688), which on long heating with fuming hydrobromic acid solution is converted into the αβ-acid (P. and T. *loc. cit.* 337). The latter on heating with water and silver oxide gives glyceric acid (Beckurts and Otto, Ber. 18, 238), which furnishes pyrotartaric acid, &c., as under F, M, and N.

Or the αα-dibrompropionic acid on heating with silver carbonate and water yields pyroracemic acid (*Ibid.* 235), which gives uvitic acid, &c., as under I and D.

Or the propionic acid can be converted into propionamide and propionitrile (Dumas, Malaguti, and Leblanc, Ann. 64, 334), and then into αα-dichlorpropionic acid, pyroracemic acid, &c., as before.

Or through propionyl chloride and β-chlorpropionic acid, which gives acrylic acid on heating with barium hydroxide solution (Michael and Garner, Ber. 34, 4047). From acrylic through α-chlorlactic to glyceric and pyrotartaric or pyroracemic acid as before.

[P.] *Lactic acid* [Vol. II] gives pyroracemic acid by oxidation of the calcium salt with potassium permanganate (Beilstein and Wiegand, Ber. 17, 840). Subsequent steps as above.

Or from lactic acid through α-chlorpropionic acid (Wurtz, Ann. Chim. [3] 49, 58; Brühl, Ber. 9, 35), which on heating with barium hydroxide solution gives acrylic acid (Michael and Garner, Ber. 34, 4050). From the latter through α-chlorlactic to glyceric and pyrotartaric or pyroracemic acid as before.

[Q.] *Isovaleric acid* [Vol. II] gives mesitylenic acid among other products when the dry sodium salt mixed with sodium ethoxide is heated in the presence of carbon monoxide at 160° (Loos, Ann. 202, 321). Mesitylenic acid gives uvitic acid on oxidation (Fittig and v. Furtenbach, Zeit. [2] 4, 1; Ann. 147, 295), and the latter yields toluene as under D.

NOTE:—Allylene is among the products formed when the vapours of *acetone* [106], *ethyl* [14], *propyl* [15], *isobutyl* [18], and *amyl* [22] *alcohols* are passed over hot magnesium, and the product decomposed by water (Keiser and Breed, Ch. News, 71, 118; Keiser, Am. Ch. Journ. 18, 328).

Generators of Toluene through Toluic Acid.

[R.] *Naphthalene* [12] and derivatives by various processes of oxidation give phthalic acid (Laurent, Ann. 19, 38; Ann. Chim. [2] 61, 113; Marignac,

Ann. **42**, 215; Häussermann, Jahresber. **1877**, 763; 1158; Fischer, Ber. **11**, 738; Depouilly, Ann. **137**, 373; Beilstein and Kurbatoff, Ann. **202**, 215; Lüddens, Chem. Zeit. **15**, 585; Fuchs, *Ibid.* 735; Graebe, Ber. **29**, 2806; Procházka, Ber. **30**, 3108; Tcherniac, Ber. **31**, 139: for electrolytic oxidation see Darmstädter, Germ. Pat. 109012 of 1897; Ch. Centr. 1900, **2**, 151: for technical process see Germ. Pat. 91202 of the Bad. An. Sod. Fab. and Brunck, Ber. **33**, Suppl. lxxx: for production by oxidation of the naphthols see Eng. Pat. 15527 of 1901, Basle Ch. Co.; from α-nitronaphthalene *via* the 2- and 4-nitronaphthols, *Ibid.* Germ. Pat. 136410 of 1901; Ch. Centr. 1902, **2**, 1371). Phthalic acid on distillation with phosphorus pentachloride is converted into phthaloyl chloride (Müller, Zeit. **1863**, 257; Graebe, Ann. **238**, 329; Auger, Ann. Chim. [6] **22**, 295; Claus and Hoch, Ber. **19**, 1187), which by reduction with zinc and hydrochloric acid or magnesium and acetic acid gives phthalide (Kolbe and Wischin, Zeit. [2] **2**, 315; Journ. Ch. Soc. **19**, 339; Hessert, Ber. **10**, 1445; Baeyer, Zeit. [2] **5**, 399; **10**, 123; 1445; **11**, 637).

Or phthalic acid can be converted into phthalide through phthalimide by heating the acid ammonium salt (Laurent, Ann. **41**, 110; Ann. Chim. [2] **61**, 121; [3] **23**, 119; Lansberg, Ann. **215**, 181: also Matthews, Journ. Am. Ch. Soc. **18**, 679), reduction to phthalimidine by tin and hydrochloric acid (Graebe, Ber. **17**, 2598; Ann. **247**, 291), formation of nitroso-derivative by the action of sodium nitrite and acid (*Ibid.* Ann. **247**, 297), and action of sodium hydroxide solution on the nitroso-derivative (*Ibid.* 292). By heating phthalide with hydriodic acid solution and phosphorus, orthotoluic acid is formed (Hessert, Ber. **11**, 238; Racine, Ann. **239**, 72), and this by distillation with lime or soda-lime gives toluene.

Naphthalene also can be sulphonated so as to give a mixture of disulphonic acids, the product nitrated and reduced, and the 1 : 3 : 8-naphthylamine-disulphonic acid converted into 1 : 3-naphthylaminesulphonic acid by sodium amalgam, or by heating with sulphuric acid of 75 per cent. (Friedländer and Lucht, Ber. **26**, 3028; Kalle & Co., Germ. Pat. 64979 of 1892). The 1 : 3-sulpho-acid is converted by potash fusion into 1 : 3-aminonaphthol (Friedländer, Ber. **28**, 1952). The latter on sulphonation gives 1 : 3-aminonaphthol-4-sulphonic acid, and this on heating with water or dilute sulphuric acid at 120° yields 1 : 3-dihydroxynaphthalene (*Ibid.* **29**, 1609), which on heating with 60 per cent. sodium hydroxide solution at 180–190° breaks down into o-toluic and acetic acids (*Ibid.* 1611).

Other naphthalene derivatives such as the 1 : 3-disulphonic acid, 1 : 3-naphthylamine-sulphonic acid, &c., give o-toluic acid on heating with alkali (Kalle & Co., Germ. Pat. 79028 of 1893; Ber. **28**, Ref. 364).

[S.] *Cymene* [6] on oxidation with dilute nitric acid gives paratoluic acid (Noad, Phil. Mag. [3] **32**, 19; Ann. **63**, 289), which on distillation with baryta gives toluene (*Ibid.* Ann. **63**, 305).

Miscellaneous Generators of Toluene.

[T.] *Heptane* [2] gives toluene among other products when the vapour is heated to 900° (Worstall and Burwell, Am. Ch. Journ. **19**, 815).

[U.] *Mannoheptol* [53] on heating with hydriodic acid gives among other products a 'heptine,' C_7H_{12} (Maquenne, Bull. Soc. [2] **50**, 548). If, as is probable, this hydrocarbon is tetrahydrotoluene, it can be converted (partially) into toluene by the action of strong sulphuric acid.

[V.] From the *cresols* [61; 62; 63] through toluene (see under quinol [71; G]).

[W.] From *phenylacetic acid* [Vol. II] through toluene by the action of heat on the acid (Engler and Löw, Ber. **26**, 1438).

[X.] From *aconitic acid* [Vol. II] through itaconic acid (Pébal, Ann. **98**, 94), and then as above under M, &c.

[Y.] From *pulegone* [128] through methylcyclohexanone (see under phenol [60; S]). The latter gives an oxime

which on heating with phosphorus pentoxide yields toluene among other products (Wallach, Ann. **309**, 7).

Pulegone and *menthone* [**129**] give pyrotartaric acid among the products of oxidation by potassium permanganate (Markownikoff, Ber. **33**, 1909). Subsequent steps as above under **N**.

[**Z.**] From *malic acid* [Vol. II] through coumalic acid and *crotonic aldehyde* [**102**], and then as above under **H**.

Malic acid also gives oxalacetic acid on oxidation with hydrogen dioxide in presence of ferrous salts. If the temperature is not kept low pyroracemic acid is produced (Fenton and Jones, Trans. Ch. Soc. **77**, 77). From oxalacetic acid through pyrotartaric acid, &c., as before (see under n-propyl alcohol [**15**; **Z**]).

[**AA.**] From *mannitol* [**51**], which gives *acroleïn* [**101**] among the products of oxidation by sulphuric acid and manganese dioxide (Backhaus, Jahresber. **1860**, 522). Subsequent steps *via* acrylic acid as under **I**, &c.

[**BB.**] From *alanine* [Vol. II], which gives acrylic acid on treatment with *methyl iodide* in the presence of alkali (Körner and Menozzi, Gazz. **11**, 258; 549; **13**, 350).

[**CC.**] From *oxalic* and *acetic acids* [Vol. II] and *alcohol* [**14**] through diethyloxalacetate and pyrotartaric acid (see under n-propyl alcohol [**15**; **Z**]).

[**DD.**] From *succinic acid* [Vol. II] through the dibromo-acid, ethoxyfumaric acid, and oxalacetic acid (see under n-propyl alcohol [**15**; **Y**]). From the latter to pyrotartaric acid, &c., as under n-propyl alcohol [**15**; **Z**].

[**EE.**] From *fumaric* or *maleïc acid* [Vol. II] through dibromsuccinic acid (n-propyl alcohol [**15**; **EE**]), and then as above under **DD**.

[**FF.**] From *hydracrylic acid* [Vol. II] through acrylic acid (n-propyl alcohol [**15**; **S**]). From acrylic acid through α-chlorlactic acid, glyceric acid, &c., as above under **I**, &c.

[**GG.**] From *isobutyl* [**18**] or *tertiary butyl alcohol* [**19**] through isobutylene [**18**; **A**; **19**; **B**]. Toluene is among the products formed by passing isobutylene through a hot tube (Noyes; Beilstein, I, 115).

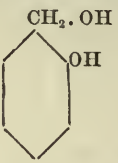
Note:—Generators of isobutylene thus become generators of benzyl alcohol.

[**HH.**] From *lysine* [Vol. II] through pyrotartaric acid (see under n-propyl alcohol [**15**; **II**]).

[**II.**] From *catechol* [**69**] and *hydrogen cyanide* [**172**] through dioxytartaric acid and glyoxal (see under hydrogen cyanide [**172**; **P**]), and the pyroracemic nitrile and acid as above under **H**.

[**JJ.**] From *protocatechuic acid* [Vol. II] through dioxytartaric acid and glyoxal, &c., as under hydrogen cyanide [**172**; **Q**], and as above under **H**.

55. Saligenin; Orthohydroxybenzyl Alcohol; Phenol-2-Methylol.



Natural Sources.

Occurs as the glucoside (*salicin* [**157**]) in bark, twigs, and leaves of various species of willow (*Salix helix*, *S. purpurea*, *S. alba*, *S. lambertina*, *S. incana*, *S. fissa*, *S. hastata*, *S. polyandra*, *S. fragilis*, *S. amygdalina*, *S. pentandra*, *S. præcox*, &c.), in poplar (*Populus tremula*, *P. alba*, *P. balsamifera*, and *P. græca*), and in flower buds of the meadowsweet (*Spiræa ulmaria*).

Salicin is found also in the buds of *Populus pyramidalis*, *P. nigra*, and *P. monilifera*. (For liberation of saligenin from salicin see Piria, Ann. **56**, 37: for distribution of salicin in vegetable kingdom, Leroux, Ann. Ch. [2] **43**, 440; Tischhauser, Ann. **7**, 280; Braconnot, Ann. Chim. [2] **44**, 296; Pelouze and Gay-Lussac, *Ibid.* 220; **48**, 111; Piria, *Ibid.* **69**, 281; [3] **14**, 257; Gerhardt, *Ibid.* [3] **7**, 215; Bouchardat, Comp. Rend. **18**, 299; **19**, 602; 1179; **20**, 610; 1635; in *Spiræa* flowers, Buchner, Ann. **88**, 224: see

also Van Rijn's 'Die Glycoside,' p. 143, and Jowett and Potter, Pharm. Journ. [4] **15**, 157.)

Salicin liberates saligenin under the influence of certain moulds, such as *Aspergillus niger* (Puriewitsch, Ber. deutsch. bot. Gesell. **16**, 368) and *A. oryzæ* (Brunstein, Abst. in Journ. Fed. Inst. **7**, 367; **8**, 507). *Populin* [**158**], which is benzoylsalicin, liberates benzoylsaligenin under the influence of an enzyme (? emulsin) contained in *Aspergillus niger*.

Salicin is said to occur also in castoreum from glands of the beaver (Wöhler, Ann. **67**, 360).

Synthetical Processes.

[**A.**] From *salicylic aldehyde* [**117**] by reduction with sodium amalgam (Beilstein and Reineke, Ann. **128**, 179).

[**B.**] From *salicylic acid* [Vol. II] through the amide (Limpricht, Ann. **98**, 258), and reduction of the latter with sodium amalgam in acid solution (Hutchinson, Ber. **24**, 175).

[**C.**] From *toluene* (see under benzyl alcohol [**54**; **A**, &c.]), o-nitrotoluene, which is formed (with p-nitrotoluene) by nitration, o-nitrobenzyl chloride by chlorination at 120–130° in the presence of sulphur (Häussermann and Beck, Ber. **25**, 2445), o-nitrobenzyl alcohol by heating the chloride with potassium carbonate solution or with chalk and water (Söderbaum and Widman, Ber. **25**, 3291; Häussermann and Beck, Journ. pr. Ch. [2] **47**, 400: see also Paal and Bodewig, Ber. **25**, 2962; Fischer, Germ. Pat. 48722 of 1888; Ber. **22**, Ref. 788; Kalle & Co., Germ. Pat. 10436 of 1897; Ch. Centr. 1899, **2**, 950; Ch. Fab. Griesheim-Elektron, Germ. Pat. 128046 of 1900; Ch. Centr. 1902, **1**, 445; Germ. Pat. 128998 of 1900; Ch. Centr. 1902, **1**, 686). From o-nitro- to o-aminobenzyl alcohol by reduction (Friedländer and Henriques, Ber. **15**, 2109) and diazo-reaction with latter (Paal and Senninger, Ber. **27**, 1084).

Note:—For references to processes for oxidising o-nitrotoluene to o-nitrobenzaldehyde, which gives the alcohol as below under **D**, see under indigo [Vol. II]. Orthonitrotoluene also gives o-nitrobenzaldoxime by interaction with amyl nitrite and dry sodium ethoxide (Lapworth, Trans. Ch. Soc. **79**, 1274). o-Nitrotoluene gives o-nitrobenzyl alcohol by electrolytic oxidation (Pierron, Bull. Soc. [3] **25**, 852).

[**D.**] From *cinnamic acid* [Vol. II] through the o-nitro-acid which is formed (with the p-nitro-acid) by nitration (Beilstein and Kuhlberg, Ann. **163**, 126), o-nitrobenzaldehyde by oxidising the acid with potassium permanganate (Einhorn, Ber. **17**, 121), and o-nitrobenzyl alcohol, which is formed (with o-nitrobenzoic acid) by the action of cold aqueous caustic alkali on the aldehyde (Friedländer and Henriques, Ber. **14**, 2804). Subsequent steps as above.

Note:—One of the products of nitration of ω-bromstyrene from cinnamic acid (see under p-hydroxybenzaldehyde [**119**; **B**]), viz. α-o-nitrophenyl-β-bromnitroethylene, gives o-nitrobenzaldehyde on boiling with water (Flürscheim, Journ. pr. Ch. [2] **66**, 16).

[**E.**] From *phenol* [**60**] by the action of methylene chloride in the presence of alkali (Greene, Am. Ch. Journ. **2**, 19). Methylene chloride can be prepared from *chloroform* [**1**; **D**, &c.] by reducing the alcoholic solution with zinc and hydrochloric acid (Greene, *Ibid.* **1**, 522; Ch. News, **50**, 75; Comp. Rend. **89**, 1077).

Also from phenol and *formic aldehyde* [**91**] by the action of caustic alkaline solution on a mixture (Manasse, Ber. **27**, 2411; Lederer, Journ. pr. Ch. [2] **50**, 225: see also Farbenfab. vorm. F. Bayer & Co., Germ. Pat. 85588 of 1894). Parahydroxybenzyl alcohol is formed simultaneously in this process.

56. Parahydroxybenzyl Alcohol; Phenol-4-Methylol.

Natural Source.

The p-hydroxybenzyl complex occurs in sinalbin, a glucoside found in white mustard seed (see under p-hydroxybenzyl mustard oil [**171**]).

Synthetical Processes.

[A.] From *phenol* [60] through *p-hydroxybenzaldehyde* [119] by the action of chloroform in the presence of caustic alkali, the o-hydroxy-aldehyde being also formed (Reimer and Tiemann, Ber. **9**, 824; Tiemann and Herzfeld, Ber. **10**, 63), and reduction of the aldehyde with sodium amalgam and dilute sulphuric acid (Biedermann, Ber. **19**, 2374).

Also from *phenol*, together with saligenin, by the action of *formic aldehyde* in the presence of alkali (see under saligenin [55; E]).

[B.] *Parahydroxybenzoic acid* [Vol. II], by heating its ethyl ester with aqueous ammonia, is converted into p-hydroxybenzamide (Hartmann, Journ. pr. Ch. [2] **16**, 50), and the latter on reduction with sodium amalgam in acid solution gives p-hydroxybenzyl alcohol (Hutchinson, Ber. **24**, 175; Auwers and Daecke, Ber. **32**, 3373).

57. Phenylethyl Alcohol; Benzyl Carbinol; 1^2-Phenethylol.

$C_6H_5 . CH_2 . CH_2 . OH$

Natural Sources.

In small quantity in the steam distillate from German oil of rose (v. Soden and Rojahn, Ber. **33**, 1720; 3063; Walbaum and Stephan, *Ibid.* 2305; v. S. and R. Ber. **34**, 2803). In dried and in fresh rose petals (Walbaum, Ber. **33**, 1904; 2299), and to a small extent in Bulgarian oil of rose (v. Soden and Rojahn, Ber. **33**, 3065).

In the aqueous distillate from orange flowers (Hesse and Zeitschel, Journ. pr. Ch. [2] **64**, 245). Esters of this alcohol occur in French néroli oil (Schimmel's Ber. Oct. 1902; Ch. Centr. 1902, **2**, 1208).

Synthetical Processes.

[A.] From *phenylacetic* and *formic acids* [Vol. II] by distilling a mixture of the calcium salts (Cannizzaro, Ann. **119**, 254) which gives *a*-toluic = phenylacetaldehyde. The latter yields the alcohol on reduction with sodium amalgam (Radziszewski, Ber. **9**, 373) or, preferably, with zinc and acetic acid (v. Soden and Rojahn, Ber. **33**, 1723).

The generators of *a*-toluic aldehyde given under phenylethyl mustard oil [170] thus become generators of this alcohol:—

[B.] From *benzene* or *toluene* through *a*-toluic aldehyde (phenylethyl mustard oil [170; A]).

[C.] From *styrene* [7] through *a*-toluic aldehyde (170; B).

[D.] From *benzoic aldehyde* [114], *alcohol* [14], and *acetic acid* [Vol. II] through *a*-toluic aldehyde (170; C).

[E.] From *cinnamic acid* [Vol. II] through *a*-toluic aldehyde (170; E).

[F.] From *benzoic* and *acetic acids* [Vol. II] through *a*-toluic aldehyde (170; F).

[G.] From *tartaric* or *racemic acid* [Vol. II] and *n-propyl alcohol* [15] through *a*-toluic aldehyde (170; D).

[H.] From *cymene* [6] through acetophenone and *a*-toluic aldehyde (170; G).

58. Methylphenyl Carbinol; 1^1-Phenethylol; Styrolyl Alcohol.

$C_6H_5 . CH(OH) . CH_3$

Natural Source.

Occurs as acetate in *Gardenia* oil (Parone, Boll. Ch. Farm. **41**, 489; Ch. Centr. 1902, **2**, 704).

Synthetical Processes.

[A.] From *benzene* [6] and *ethyl alcohol* [14] through ethylbenzene (see under phlorol [64; A]). The latter on bromination at its boiling-point or in presence of strong light gives 1^1-bromethylbenzene (see under styrene [7; A]). The latter gives the alcohol acetate by interaction with silver acetate (Radziszewski, Ber. **7**, 141; Berthelot, Zeit. [2] **4**, 589).

[B.] From *styrene* [7] through 1^1-bromethylbenzene by combination with hydrogen bromide (Schramm, Ber. **26**, 1710), and then as above.

[C.] From *benzoic* and *acetic acids* [Vol. II], or from *benzene* and *acetyl*

chloride through acetophenone. The latter is reduced to the alcohol by sodium amalgam (Emmerling and Engler, Ber. **6**, 1006: see also under styrene [**7**; **A** and **D**]), or by sodium and alcohol (Klages and Allendorf, Ber. **31**, 1003).

[**D.**] From *benzoic aldehyde* [**114**] and *methyl alcohol* [**13**] by the interaction of the aldehyde and magnesium methiodide (Klages and Keil, Ber. **36**, 1632).

59. Phenylpropyl Alcohol; 1^3-Phenepropylol.

$C_6H_5 . CH_2 . CH_2 . CH_2 . OH$

Natural Sources.

Phenylpropyl cinnamate occurs in storax from *Liquidambar orientalis* and from the American *L. styraciflua* (v. Miller, Ann. **188**, 184; Arch. Pharm. **220**, 648; Tschirch and Van Itallie, *Ibid.* **239**, 506; 532; Ch. Centr. 1901, **2**, 553; 856).

Synthetical Process.

[**A.**] From *benzene*, [**6**] *trimethylene glycol* [**46**], and *ethyl alcohol* [**14**]. The monosodium glycol is converted into the ethyl ether by means of ethyl iodide and the hydroxyl-group replaced by bromine by means of phosphorus tribromide. A mixture of ethyl-γ-brompropyl ether and monobrombenzene on treatment with sodium in ethereal solution gives the ethyl ether of phenylpropyl alcohol = phenylpropyl-γ-ethyl ether (Noyes, Am. Ch. Journ. **19**, 766, &c.). The ether would yield the alcohol by de-ethylation.

60. Phenol; Carbolic Acid.

Natural Sources.

In normal and pathological urine of man (Salkowski, Ber. **9**, 138; 1595; **10**, 842; Munk, Ber. **9**, 1595: see also Lewin, Beit. ch. Physiol. Path. &c., **1**, 472; Ch. Centr. 1902, **1**, 487), and in the urine of herbivorous animals (Städeler, Ann. **77**, 18; Lieben, Ann. Suppl. **7**, 240; Hoppe-Seyler, Pflüger's Arch. **5**, 470).

The phenol is said to exist in urine as a salt of phenylsulphuric acid (Baumann, Ber. **9**, 54; 1389; 1715; Brieger, Zeit. physiol. Ch. **4**, 204) or (in normal urine) as glycuronate (Mayer and Neuberg, Zeit. physiol. Ch. **29**, 271). Phenol (combined) has been found in sweat of sheep (Buisine, Comp. Rend. **103**, 66) and of man (Kast, Zeit. physiol. Ch. **11**, 501). Occurs also in minute quantity in castoreum (Wöhler, Ann. **67**, 360).

Phenol is among the products of the putrefaction of many proteids (Baumann, Ber. **10**, 685; **12**, 2166; Zeit. physiol. Ch. **1**, 60; **3**, 250; Weyl, *Ibid.* **1**, 339; Brieger, Ber. **10**, 1028; Zeit. physiol. Ch. **3**, 134; Journ. pr. Ch. [2] **17**, 134; Odermatt, *Ibid.* **18**, 249; Salkowski, Ber. **10**, 842; Zeit. physiol. Ch. **12**, 215).

Among the products of putrefaction of *tyrosin* and of *hydroparacoumaric acid* (Baumann, Ber. **13**, Ref. 1881) and among the products of anaerobic putrefaction of milk by *Bacillus putrificus* and by the *Bacilli* of malignant œdema and of symptomatic anthrax (Bienstock, Ch. Centr. 1901, **1**, 1209).

A product of putrefaction of wheat gluten by *Proteus vulgaris* and of egg albumin by *Staphylococcus pyogenes aureus* (Emmerling, Ber. **29**, 2722; 2725). Occurs among the products of fermentation of the aqueous extract obtained by washing wool (A. and P. Buisine, Comp. Rend. **125**, 777).

Said to occur in the trunk, leaves, and sap of Scotch fir, *Pinus sylvestris* (Griffiths, Ch. News, **49**, 59).

The phenol complex may be considered to exist in certain natural products of the flavone group, such as *apigenin* [**140**], genistein, and kampherol (see under phloroglucinol [**86**]).

Synthetical Processes.

[A.] From *acetylene* (see under methane [1; A]), the sulphonic acid formed by absorbing the latter in fuming sulphuric acid, and fusion of the sulphonic acid salt with potash (Berthelot, Comp. Rend. **68**, 539: could not be confirmed by Schroeter, Ber. **31**, 2189; Ann. **303**, 132). According to later experiments by Berthelot (Comp. Rend. **127**, 908; **128**, 335), the 'potassium-acetylene sulphonate' is heated to 180-200° in an atmosphere of hydrogen, and then distilled with dilute sulphuric acid, when phenol passes over. A further quantity is obtained from the residue by fusion with potash at 250° (see also Ann. Chim. [4] **19**, 432 and [7] **17**, 289.)

Or from acetylene through *benzene* (see under cymene [6; A]), benzenesulphonic acid (Mitscherlich, Pogg. Ann. **31**, 283; 634; Stenhouse, Proc. Roy. Soc. **14**, 351; Wurtz, Comp. Rend. **64**, 749; Michael and Adair, Ber. **10**, 585), and fusion of the potassium salt with excess of potash (Wurtz, Ann. **144**, 121; Bull. Soc. [2] **8**, 197; Kekulé, Lehrb. d. org. Ch. **3**, 13; Dusart, Zeit. [2] **3**, 299). Benzene is said to be oxidised by atmospheric air in the presence of alkali with the formation of phenol (Nencki, Ber. **14**, 1144).

Also from benzene by passing air through the boiling hydrocarbon in presence of aluminium chloride (Friedel and Crafts, Ann. Chim. [6] **14**, 435; Bull. Soc. [2] **31**, 463); by the action of palladium hydride, water, and air (Hoppe-Seyler, Ber. **12**, 1552); or by oxidation with hydrogen peroxide or nascent ozone (Leeds, Ber. **14**, 976; Cross, Bevan, and Heiberg, Trans. Ch. Soc. **75**, 751).

Also from benzene through nitrobenzene, aniline, and action of nitrous acid (diazo-reaction) on latter (Hofmann, Ann. **75**, 356; Hunt, Silliman's Am. Journ. [2] **8**, 372; Jahresber. **1849**, 391; Griess, Ann. **137**, 39: for direct production of aniline from benzene by the action of hydroxylamine in presence of aluminium chloride see Graebe, Ber. **34**, 1778; Jaubert, Comp. Rend. **132**, 841).

A synthesis of phenol from carbon is possible through mellitic (benzenehexacarboxylic) acid, which is obtained by oxidising charcoal with alkaline permanganate (Schulze, Ber. **4**, 802; 806), by the electrolysis of dilute acid or alkali with retort carbon for the positive electrode (Bartoli and Papasogli, Gazz. **11**, 468; Ch. Centr. **1881**, 327), by the oxidation of animal charcoal or lampblack with alkaline hypochlorite (*Ibid.* Gazz. **15**, 446), or by heating wood charcoal with strong sulphuric acid (Verneuil, Bull. Soc. [3] **11**, 121).

Mellitic acid is converted by dry distillation into pyromellitic (1 : 2 : 4 : 5-benzenetetracarboxylic) acid (Erdmann, Ann. **80**, 281), which by reduction in alkaline solution with sodium amalgam is converted into hydropyromellitic acid (Baeyer, Ann. Suppl. **7**, 38; **166**, 337; **258**, 205). The latter on heating with strong sulphuric acid gives isophthalic acid (*Ibid.* Ann. Suppl. **7**, 4), which can be converted into 5-sulpho- and 5-hydroxyisophthalic acid by sulphonation and potash fusion (Heine, Ber. **13**, 493). The latter acid gives phenol on distillation with lime (see also under L).

Mellitic acid can be obtained also by the oxidation of charcoal with fuming nitric acid (Dickson and Easterfield, Proc. Ch. Soc. **14**, 163).

Phenylsulphuric acid (potassium salt) is obtained by the action of potassium pyrosulphate on phenol in potassium hydroxide solution (Baumann, Ber. **9**, 54 and 1715; **11**, 1907; Brieger, Zeit. physiol. Ch. **8**, 311; Drechsel, Journ. pr. Ch. [2] **29**, 234). The acid is also among the products of the electrolysis of phenol by an alternating current in the presence of magnesium sulphate and acid magnesium carbonate (Drechsel, *loc. cit.*).

[B.] *Glycerol* [48] is said to give phenol when distilled with calcium chloride (Linnemann and Zotta, Ann. **174**, 87; Suppl. **8**, 254).

[C.] From *salicylic acid* [Vol. II] by distillation with lime (Gerhardt, Rev. Scien. **10**, 210; Rosenthal, Zeit. [2] **5**, 627); also by heating *per se*, or with

water at 220–230°, or with strong hydrochloric or hydriodic acid, or with dilute sulphuric acid at 140–150° (Graebe, Ann. **139**, 143).

Methyl salicylate gives phenol when heated with dry aniline (Tingle, Am. Ch. Journ. **24**, 45).

[D.] *Parahydroxybenzoic acid* [Vol. II] gives phenol when distilled with lime; also when heated *per se*, or by heating with sodium hydroxide, or by the dry distillation of the sodium salt at 240–250° (Gerhardt, Rev. Scien. **10**, 210; Rosenthal, Zeit. [2] **5**, 627; Klepl, Journ. pr. Ch. [2] **28**, 194; Barth and Schreder, Ber. **12**, 1257; Kupferberg, Journ. pr. Ch. [2] **16**, 425; Goldschmiedt and Herzig, Monats. **3**, 132). Also by heating in sealed tube with dilute sulphuric acid (Klepl, Journ. pr. Ch. [2] **25**, 464).

p-Methoxybenzoic = anisic acid [Vol. II] gives phenol among the products of the distillation of the calcium salt (Goldschmiedt and Herzig, Monats. **3**, 127).

[E.] From *benzoic acid* [Vol. II] by fusion with caustic potash (Barth and Schreder, Monats. **3**, 802).

Also through metasulphobenzoic acid by sulphonation (Mitscherlich, Pogg. Ann. **31**, 287; **32**, 227; Offermann, Ann. **280**, 5; Barth, Ann. **148**, 33), and m-hydroxybenzoic acid by fusion of the sulpho-acid with caustic potash (Barth, *loc. cit.*; Remsen, Zeit. [2] **7**, 81; 199). Or from benzoic acid through metachlorbenzoic acid by chlorination (Scharling, Ann. **41**, 49; **42**, 268; Stenhouse, Phil. Mag. **27**, 129; Ann. **55**, 10; Field, Ann. **65**, 55; Otto, Ann. **122**, 157; Hübner and Weiss, Ber. **6**, 175), and fusion of the chloro-acid with caustic potash (Dembey, Ann. **148**, 222).

Or from benzoic acid through the metanitro-acid by nitration (Mulder, Ann. **34**, 297; Gerland, Ann. **91**, 186; Hübner, Ann. **222**, 72; Holleman, Zeit. physik. Ch. **31**, 79), m-amino-acid by reduction (Zinin, Berz. Jahresber. **26**, 450; Journ. pr. Ch. **36**, 103; Gerland, Ann. **86**, 143; **91**, 188; Schiff, Ann. **101**, 94; Beilstein and Wilbrand, Ann. **128**, 265; Holleman, Rec. Tr. Ch. **21**, 56), and m-hydroxybenzoic acid by the action of nitrous acid (Gerland, Ann. **91**, 189; Graebe and Schultzen, Ann. **142**, 350).

In all these cases the metahydroxybenzoic acid can be best converted into phenol by heating the barium salt with excess of baryta at 350° (Klepl, Journ. pr. Ch. [2] **27**, 159).

[F.] *Cinnamic acid* [Vol. II] on treatment with bleaching powder is said to give metachlorbenzoic acid (Stenhouse, Ann. **55**, 1), which can be converted into m-hydroxybenzoic acid and phenol as under **E**.

Or cinnamic acid can be converted by nitration into o- (with p-) nitrocinnamic acid (Beilstein and Kuhlberg, Ann. **163**, 126; Müller, Ann. **212**, 124), the o-nitro-acid oxidised to o-nitrobenzoic acid (B. and K. *loc. cit.* 134; Widnmann, Ber. **8**, 393), reduced to *anthranilic acid* [Vol. II], the latter converted into *salicylic acid* [Vol. II] by the diazo-method, and then into phenol as under **C**.

Or cinnamic acid can be sulphonated, the ortho- (? meta-) separated from the parasulphonic acid, giving m-hydroxybenzoic acid on fusion with alkali (Rudneff, Ann. **173**, 8).

[G.] From *gallic acid* [Vol. II] by heating the acid or its ester with strong sulphuric acid so as to form rufigallic acid = 1 : 2 : 3 : 5 : 6 : 7-hexahydroxyanthraquinone (Robiquet, Ann. **19**, 204; Wagner, Jahresber. **1860**, 288; Ch. Centr. **1861**, 47; Löwe, Journ. pr. Ch. **107**, 296; Zeit. [2] **6**, 128; Jaffé, Ber. **3**, 694; Widman, Ber. **9**, 856; Klobukowski and Noelting, Ber. **8**, 819; **9**, 1256; **10**, 880). Rufigallic acid on fusion with potash gives (with m-hydroxybenzoic acid) 5-hydroxyisophthalic acid (Schreder, Monats. **1**, 437), and the latter on distillation with lime gives phenol. Hydroxyterephthalic acid is also among the products of fused potash on rufigallic acid (*Ibid.* 439), and this also gives phenol on heating with sand.

[H.] From *benzoic aldehyde* [114] through the m-nitro-derivative by nitration (Bertagnini, Ann. **79**, 259; **86**, 190; Lippmann and Hawliczek,

Ber. **9**, 146; Friedländer and Henriques, Ber. **14**, 2802; Ehrlich, Ber. **15**, 2010), m-nitrobenzylidene chloride ($1^1:1^1$-dichlor-3-nitrotoluene) by the action of phosphorus pentachloride (Widman, Ber. **13**, 676), m-toluidine by reduction (Vienne and Steiner, Bull. Soc. [2] **35**, 428; Widman, *loc. cit.* 677; Bull. Soc. [2] **36**, 216; Ehrlich, Ber. **15**, 2011; Harz, Ber. **18**, 3398), m-chlortoluene by the diazo-reaction (Wroblewski, Ann. **168**, 199), m-chlorbenzoic acid by oxidation (*Ibid.* 200), m-hydroxybenzoic acid, &c., as under **E**.

Or the m-nitrobenzoic aldehyde might be directly oxidised to m-nitrobenzoic acid, reduced to m-aminobenzoic acid, and then converted into m-hydroxybenzoic acid and phenol as under **E**. The aldehyde can also be converted (partially) into m-chlorbenzaldehyde by the action of iodine and antimony pentachloride (Gnehm and Bänziger, Ber. **29**, 875), and then oxidised to m-chlorbenzoic acid and treated as under **E**.

[I.] *Metacresol* [62] is said to give m-hydroxybenzoic acid on fusion with potash (Barth, Ann. **154**, 361; Monats. **3**, 802), and this can be converted into phenol as under **E**.

[J.] *Naphthalene* [12] when nitrated gives α-nitronaphthalene (Laurent, Ann. Chim. [2] **59**, 378; Piria, Ann. **78**, 32; Beilstein and Kuhlberg, Ann. **169**, 83), which on oxidation yields 3-nitrophthalic acid (Guareschi, Ber. **10**, 294; Beilstein and Kurbatoff, Ann. **202**, 217). The latter on reduction with tin and hydrochloric acid gives m-aminobenzoic acid (Faust, Ann. **160**, 61; Miller, Ann. **208**, 245), which can be converted into m-hydroxybenzoic acid and phenol as under **E**.

Or the reduction can be regulated so as to give 3-aminophthalic acid (Miller, *loc. cit.*), from which, by the diazo-method, 3-hydroxyphthalic acid can be obtained (Bernthsen and Semper, Ber. **18**, 167; **20**, 937), and this gives phenol on heating.

Or from naphthalene through phthalic acid, phthalide, &c., to o-toluic acid (see under benzyl alcohol [54; **R**]), or through 1 : 3 : 8-naphthylaminedisulphonic acid, &c., to o-toluic acid (*Ibid.*). The latter on sulphonation gives 6-sulpho-o-toluic acid (Jacobsen and Wierss, Ber. **16**, 1959), from which, by potash fusion, 6-hydroxy-o-toluic acid can be obtained (*Ibid.* 1963).

Or o-toluic acid can be converted into the 6-hydroxy-acid through the 6-nitro- and 6-amino-acid and diazo-method (*Ibid.* **17**, 163). The 6-hydroxy-o-toluic acid is converted into the methoxy-o-toluic acid by methylation, and the latter on oxidation with alkaline permanganate gives 3-methoxyphthalic (3-methoxy-1 : 2-dicarboxylic) acid, which yields 3-hydroxyphthalic acid on fusion with alkali (Jacobsen, Ber. **16**, 1965). The latter acid gives phenol when heated.

Phthalic acid also may be nitrated, and the 4-nitro- (separated from the 3-nitro-) acid (Miller, Ann. **208**, 224) converted into ester and reduced to 4-aminophthalic ester, which by the diazo-method and hydrolysis gives 4-hydroxyphthalic acid (Baeyer, Ber. **10**, 1079; Miller, Ber. **11**, 1191; Ann. **208**, 237). The latter on heating with hydrochloric acid yields m-hydroxybenzoic acid, from which phenol can be obtained as under **E**.

Or phthalic acid may be sulphonated by fuming sulphuric acid (Loew, Ann. **143**, 257; Rée, Ann. **233**, 219), the 4-sulphophthalic acid converted into 4-hydroxyphthalic acid by fusion with alkali (Graebe, Ber. **18**, 1130; Rée, *loc. cit.*), and the latter converted into m-hydroxybenzoic acid and phenol as above.

Naphthalene may also be converted into α-sulphonic acid and α-naphthol (Eller, Ann. **152**, 275), the latter into acetate, and the acetate oxidised by chromic acid into 3-hydroxyphthalic acid (Miller, Ann. **208**, 247), from which phenol can be obtained as above. [The acid thus obtained by Miller is said to have been 2-hydroxyisophthalic acid, but from its mode of formation must be 3-hydroxyphthalic acid (Beilstein, II, 1936 and errata, 2209).]

Or naphthalene-α-sulphonic acid may be converted into the sulphonamide,

the latter oxidised by permanganate to 3-sulphophthalic acid (Remsen and Comstock, Am. Ch. Journ. **5**, 107), and the sulpho-acid converted into 3-hydroxyphthalic acid by potash fusion (Remsen and Stokes, Am. Ch. Journ. **6**, 282), and then into phenol as before.

Or α-naphthol may be sulphonated and nitrated so as to form dinitro-α-naphtholsulphonic (2 : 4-dinitro-1-naphthol-7-sulphonic) acid (Caro, Ber. **14**, 2029), which on oxidation with nitric acid gives 4-sulphophthalic acid (Graebe, Ber. **18**, 1127), from which 4-hydroxyphthalic acid, m-hydroxybenzoic acid, and phenol can be obtained as above.

Naphthalene-β-sulphonic acid, when converted into its amide and the latter oxidised with potassium permanganate, also gives 4-sulphophthalic acid (Remsen and Comstock, Am. Ch. Journ. **5**, 110).

[**K.**] *Indigo* [Vol. II] on distillation with potash gives aniline (Fritzsche, Ann. **39**, 76), which can be converted into phenol as under **A**.

[**L.**] From *acetone* [**106**] through mesitylene and uvitic or mesitylenic acid (see under benzyl alcohol [**54**; **D**]), m-toluic acid or m-xylene (see under o-cresol [**61**; **B**]), and isophthalic acid by oxidation of either the acid or hydrocarbon (Weith and Landolt, Ber. **8**, 721; Fittig and Velguth, Ann. **148**, 11).

Isophthalic acid on nitration gives a mixture of 4- and 5-nitro-acids (Beyer, Journ. pr. Ch. [2] **22**, 352; **25**, 470; Storrs and Fittig, Ann. **153**, 285). The 5-nitro-acid on reduction and application of the diazo-method yields 5-hydroxyisophthalic acid (Beyer, *loc. cit.* **25**, 515), and this gives phenol on heating with lime.

Or isophthalic acid can be sulphonated (Heine, Ber. **13**, 493), the 5-sulpho-acid converted into the 5-hydroxy-acid by potash fusion (*Ibid.*), and then into phenol as above.

Or from acetone through phorone and pseudocumene (see under o-cresol [**61**; **B**]), methylterephthalic (α-xylidic) acid by oxidising the latter with nitric acid (Fittig and Laubinger, Ann. **151**, 276), and isophthalic acid, which is formed (with trimellitic acid) by further oxidation with potassium permanganate (Krinos, Ber. **10**, 1494).

Or pseudocumene may be sulphonated, the sulphonamide oxidised with alkaline permanganate so as to form 4-sulphamide-α-xylic acid (Jacobsen and Meyer, Ber. **16**, 190), which by further oxidation with the same reagent gives 5-sulphotrimellitic acid (*Ibid.* 192). The latter on potash fusion yields 5-hydroxytrimellitic acid (*Ibid.*), and this gives phenol on distillation with lime.

Or mesitylene may be sulphonated, and the sulphonamide oxidised with chromic acid mixture or alkaline permanganate so as to form o- and p-sulphamidemesitylenic acid (Hall and Remsen, Ber. **10**, 1040; Jacobsen, Ann. **206**, 167). The latter acids on further oxidation with potassium permanganate give sulphamidetrimesic acid (Jacobsen, *loc. cit.* 203), which by potash fusion yields hydroxytrimesic acid (*Ibid.*), and the latter gives phenol by heating with lime.

Note :—Generators of mesitylene and uvitic acid (see under benzyl alcohol [**54**; **D** to **P**]) thus become generators of phenol.

[**M.**] From *cymene* [**6**] through terephthalic acid by oxidation (De la Rue and Müller, Ann. **121**, 87; Schwanert, Ann. **132**, 257; Homeyer, Arch. Pharm. [3] **5**, 326; Beilstein, Ann. **133**, 41). The latter can be converted into nitro- and aminoterephthalic acid by nitration and reduction, and into hydroxyterephthalic acid by the diazo-method (Burkhardt, Ber. **10**, 145), the latter giving phenol on heating with sand.

Or terephthalic acid may be brominated, the bromo-acid fused with potash (Fischli, Ber. **12**, 621), and the hydroxyterephthalic acid thus formed converted into phenol as above.

[**N.**] *Carvacrol* [**66**] when fused with potash gives hydroxyterephthalic acid (Jacobsen, Ber. **11**, 570), and this can be converted into phenol as above.

[**O.**] *Thymol* [**67**] also gives hydroxyterephthalic acid when fused with potash (Jacobsen, *loc. cit.*).

[**P.**] *Phenylacetic acid* [Vol. II] on nitration gives the 2 : 4-dinitro-acid, which can be converted into o-nitro-

benzoic acid (as under quinol [71; I]), into *anthranilic acid*, *salicylic acid*, and phenol as under C.

[Q.] *Hydrojuglone* [90] gives phenol among the products of its fusion with potash (Mylius, Ber. 18, 475).

[R.] *Acetic aldehyde* [92] gives phenol in small quantity by the action of fuming sulphuric acid and fusion of the product with alkali (Berthelot, Comp. Rend. 128, 336).

[S.] *Pulegone* [128] on heating with formic acid or with water under pressure gives (with acetone) methylcyclohexanone (Wallach, Ann. 289, 338; 340; Klages, Ber. 32, 2567). The latter by the action of phosphorus pentachloride yields (as final product) tetrahydrochlortoluene, and this by the action of bromine gives m-chlortoluene (Klages, Ber. 32, 2567). Subsequent steps as under H and E.

Mineral acids (especially sulphuric) may also be used for converting pulegone into the cycloketone (Zelinsky, Ber. 30, 1532; Wallach, Ber. 32, 3338).

[T.] From *o-coumaric acid* [Vol. II], which gives phenol on dry distillation.

[U.] From *malonic acid* [Vol. II] and *ethyl alcohol* [14] through dicarboxyglutaconic ester and glutaconic ester. The sodium derivative of the latter on heating with alcohol at 150° gives hydroxyisophthalic acid (Lawrence and W. H. Perkin, junr., Proc. Ch. Soc. 17, 47: see also under cymene [6; XV]). The latter gives phenol on distillation.

Note:—Generators of dicarboxyglutaconic ester are given under cymene as above. Glutaconic acid is formed by the action of alcoholic soda or hydrochloric acid on the dicarboxyglutaconic ester (Conrad and Gutzeit, Ann. 222, 253; Gutzeit and Bolam, Journ. pr. Ch. [2] 54, 372).

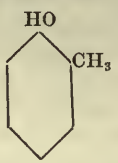
Also from *formic* and *acetic acids* and *alcohol* or from *malic acid* through coumalic acid = formylglutaconic anhydride (see under n-butyl alcohol [17; J; O, &c.]). Coumalic acid gives glutaconic acid on heating with barium hydroxide solution (v. Pechmann, Ann. 264, 301).

Or *citric acid* can be converted into acetonedicarboxylic acid (see under n-secondary amyl alcohol [21; H]) and this, by reduction with sodium amalgam, gives β-hydroxyglutaric acid (v. Pechmann and Jenisch, Ber. 24, 3250) which, on distillation in a vacuum or with sulphuric acid, yields glutaconic acid (*Ibid.* 3256).

Or from *acetic acid* (ester) and *acrylic acid* (ester) through pyrazolin-3:5-dicarboxylic ester by the interaction of diazoacetic and acrylic esters (Buchner and Papendieck, Ann. 273, 232: generators of acrylic acid are referred to under benzyl alcohol [54; E], under resorcinol [70; F], and under acetone [106; S]). Glutaconic ester is formed by the distillation of pyrazolindicarboxylic ester (Buchner, Ber. 23, 703).

α-Hydroxyglutaric acid [Vol. II] on dehydration gives glutaconic acid among other products (Paolini, Gazz. 32, 402).

61. Orthocresol; 2-Methylphenol.



Natural Sources.

Occurs as a salt of o-cresylsulphuric acid in urine of herbivorous animals and, to a small extent, in human urine. Found also among the products of putrefaction of horse liver (Baumann, Ber. 9, 1389; Zeit. physiol. Ch. 2, 335; Preusse, *Ibid.* 355; Baumann and Brieger, *Ibid.* 3, 149; 252; Brieger, *Ibid.* 4, 204; Baumann, *Ibid.* 304; Baumann and Brieger, Ber. 12, 804; Baumann, Zeit. physiol. Ch. 6, 183; Brieger, *Ibid.* 8, 311: see also Salkowski, *Ibid.* 12, 215).

The o-cresol complex exists possibly in bebeerine, an alkaloid found in the bark of *Nectandra rodioei* from British Guiana, in the bark and leaves of *Buxus sempervirens*, and in the root of *Cissampelos pareira* (see Scholtz, Ber. 29, 2054, and Arch. Pharm. 236, 530; Ch. Centr. 1898, 2, 983).

A cresol (? isomeride) has been found in cascarilla oil from the bark of *Croton eluteria* (Fendler, Arch. Pharm. 238, 671).

Synthetical Processes.

[A.] From *toluene* (see under benzyl alcohol [54; A and D to T]). Toluene on sulphonation gives (with para-) orthosulphonic acid (Engelhardt and Latschinoff, Zeit. [2] 5, 617; Wolkoff, *Ibid.* 6, 321; Claesson and Wallin, Ber. 12, 1848; Noyes, Am. Ch. Journ. 8, 176), and this gives o-cresol by potash fusion (Engelhardt and Latschinoff, *loc. cit.* 620).

Toluene on nitration gives a mixture of p- and o-nitrotoluenes (Glénard and Boudault, Comp. Rend. **19**, 505; Hofmann and Muspratt, Ann. **53**, 221; Kekulé, Zeit. [2] **3**, 225; Rosenstiehl, Ann. Chim. [4] **27**, 433; Reverdin and La Harpe, Bull. Soc. **50**, 44: for direct production of o- and p-toluidine from toluene and hydroxylamine in presence of aluminium chloride see Graebe, Ber. **34**, 1778). The latter can be reduced to o-toluidine, and this by the diazo-reaction gives o-cresol (Kekulé, Ber. **7**, 1006).

Or o-nitrotoluene gives o-cresol directly among the products of pyrogenic (electric) decomposition when mixed with steam and heated to 500–1000° (Löb, Zeit. Elektroch. **8**, 775).

Or p-nitrotoluene can be reduced to p-toluidine, the latter converted into 3-brom-p-toluidine (Wroblewski, Ann. **168**, 153), into 3-brom-p-toluic nitrile by the diazo-method (Claus and Kunath, Journ. pr. Ch. [2] **39**, 486), the acid by hydrolysis, 3-brom-6-nitro-p-toluic acid by nitration (Claus and Herbabny, Ann. **265**, 364), and then through 6-nitro-3-amino-p-toluic acid, 6-nitro-m-toluidine, o-nitrotoluene, and o-toluidine to o-cresol as above and under **C** and **F**.

Toluene can be converted into paratoluic acid by several processes:—By heating p-bromtoluene with sodium in an atmosphere of carbon dioxide (Kekulé, Ann. **137**, 184), or by treatment with sodium and ethyl chlorocarbonate and hydrolysing the ester (Wurtz, Comp. Rend. **68**, 1298; Ann. Supp. **7**, 126).

By the action of aluminium chloride on a solution of phosgene in toluene and decomposition of the chloride with water (Ador and Crafts, Ber. **10**, 2176).

By nitration, reduction of p-nitrotoluene to p-toluidine, the formation of the nitrile by the diazo- (Sandmeyer) reaction and hydrolysis (Herb, Ann. **258**, 9; Glock, Ber. **21**, 2650; Van Scherpenzeel, Rec. Tr. Ch. **20**, 149).

By the action of aluminium chloride on a mixture of toluene and chlorocarbamide (urea chloride) dissolved in carbon disulphide, and hydrolysis of the p-toluic amide thus formed (Gattermann and Schmidt, Ann. **244**, 51).

By heating toluene with zinc chloride, acetic acid, and phosphorus oxychloride, and treating the product with dilute sodium hydroxide solution (Frey and Horowitz, Journ. pr. Ch. [2] **43**, 116).

By the action of aluminium chloride on a mixture of toluene and phthalic anhydride (see under benzyl alcohol [**54**; **R**]), and potash fusion of the p-toluyl-o-benzoic acid thus formed (Friedel and Crafts, Ann. Chim. [6] **14**, 449; Bull. Soc. [2] **35**, 508).

By passing cyanic acid and hydrogen chloride into toluene at 100° in presence of aluminium chloride (Gattermann and Rossolymo, Ber. **23**, 1195).

By passing carbon monoxide and hydrogen chloride through toluene in the presence of aluminium and cuprous chlorides and oxidising the p-toluic aldehyde thus formed (Gattermann and Koch, Ber. **30**, 1622).

Paratoluic acid can be converted into 2-hydroxy-p-toluic acid (2-methylphenol-4-carboxylic acid) by several processes:—

By sulphonation and potash fusion of the 2-sulpho-acid (Weinreich, Ber. **20**, 981).

By conversion into 2-brom-p-toluic acid (Brückner, Ber. **9**, 407) and potash fusion of the latter (Vongerichten, Ber. **11**, 368).

By converting the acid (or nitrile) into 2-nitro-p-toluic acid by nitration (Fittig and Ramsay, Ann. **168**, 251; Banse, Ber. **27**, 2162; Van Scherpenzeel, *loc. cit.*), reducing to amino-acid and applying the diazo-reaction (Fittica, Ber. **7**, 927; Vongerichten and Rössler, Ber. **11**, 705).

The 2-hydroxy-p-toluic acid thus formed gives o-cresol when distilled with lime.

From Toluene through m-Xylene and the Hydroxytoluic Acids.

Metaxylene is formed (among other methylbenzenes) when methyl chloride is passed into toluene in presence of aluminium chloride (Friedel and Crafts, Ann. Chim. [6] **1**, 461; Ador and Rilliet, Ber. **11**, 1627), and this on sulphonation gives (chiefly) m-xylene-4-sulphonic acid (Jacobsen, Ann. **184**,

188; Ber. **11**, 18), the amide of which gives on oxidation with chromic acid or potassium permanganate 6-sulphamide-m-toluic acid (Remsen and Iles, Am. Ch. Journ. **1**, 41; Jacobsen, Ber. **11**, 895; Coale and Remsen, Am. Ch. Journ. **3**, 205). The latter on potash fusion yields 6-hydroxy-m-toluic acid (Jacobsen, *loc. cit.* 897; Remsen and Iles, *loc. cit.* 48; 114; Ber. **11**, 462; Mahon, Am. Ch. Journ. **4**, 186), which on heating with hydrochloric acid at 180–185° gives o-cresol.

Or m-xylene can be nitrated, the 6-nitro-m-xylene oxidised to 6-nitro-m-toluic acid by chromic acid (Beilstein and Kreusler, Ann. **144**, 168), reduced to the amino-acid (*Ibid.* 177), the latter converted into the 6-hydroxy-m-toluic acid by the diazo-reaction (Remsen and Kuhara, Am. Ch. Journ. **3**, 428), and the hydroxy-acid converted into o-cresol as above.

Or m-xylene may be brominated, the product oxidised to 6-brom-m-toluic acid by chromic acid (Fittig, Ahrens, and Mattheides, Ann. **147**, 32; Jacobsen, Ber. **14**, 2352), the 6-hydroxy-acid formed by potash fusion of the bromo-acid (Jacobsen, *loc. cit.*), and then converted into o-cresol as before.

When m-xylene is sulphonated the 2-sulphonic acid is produced as well as the 4-sulphonic acid (Jacobsen, Ann. **184**, 188; Ber. **10**, 1015; **11**, 19), and the amide of the former on oxidation with chromic acid gives 2-sulphamide-m-toluic acid (*Ibid.* Ber. **11**, 901), which on fusion with potash yields 2-hydroxy-m-toluic (β-cresotic = o-homosalicylic) acid. The latter on heating with strong hydrochloric acid is converted into o-cresol.

Or m-xylene can be directly oxidised to m-toluic acid by dilute nitric acid (Tawildaroff, Zeit. [2] **6**, 419; Ber. **4**, 410; Brückner, Ber. **9**, 406; Reuter, Ber. **17**, 2028). m-Toluic acid on nitration gives (with much 4-nitro-acid) a small quantity of 2-nitro-m-toluic acid (Jacobsen, Ber. **14**, 2353; Van Scherpenzeel, Rec. Tr. Ch. **20**, 149), and this on reduction to the amino-acid and application of the diazo-reaction yields 2-hydroxy-m-toluic acid (Jacobsen, *loc. cit.*), which can be converted into o-cresol as before.

Or m-toluic acid may be brominated with the formation of 4-brom- and 6-brom-m-toluic acid (Jacobsen, *loc. cit.*), the latter being convertible into 6-hydroxy-m-toluic acid by potash fusion and then into o-cresol as above.

NOTE :—All the generators of toluene referred to under benzyl alcohol (**54**; **A** and **D** to **T**, &c.) by the foregoing methods become generators of o-cresol.

[**B.**] From *acetone* [**106**] through mesitylene (see under benzyl alcohol; [**54**; **D**]), mesitylenic acid by oxidation with dilute nitric acid (Fittig, Ann. **141**, 144; Fittig and Brückner, Zeit. [2] **4**, 493; Ann. **147**, 45), m-xylene by distilling mesitylenic acid with lime (Fittig and Velguth, Ann. **148**, 10), and then as under the foregoing methods. Or from acetone through phorone (2 : 6-dimethyl-2 : 5-heptadienone-4) by the action of lime or acids (Fittig, Ann. **110**, 32; Baeyer, Ann. **140**, 301), pseudocumene (1 : 2 : 4-trimethylbenzene) by the action of phosphorus pentoxide or zinc chloride on phorone (Jacobsen, Ber. **10**, 855), xylic acid (1 : 3-dimethyl-4-benzoic acid) by the oxidation of pseudocumene by dilute nitric acid (Fittig and Laubinger, Ann. **151**, 269), m-xylene by distilling xylic acid with lime (Fittig and Bieber, Ann. **156**, 236), and then as above. Or from acetone through triacetonamine by the action of ammonia (Heintz, Ann. **178**, 305; **189**, 214), nitrosotriacetonamine by the action of nitrous acid (*Ibid.* **185**, 1; **187**, 233), phorone by the action of caustic alkali on the nitrosamine (*Ibid.* **187**, 250), and then as above.

NOTE :—Mesitylenic acid is formed also in small quantity by passing carbon monoxide over a mixture of *sodium ethylate* and *sodium acetate* heated to 205°, or by heating this same mixture with zinc dust (Geuther and Fröhlich, Ann. **202**, 310). Also under similar conditions from sodium *isovalerate* and *ethylate* at 160° (Loos, *Ibid.* 321).

Mesitylene also is converted by further oxidation into uvitic acid (see under benzyl alcohol [**54**; **D**]), and this on heating the calcium salt with a small quantity of lime gives m-toluic acid (Böttinger and Ramsay, Ann. **168**, 255),

which can be converted into 2-hydroxy-m-toluic acid and o-cresol as under **A**.

NOTE :—The generators of mesitylene and uvitic acid referred to under benzyl alcohol (54 ; D to Q) thus become generators of o-cresol.

[C.] From *cymene* [6] through the *a*-sulphonic acid (Claus and Cratz, Ber. **13**, 901; Spica, Ber. **14**, 653; Claus, *Ibid.* 2139), 2-sulpho-p-toluic acid by oxidation of the sulphonic acid (Remsen and Burney, Am. Ch. Journ. **2**, 411; Meyer and Baur, Ann. **220**, 18), 2-hydroxy-p-toluic acid by potash fusion, &c., as under **A**.

Or from cymene through the 2-(*a*)-sulphonic acid (see above), 3-brom-6-sulphonic acid by bromination (Kelbe and Koschnitzky, Ber. **19**, 1730; Claus and Christ, *Ibid.* 2165), 3-bromcymene by heating the latter with sulphuric acid (*Ibid.*), 3-brom-6-nitro-p-toluic acid by the action of nitric acid on latter (Fileti and Crosa, Gazz. **16**, 297), 6-nitro-3-amino-p-toluic acid by heating the brom-nitro acid with alcoholic ammonia (*Ibid.* **18**, 303), 6-nitro-m-toluidine by heating the nitramino-p-toluic acid with hydrochloric acid at 150° (*Ibid.*), and then through o-nitrotoluene and o-toluidine to o-cresol as under **F** and **A**.

Or 3-bromcymene may be nitrated (Mazzara, Gazz. **16**, 193; Fileti and Crosa, *Ibid.* **18**, 289), the 3-brom-6-nitrocymene oxidised to 3-brom-6-nitro-p-toluic acid (F. and C. *Ibid.* 300), and then treated as above.

[D.] From *thymol* [67] through 3-amino-p-cymene (cymidine) by heating with ammonium bromide and ammonio-zinc bromide at 350–360° (Lloyd, Ber. **20**, 1260), and then as under **G**.

Or thymol can be converted directly into 3-bromcymene by phosphorus pentabromide (Fileti and Crosa, Gazz. **16**, 291), and then into o-cresol as under **C**.

[E.] *Carvacrol* [66] on heating with phosphorus pentoxide and hydrolysis of the phosphate gives o-cresol (Kekulé, Ber. **7**, 1006).

Or carvacrol by the action of phosphorus pentasulphide can be converted into thiocarvacrol (Roderburg, Ber. **6**, 669), which by oxidation with nitric acid gives 2-sulpho-p-toluic acid (Flesch, Ber. **6**, 480; Bechler, Journ. pr. Ch. [2] **8**, 170). The latter can be converted into the hydroxy-acid and o-cresol as before.

[F.] *Metacresol* (see below) on heating with ammonio-zinc chloride and ammonium chloride at 330–340° is converted into m-toluidine (Merz and Müller, Ber. **20**, 548), the acetyl-derivative giving on nitration 6-nitro-m-toluidine (Beilstein and Kuhlberg, Ann. **158**, 348 : see also Noelting and Stöcklin, Ber. **24**, 564), which by the diazo-method gives o-nitrotoluene (B. and K.). The latter can be reduced to o-toluidine and converted into o-cresol as under **A**.

Or m-cresol may be ethylated, the ether nitrated (Städel, Ann. **217**, 161), the 6-nitro-m-cresol ether converted into 6-nitro-m-toluidine by heating with strong ammonia (Städel and Kolb, Ann. **259**, 214), and the latter converted into o-cresol as before.

[G.] From *cumic aldehyde* [116] through the 3-nitro-derivative by nitration, nitrocymylidene chloride by the action of phosphorus pentachloride, 3-amino-p-cymene (cymidine) by reduction, 3-amino-p-cymene-6-sulphonic acid by sulphonation, 3-brom-p-cymene-6-sulphonic acid by the diazo-method, and then through 3-bromcymene, 3-brom-6-nitro-p-toluic acid, 6-nitro-3-amino-p-toluic acid, 6-nitro-m-toluidine, and o-nitrotoluene to o-cresol as under **C**.

[H.] From *phenylacetic acid* [Vol. II] through the 2 : 4-dinitro acid, 2 : 4-dinitrotoluene and o-nitrotoluene (see under quinol [71; I]), o-toluidine, &c., as under **A**.

[I.] *Methylheptenone* [111] by heating with zinc chloride or with 75 per cent. sulphuric acid gives dihydro-m-xylene (Verley, Bull. Soc. [3] **17**, 181). The latter on nitration gives 6-nitro-m-xylene (Wallach, Ann. **258**, 330), and this can be converted into 6-amino- and 6-hydroxytoluic acid and o-cresol as under **A** above.

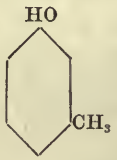
[J.] *Carvone* [127] through *carvacrol* [66] gives o-cresol (see above under **E**). Or from carvone through dihydrocarveol by reduction and the ketone-alcohol by oxidation. The latter by extreme

oxidation gives hexahydro-m-hydroxy-p-toluic acid, which is converted by bromine into 2-hydroxy-p-toluic acid (Tiemann and Semmler, Ber. **28**, 2141). The latter gives o-cresol as above under **A**.

[**K.**] From *acetylene* [**1**; **A**, &c.], the copper compound of which gives a mixture of cresols among the products of distillation with zinc dust (Erdmann and Köthner, Zeit. anorg. Ch. **18**, 48).

NOTE:—Orthocresylsulphuric acid is obtained from o-cresol by treating the potassium salt with potassium pyrosulphate (Baumann, Ber. **11**, 1911).

62. Metacresol; 3-Methylphenol.



NATURAL SOURCE.

Possibly occurs (as salt of cresylsulphuric acid) in urine of horse (Preusse, Zeit. physiol. Ch. **2**, 356).

SYNTHETICAL PROCESSES.

[**A.**] From *toluene* (see under benzyl alcohol [**54**; **A**]) by passing air through the boiling hydrocarbon in presence of aluminium chloride (Friedel and Crafts, Ann. Chim. [6] **14**, 436).

Toluene on sulphonation (preferably with chlorosulphonic acid) gives o- (with p-) toluenesulphonic acid (Claesson and Wallin, Ber. **12**, 1848; Noyes, Am. Ch. Journ. **8**, 176: see also under **61**; **A**), which can be converted into o-cyanotoluene (nitrile) by distilling the potassium salt with *potassium cyanide* [**172**] (Fittig and Ramsay, Zeit. [2] **7**, 584; Ann. **168**, 246) and into o-toluic acid by hydrolysis (Cahn, Ann. **240**, 280). The latter on bromination gives 3-brom-o-toluic acid (Jacobsen and Wierss, Ber. **16**, 1956; Racine, Ann. **239**, 74), which by potash fusion yields the corresponding hydroxytoluic acid (Jacobsen, Ber. **16**, 1963), and this on heating with strong hydrochloric acid at 200° gives m-cresol (*Ibid.*).

Or toluene can be nitrated, the o-nitrotoluene (separated from the para-) reduced to o-toluidine, converted into the nitrile by the diazo- (Sandmeyer) method and the nitrile converted into the acid (Cahn, *loc. cit.*), the bromo-acid, &c., as before.

From Toluene through the Xylenes and Hydroxytoluic Acids.

Toluene can be converted into o-xylene by the action of sodium on a mixture of o-bromtoluene and *methyl iodide* (Jannasch and Hübner, Ann. **170**, 117; Reymann, Bull. Soc. [2] **26**, 532) or by passing *methyl chloride* into warm toluene in presence of aluminium chloride (Jacobsen, Ber. **14**, 2625). Orthoxylene gives o-toluic acid on oxidation with dilute nitric acid (Fittig and Bieber, Zeit. [2] **6**, 496; Ann. **156**, 242), and this can be treated as above.

Orthoxylene also on sulphonation (Jacobsen, Ber. **11**, 22) and conversion into the sulphonamide gives on oxidation of the latter with alkaline permanganate a mixture of 4- and 5-sulphamide-o-toluic acid (*Ibid.* Ber. **14**, 39); the latter on fusion with potash gives 5-hydroxy-o-toluic acid, which on heating with hydrochloric acid at 200° yields m-cresol (*Ibid.*).

Or from o-xylene through 5-nitro-o-xylene (Jacobsen, Ber. **17**, 160), 5-nitro-o-toluic acid by oxidising the latter with dilute nitric acid (*Ibid.* 162), 5-amino-o-toluic acid by reduction (*Ibid.* 164), 5-hydroxy-o-toluic acid by the diazo-method (*Ibid.*), and then as above.

From toluene through m-xylene (see under orthocresol [**61**; **A**]), m-toluic acid by oxidation with dilute nitric acid (Tawildaroff, Zeit. [2] **6**, 419; Ber. **4**, 410; Brückner, Ber. **9**, 406; Reuter, Ber. **17**, 2028), 5-sulpho-m-toluic acid by sulphonation (Jacobsen, Ber. **14**, 2355), 5-hydroxy-m-toluic acid by potash fusion (*Ibid.* 2357), and decomposition of the latter by heating with lime.

Or toluene can be nitrated, the p-nitrotoluene reduced to p-toluidine, the latter acetylated, nitrated, and hydrolysed to 3-nitro-p-toluidine (Beilstein

and Kuhlberg, Ann. **155**, 23; Ehrlich, Ber. **15**, 2009; Gattermann, Ber. **18**, 1483), the latter converted into m-nitrotoluene by the diazo-method (*Ibid.* **158**, 346), reduced to m-toluidine, and converted into m-cyanotoluene by the diazo-(Sandmeyer) reaction (Buchka and Schachtebeck, Ber. **22**, 841), m-toluic acid by hydrolysis, and then as above. o-Nitrotoluene can be converted into m-toluic acid by a similar series of processes.

Or p-toluidine can be sulphonated (v. Pechmann, Ann. **173**, 195; Nevile and Winther, Ber. **13**, 1947), the p-toluidine-3-sulphonic acid converted into the nitrile by Sandmeyer's process (Randall, Am. Ch. Journ. **13**, 258), and the latter hydrolysed to 3-sulpho-p-toluic acid, which, by potash fusion, gives 3-hydroxy-p-toluic = γ-cresotic acid (Weber, Ber. **25**, 1743). The latter on heating with hydrochloric acid is converted into m-cresol.

Or toluene can be converted into 3-nitro-p-toluidine as above, the latter converted into the nitrile (Leuckart, Ber. **19**, 175; Niementowski and Rozanski, Ber. **21**, 1993; Noyes, Am. Ch. Journ. **10**, 476), then into 3-nitro-p-toluic acid by hydrolysis, into 3-amino-p-toluic = homoanthranilic acid by reduction, and then into 3-hydroxy-p-toluic = γ-cresotic acid by the diazo-method (N. and R. *loc. cit.* 1998).

From toluene through p-xylene by the action of sodium on p-bromtoluene and methyl iodide (Fittig and Glinzer, Ann. **136**, 303; Jannasch, Ann. **171**, 79), p-xylenesulphonic acid and 1 : 4 : 2-xylenol (Jacobsen, Ber. **11**, 26; Wurtz, Ann. **147**, 373), 3-hydroxy-p-toluic acid by potash fusion of latter (Jacobsen, *loc. cit.* 570), and m-cresol as above.

Or p-xylene may be nitrated, reduced to the corresponding xylidine, the latter converted into p-xylenol by the diazo-method (Noelting, Witt, and Forel, Ber. **18**, 2665), and then as above.

NOTE:—All generators of toluene thus become generators of m-cresol.

[B.] From *acetone* [**106**] through mesitylene, mesitylenic acid (see under o-cresol [**61**; **B**]), and m-xylene, and then as under **A**. Or from mesitylene through uvitic acid and m-toluic acid and then as under **A** (see also under o-cresol [**61**; **B**]).

Or from acetone through phorone, pseudocumene, 1 : 3-dimethyl-4-benzoic (xylic) acid, and m-xylene as under o-cresol (**61**; **B**).

NOTE:—Generators of mesitylene and uvitic acid (see under benzyl alcohol [**54**; **D** to **Q**]) thus also become generators of m-cresol.

From acetone and *oxalic acid* [Vol. II] and *ethyl alcohol* [**14**] through acetone-oxalic ester by the action of sodium ethylate on a mixture of acetone and oxalic ester (Claisen and Stylos, Ber. **20**, 2188). This acetoneoxalic ester (= acetylpyroracemic ester) on heating with baryta water is converted into 5-hydroxy-m-toluic acid (Claisen, Ber. **22**, 3271), from which m-cresol can be obtained as under **A**.

[C.] From *acetic acid* [Vol. II] and *ethyl alcohol* [**14**] through 5-methylphenol-2 : 4-dicarboxylic acid (= m-hydroxyuvitic acid) by the action of chloroform, chloral, trichloracetic ester or carbon tetrachloride on sodio-acetoacetic ester (Oppenheim and Pfaff, Ber. **7**, 929; **8**, 884; Oppenheim and Precht, Ber. **9**, 321; Conrad and Guthzeit, Ann. **222**, 249), and hydrolysis of the ester thus formed. The acid on distillation with baryta gives m-cresol (Oppenheim and Pfaff, Ber. **8**, 886).

Or acetoacetic ester on treating the sodium compound with methylene iodide (Hagemann, Ber. **26**, 876), or the ester with formic aldehyde (Knoevenagel, *Ibid.* 1090) and hydrolysis of the product, gives 3-methyl-Δ_2-keto-R-hexene (1-methylcyclo-3-hexenone) (Hagemann, *loc. cit.*; Knoevenagel, *loc. cit.* 1085; K. and Klages, Ann. **281**, 97). The latter forms a dibromide (Hagemann, *loc. cit.* 884; Knoevenagel, *loc. cit.* 1951), which readily decomposes into hydrogen bromide and m-cresol (K. *Ibid.*).

Acetoacetic ester through its methylene derivative can also be converted by the action of ammonia under various conditions into dihydrolutidine-dicarboxylic ester (Knoevenagel and Klages,

Ann. **281**, 96; Schiff and Prosio, Gazz. **25**, 70: see also Griess and Harrow, Ber. **21**, 2740). The latter on heating with alcoholic potash gives the above methylcyclohexenone among other products (S. and P. *loc. cit.* 76), and this can be converted into m-cresol as before.

[**D.**] From *naphthalene* [**12**] through o-toluic acid (see under benzyl alcohol [**54**; **R**]), and from the latter as under **A**.

Phthalic acid may also be converted into phthalimidine (*loc. cit.*), the latter nitrated (Hönig, Ber. **18**, 3447), reduced to 5-amino-o-toluic acid by heating with hydriodic acid and phosphorus (*Ibid.* 3449), and the latter converted into 5-hydroxy-o-toluic acid and m-cresol as under **A**.

Also from naphthalene through the trisulphonic acids (heteronucleal) derived from the m-disulphonic acid, which, on fusion with alkali, give m-hydroxytoluic acid and m-cresol (Kalle & Co., Germ. Pat. 81484 of 1894; Ber. **28**, Ref. 694; also Ref. 364). The 1 : 6-dihydroxynaphthalene-3-sulphonic acid on fusion with alkali gives the corresponding trihydroxynaphthalene, which yields m-cresol on further heating (Kalle & Co., Germ. Pat. 112176 of 1899; Ch. Centr. 1900, **2**, 700: see also Ber. **28**, Ref. 671 and 693, relating to Germ. Pats. 81281 and 81333 of 1893 of Meister, Lucius, and Brüning, and also Ch. Centr. 1897, **1**, 1039).

[**E.**] *Orthocresol* [**61**] on heating with ammonium chloride and ammonio-zinc chloride at 330–340° gives o-toluidine (Merz and Müller, Ber. **20**, 547). The latter can be converted into o-toluic acid, and m-cresol as under **A**.

Or o-toluidine may be acetylated, nitrated, hydrolysed, and thus converted into 5-nitro-o-toluidine (Beilstein and Kuhlberg, Ann. **158**, 345), from which, by the diazo-method, m-nitrotoluene can be obtained (*Ibid.*), and from this m-toluidine. The latter might be directly converted into m-cresol by the diazo-method, or indirectly through m-toluic acid, &c., as under **A**.

[**F.**] *Paracresol* [**63**] on nitration gives 3-nitro-p-cresol (Armstrong and Thorpe, B. A. Rep. 1875, 112; Hofmann and Miller, Ber. **14**, 573; Städel, Ann. **217**, 53; Frische, Ann. **224**, 138), which, by heating with ammonia, gives 3-nitro-p-toluidine (Barr, Ber. **21**, 1543). The latter can be converted into m-nitrotoluene, m-toluidine, and m-cresol as under **A**.

[**G.**] From *benzoic aldehyde* [**114**] through the m-nitro-derivative, m-toluidine (see under phenol [**60**; **H**]), and then as above.

[**H.**] From *thymol* [**67**] by heating with phosphorus pentoxide and decomposition of the m-cresyl phosphate by heating with alkali (Engelhardt and Latschinoff, Zeit. [2] **5**, 621; Southworth, Ann. **168**, 268; Städel and Kolb, Ann. **259**, 209; Tiemann and Schotten, Ber. **11**, 769).

Or thymol can be converted into thiothymol by the action of phosphorus pentasulphide (Fittica, Ann. **172**, 328), 3-sulpho-p-toluic acid by oxidation of thiothymol with nitric acid (*Ibid.* 329), and then through 3-hydroxy-p-toluic acid and m-cresol as under **A**.

[**I.**] From *menthone* [**129**], which gives tetrabrom-m-cresol among the products of the action of bromine. The tetrabrom-derivative gives m-cresol on reduction with sodium in alcoholic solution (Baeyer and Seuffert, Ber. **34**, 40).

[**J.**] From *pulegone* [**128**] through methylcyclohexanone (see under phenol [**60**; **S**]). The latter gives m-cresol on treatment with a chloroform solution of bromine (Klages, Ber. **32**, 2567: see also Wallach, *Ibid.* 3338).

63. Paracresol; 4-Methylphenol.

Natural Sources.

Occurs as a salt of cresylsulphuric acid in urine of herbivorous animals, and, in certain diseases, in human urine (Baumann, Ber. **9**, 1389; Städeler,

Ann. **77**, 18; Brieger, Zeit. physiol. Ch. **4**, 204: see also under o-cresol [**61**] for further references).

A product of putrefaction of animal proteids (Baumann and Brieger, Zeit. physiol. Ch. **3**, 149; Ber. **12**, 706), of *p-hydroxyphenylacetic* and *hydroparacoumaric acids* [Vol. II] (Baumann, Zeit. physiol. Ch. **4**, 304), and of *tyrosin* [Vol. II] (Weyl, Zeit. physiol. Ch. **3**, 312; Baumann, *Ibid.* **4**, 304).

The p-cresol complex may be contained in podocarpic acid, which constitutes the chief portion of the resin of *Podocarpus cupressina*, var. *imbricata* (Oudemans, Ann. **170**, 259).

The methyl ether appears to exist in the perfume 'Cananga Essence' (ylang-ylang) from *Cananga odorata* (Reychler, Bull. Soc. [3] **13**, 140). p-Cresyl acetate exists also in this oil (Darzens, Bull. Soc. [3] **37**, 83).

Synthetical Processes.

[**A.**] From *toluene* [**54**; **A**, &c.] through p-nitrotoluene (see under orthocresol [**61**; **A**]), p-toluidine by reduction, and the diazo-reaction with latter (Griess, Jahresber. **1866**, 458; Körner, Zeit. [2] **4**, 326).

Or p-nitrotoluene on mild reduction gives p-toluylhydroxylamine (see under toluquinol [**72**; **A**]), and this gives p-cresol among the products of decomposition by hot dilute sulphuric acid (Bamberger, Ber. **28**, 246; for production of p-toluylhydroxylamine by the oxidation of p-toluidine by monopersulphuric acid see Bamberger and Tschirner, Ber. **32**, 1677).

Or from toluene through the p-sulphonic acid and potash fusion of the latter (Wurtz, Ann. **144**, 122; **156**, 258; Engelhardt and Latschinoff, Zeit. [2] **5**, 618).

From toluene through m-xylene (see under orthocresol [**61**; **A**]), m-xylene-4-sulphonic acid by sulphonation (Jacobsen, Ann. **184**, 188; Ber. **10**, 1015; **11**, 19), and potash fusion of latter so as to form 4-hydroxy-m-toluic (α-cresotic = p-homosalicylic) acid (Engelhardt and Latschinoff, *loc. cit.* 712). The latter acid on heating with strong hydrochloric acid at 180–185° gives p-cresol.

Or m-xylene may be oxidised to m-toluic acid (Tawildaroff, Zeit. [2] **7**, 419; Ber. **4**, 410; Brückner, Ber. **9**, 406; Reuter, Ber. **17**, 2028), the latter brominated (Jacobsen, Ber. **14**, 2351), and the 4-brom-m-toluic acid thus formed fused with potash (*Ibid.*).

Or m-toluic acid may be sulphonated (Jacobsen, *loc. cit.* 2355), the 4-sulpho-m-toluic acid converted into 4-hydroxy-m-toluic acid by potash fusion (*Ibid.*), and then into p-cresol as before.

Or m-toluic acid may be nitrated (*Ibid.* 2353), the 4-nitro- reduced to the 4-amino-m-toluic (methylanthranilic) acid (*Ibid.*), the latter converted into 4-hydroxy-m-toluic acid by the diazo-reaction (*Ibid.*: see also Panaotovic, Journ. pr. Ch. [2] **33**, 64), and into p-cresol as before.

Or m-xylene-4-sulphonic acid (see above) may be converted into 1 : 3 : 4-xylenol by potash fusion (Jacobsen, Ber. **11**, 28), or the corresponding 1 : 3 : 4-nitroxylene into 1 : 3 : 4-xylidine and into the same xylenol by the diazo-reaction (Harmsen, Ber. **13**, 1558). This 1 : 3 : 4-xylenol (or its β-sulphonic acid) gives 4-hydroxy-m-toluic acid by potash fusion (Jacobsen, Ber. **11**, 375; Ann. **195**, 283), and this gives p-cresol as before.

Toluene may also be converted into 2 : 4-dinitrotoluene (Deville, Ann. **44**, 307), the p-nitro-group in the latter replaced by bromine (Beilstein and Kuhlberg, Ann. **158**, 340), the 4-brom-2-nitrotoluene heated with alcoholic *potassium cyanide* at 220°, and the nitrile hydrolysed to 4-brom-m-toluic acid (Richter, Ber. **5**, 425), which can be converted into 4-hydroxy-m-toluic acid and p-cresol as above. 4-Brom-2-nitrotoluene is also formed (with 4-brom-3-nitrotoluene) by the nitration of p-bromtoluene (Wroblewski, Ann. **168**, 176).

Or toluene may be converted into methyl-m-toluyl ketone by the action of acetyl chloride in presence of aluminium chloride (Essner and Gossin, Bull. Soc. [2] **42**, 95); or p-bromtoluene into p-bromtoluyl-m-methyl ketone by the same process. The latter on oxida-

tion with potassium permanganate gives 4-brom-m-toluic acid (Claus, Journ. pr. Ch. [2] **46**, 21), and this can be converted into p-cresol as before.

Toluene or m- or p-xylene can, by further methylation, be converted into pseudocumene = 1 : 2 : 4-trimethylbenzene (Fittig and Ernst, Ann. **139**, 187; Fittig and Jannasch, Ann. **151**, 286; Fittig and Laubinger, *Ibid.* 257; Jannasch, Ann. **176**, 286; Friedel and Crafts, Ann. Chim. [6] **1**, 461; Ador and Rilliet, Ber. **12**, 329), the sulphonic acid of which (Jacobsen, Ann. **184**, 199) gives a sulphonamide, which, by oxidation with alkaline permanganate, gives 4-sulphamidemethylbenzene-2 : 5-dicarboxylic (methylterephthalic = α-xylidic) acid (Jacobsen and Meyer, Ber. **16**, 190). The latter (sulphamide) on potash fusion gives methyl-4-phenol-2 : 5-dicarboxylic (s-hydroxymethylterephthalic) acid (*Ibid.*), and this on heating with lime gives p-cresol.

NOTE :—All generators of toluene thus become generators of p-cresol.

[B.] From *p-hydroxyphenylacetic acid* [Vol. II] by heating with lime (Salkowski, Ber. **12**, 1440).

[C.] From *acetone* [**106**] through mesitylene (see under benzyl alcohol [**54** ; **D**]), mesitylenesulphonic acid (Jacobsen, Ann. **146**, 95), 4-hydroxymesitylenic (1 : 3-dimethyl-4-phenol-5-carboxylic) acid by potash fusion of the sulphonic acid (Fittig and Hoogewerff, Ann. **150**, 333), 4-hydroxyuvitic (4-methylphenol-3 : 5-dicarboxylic) acid by potash fusion of hydroxymesitylenic acid (Jacobsen, Ann. **195**, 285), and decomposition of the hydroxyuvitic acid by heating with hydrochloric acid at 200° (*Ibid.* **206**, 196).

Or from mesitylene through mesitylenic acid (see under o-cresol [**61**; **B**]), 4-nitro- and 4-aminomesitylenic acid (Schmitz, Ann. **193**, 162; 171), 4-hydroxymesitylenic acid by the diazo-reaction (Jacobsen, Ber. **11**, 2055), and then 4-hydroxyuvitic acid and p-cresol as above.

Or 4-hydroxymesitylenic acid may be converted into 1 : 3 : 4-xylenol by heating with hydrochloric acid at 200° (Jacobsen, Ber. **11**, 2052; Fittig and Hoogewerff, Ann. **150**, 330), and the xylenol converted into 4-hydroxy-m-toluic acid and p-cresol as under **A**.

Or mesitylene may be converted into mesitol (1 : 3 : 5-trimethyl-2-phenol) by potash fusion of mesitylenesulphonic acid, or by the diazo-reaction from aminomesitylene (Biedermann and Ledoux, Ber. **8**, 59 and 250; Jacobsen, Ann. **195**, 268). Mesitol on potash fusion gives 4-hydroxymesitylenic acid (Jacobsen, *loc. cit.* 274), from which p-cresol can be obtained as above.

Or from mesitylenic acid through α-sulphomesitylenic acid by sulphonation (Remsen and Brown, Am. Ch. Journ. **3**, 218), 4-hydroxymesitylenic acid by potash fusion (*Ibid.* 220), and then as above.

Or mesitylene may be oxidised to uvitic acid (see under benzyl alcohol [**54** ; **D**]), which, by distillation with lime, gives m-toluic acid (Böttinger and Ramsay, Ann. **168**, 255). The latter can be converted into 4-hydroxy-m-toluic acid and p-cresol as under **A**.

NOTE :—Generators of mesitylene and uvitic acid (see under benzyl alcohol [**54** ; **D** to **Q**]) thus also become generators of p-cresol.

Acetone may also be converted through phorone into pseudocumene (see under o-cresol [**61**; **B**]), and the latter into s-hydroxymethylterephthalic acid and p-cresol as under **A**.

[D.] *Parahydroxybenzoic aldehyde* [**119**] gives, among other products, p-cresol when heated with acetic acid and zinc dust (Tiemann, Ber. **24**, 3170).

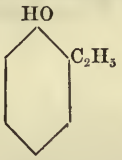
[E.] *Metacresol* [**62**] on nitration yields a mixture of 4- and 6-nitro-m-cresol (Städel, Ann. **217**, 51; **259**, 210). The ethyl ether of the former gives, on heating with strong aqueous ammonia at 140–150°, 4-nitro-m-toluidine (Städel and Kolb, Ann. **259**, 224). The latter on replacement of the NH_2-group by hydrogen by the diazo-method would give p-nitrotoluene, which can be converted into p-toluidine and p-cresol as under **A**.

[F.] *Anethole* [**68**] when heated under pressure to 250–275° gives, among other products, p-cresol methyl ether (Orn-

dorff, Terrasse, and Morton, Am. Ch. Journ. **19**, 845).

Note :—Paracresol can be converted into p-cresylsulphuric acid (potassium salt) by heating the potassium salt with a solution of potassium pyrosulphate (Baumann, Ber. **9**, 1389).

64. Phlorol; 2-Ethylphenol.



Natural Sources.

The phlorol complex probably occurs in gum-ammoniac, the dried sap of *Dorema ammoniacum*, which yields phlorol methyl ether on distillation with zinc dust (Ciamician, Ber. **12**, 1658).

Hlasiwetz obtained a phlorol by distilling barium phloretate with lime (Ann. **102**, 166), but since phloretic acid is a para-hydroxybenzene derivative, it is doubtful whether the phlorol thus obtained is the ortho-ethylphenol, although Oliveri concludes that it is identical with this modification (Gazz. **13**, 263).

Synthetical Processes.

[A.] *Benzene* [6 ; I, &c.] can be converted into ethylbenzene by several processes :—

By the action of sodium on a mixture of brombenzene and ethyl bromide (Fittig, Ann. **131**, 310 ; **133**, 222 ; **144**, 278 ; Schramm, Ber. **24**, 1333).

From benzene, ethyl iodide, bromide or chloride, and aluminium chloride (Friedel and Crafts, Ann. Chim. [6] **1**, 457 ; Söllscher, Ber. **15**, 1680 ; Sempotowski, Ber. **22**, 2662 ; Béhal and Choay, Bull. Soc. [3] **11**, 207 ; Radziewanowski, Ber. **27**, 3235).

From benzene and ethylene in the presence of aluminium chloride (Balsohn, Bull. Soc. [2] **31**, 540), or by heating benzene with ethyl ether and zinc chloride (*Ibid.* **32**, 618).

From benzene and chloracetic or chloroformic ester and aluminium chloride (Friedel and Crafts, Ann. Chim. [6] **1**, 527 ; Rennie, Trans. Ch. Soc. **41**, 33).

From benzene and ethylene through the dibromide of the latter, vinyl bromide, and the action of the latter on benzene in presence of aluminium chloride (Anschütz, Ann. **235**, 331).

Ethylbenzene when brominated (in the dark) in presence of iodine gives a mixture of o- and p-ethylbrombenzene (Schramm, Ber. **18**, 1273 ; Sempotowski, Ber. **22**, 2668). The latter on sulphonation yields ethyl-4-brombenzene-2-sulphonic acid (Sempotowski, *loc. cit.*), which on debromination by zinc dust and ammonia gives ethylbenzene-o-sulphonic acid (*Ibid.*). The latter yields phlorol on fusion with potash (Beilstein and Kuhlberg, Ann. **156**, 211 ; Sempotowski, *loc. cit.* 2672).

Or ethylbenzene may be nitrated, the o-nitro-derivative reduced, and the amino-ethylbenzene converted into phlorol by the diazo-method (Suida and Plohn, Monats. **1**, 175 ; Béhal and Choay, Bull. Soc. [3] **11**, 209 ; Sempotowski, *loc. cit.* 2672 ; for nitration of ethylbenzene and separation of isomerides see Schultz and Flachsländer, Journ. pr. Ch. [2] **66**, 153).

[B.] From *styrene* [7] through ethylbenzene by heating with hydriodic acid (Berthelot, Bull. Soc. [2] **9**, 455), or by passing the vapour mixed with hydrogen over heated copper (Sabatier and Senderens, Comp. Rend. **130**, 1761 ; **132**, 1254 ; **134**, 1127). Also by reduction with sodium in alcoholic solution (Klages and Keil, Ber. **36**, 1632), and then as under A.

[C.] *Phenol* [60] when heated with absolute alcohol and zinc chloride gives a mixture of ethylphenols (Auer, Ber. **17**, 670 ; Errera, Gazz. **14**, 484), among which phlorol is present.

Or phenol may be converted into phenoxylacetal by heating sodium phenate with chloracetal at 160° (Autenrieth, Ber. **24**, 162 ; Pomeranz, Monats. **15**, 739).

[Chloracetal is prepared by the action of chlorine on *ethyl alcohol* (Lieben, Ann. **104**, 114 ; Fritsch, Ann. **279**, 288 : see also **54**, p. 111).]

Phenoxylacetal when heated with zinc

chloride (in acetic acid solution) condenses to coumarone (Stoermer, Ber. **30**, 1703), and this can be reduced to phlorol as below under **D**.

[**D.**] From *coumarin* [Vol. II] through the chloride or bromide (Perkin, Zeit. [2] **7**, 178; Journ. Ch. Soc. **17**, 368; **24**, 37; Ann. **157**, 116; Fittig and Ebert, Ann. **216**, 163), *a*-chlor- or *a*-bromcoumarin (Perkin, *loc. cit.*; also Journ. Ch. Soc. **23**, 368), o-coumarilic acid by the action of alcoholic potash (*Ibid.* Journ. Ch. Soc. **24**, 45; Fittig and Ebert, *loc. cit.*), coumarone by heating coumarilic acid with lime (Fittig and Ebert, *loc. cit.* 168 and **226**, 347), and reduction of coumarone in hot alcoholic solution with sodium, hydrocoumarone being simultaneously formed (Alexander, Ber. **25**, 2410).

The conversion of hydrocoumarone into o-ethylphenol can also be effected by boiling with strong hydriodic acid solution (Baeyer and Seuffert, Ber. **34**, 52). Coumarone also gives o-ethylphenol among the products of its decomposition by alcoholic alkali (Stoermer and Kahlert, Ber. **35**, 1630).

[**E.**] From *salicylic aldehyde* [**117**] and *acetic acid* [Vol. II] through o-aldehydophenoxyacetic acid (aldehydophenylglycollic acid) by the action of chloracetic acid on the sodium compound of the aldehyde (Rössing, Ber. **17**, 2990), coumarone by heating the aldehyde acid with acetic anhydride and sodium acetate (*Ibid.* 3000), and then as under **D**.

[**F.**] *Cinnamic acid* [Vol. II] when nitrated gives a mixture of o- and p-nitro-acids (Beilstein and Kuhlberg, Ann. **163**, 126; Morgan, Ch. News, **36**, 269; Jahresber. **1877**, 788; Müller, Ann. **212**, 124; Drewsen, Ann. **212**, 151; Fischer and Kuzel, Ann. **221**, 265). The former, by the action of hypochlorous acid on the sodium salt, yields (with o-nitrophenylchlorlactic acid) 1^2-chlor-2-nitrostyrene = o-nitrophenyl-ω-chlorethylene (Lipp, Ber. **17**, 1070), which, by reduction and the diazo-method, gives 1^2-chlorvinylphenol = o-hydroxy-ω-chlorstyrene (Komppa, Ber. **26**, 2970). The latter when heated with strong potash solution yields coumarone (*Ibid.* 2971), which can be converted into phlorol as under **D**.

[**G.**] *Benzoic aldehyde* [**114**] on nitration gives (with much m-nitro-) a small quantity of o-nitro-aldehyde (Rudolph, Ber. **13**, 310), which, on heating with *acetic anhydride* and *sodium acetate*, yields o-nitrocinnamic acid (Gabriel and Meyer, Ber. **14**, 830). The latter can be converted into coumarone and phlorol as under **F**.

Note:—For o-nitrobenzaldehyde generators see also under indigo [Vol. II].

[**H.**] From *phenylacetic acid* [Vol. II] through the 2 : 4-dinitro-acid by nitration (Radziszewski, Ber. **2**, 210; Gabriel and Meyer, Ber. **14**, 823), 2-nitro-4-amino-acid by reduction, the diazochloride by the action of nitrous acid in presence of hydrochloric acid, o-nitrobenzaldoxime by heating the diazochloride with alcohol, o-nitrobenzaldehyde by oxidising the aldoxime with chromic acid (Gabriel and Meyer, *loc. cit.* and **15**, 3057; Gabriel, *Ibid.* **16**, 520), and then as under **G**.

[**I.**] *Acetoacetic ester* [Vol. II] and *benzene* can give rise to phlorol by the following steps:—

Benzene is brominated, the monobrombenzene converted by cold nitration into brom-2 : 4-dinitrobenzene (Kekulé, Ann. **137**, 167; Spiegelberg, Ann. **197**, 257 : see also Walker and Zincke, Ber. **5**, 117), the latter combined with sodio-acetoacetic ester so as to form 2 : 4-dinitrophenylacetoacetic ester (Heckmann, Ann. **220**, 131 : a bis-dinitrophenyl derivative is formed simultaneously). The dinitrophenyl ester on heating in alcohol with 10 per cent. sulphuric acid is converted into 2 : 4-dinitrophenylacetic acid (*Ibid.* 134), which can be treated as above.

[**J.**] *Racemic* or *tartaric acid* [Vol. II] and *n-propyl alcohol* [**15**] are generators of ethylbenzene, and therefore of phlorol, by the following steps:—

Pyroracemic acid is obtained from the above acids by dry distillation or other method (see under benzyl alcohol [**54**; **N**]), and this, when mixed with *propionic aldehyde* and barium hydroxide solution, condenses to 1 : 3 : 5-ethylisophthalic

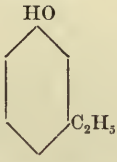
acid (Doebner, Ber. **23**, 2379; **24**, 1746), which gives ethylbenzene on distilling the calcium salt (*Ibid.* **23**, 238).

Note :—The generators of pyroracemic acid referred to under benzyl alcohol [54; F; I; O; P] thus become, with n-propyl alcohol, generators of phlorol.

[K.] *Acetophenone* [7; D and 114; A] gives dypnone [$CH_3 . C(C_6H_5) : C : CH . CO . C_6H_5$] as the first product of condensation, and this, on heating for 80 hours at 280°, yields ethylbenzene (Ameye, Bull. Acad. Roy. Belg. [3] **37**, 227; Delacre, *Ibid.* [3] **39**, 68; Ch. Centr. 1900, **2**, 256).

Ethylbenzene is also among the products of reduction of acetophenone by sodium in alcohol (Klages and Allendorff, Ber. **31**, 1003).

65. 3-Ethylphenol; Meta-ethylphenol.



Natural Source.

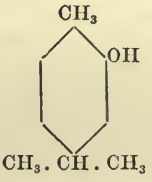
A phlorol probably occurs as isobutyrate in oil of arnica root from *Arnica montana* (Sigel, Ann. **170**, 354) which may be m-ethylphenol, but this requires confirmation.

Synthetical Processes.

[A.] From *ethylbenzene* (see under *phlorol* [64; A]) by bromination and sulphonation, whereby (with the 4-brom-2-sulphonic acid) there is formed ethyl-2-brombenzene-3- or 5-sulphonic acid. The latter on debromination with zinc dust and ammonia gives ethylbenzene-m-sulphonic acid (Sempotowski, Ber. **22**, 2673), which yields m-ethylphenol on potash fusion (*Ibid.* 2674).

Or the ethyl-p-nitrobenzene (obtained as under phlorol [64; A]) can be reduced to ethyl-p-aminobenzene, acetylated, nitrated, and hydrolysed so as to form 3-nitro-4-aminoethylbenzene, the amino-group replaced by hydrogen by the diazo-method, the ethyl-m-nitrobenzene reduced to ethyl-m-aminobenzene, and the latter converted into m-ethylphenol by the diazo-method (Béhal and Choay, Bull. Soc. [3] **11**, 212).

66. Carvacrol; Cymophenol; 6-Methyl-3-Isopropylphenol; 1 : 4-Methylmethoethyl-2-Phenol.



Natural Sources.

Occurs in oils of *Origanum hirtum* from Trieste and *O. smyrnæum* from Smyrna (Jahns, Arch. Pharm. **215**, 1; Gildemeister, *Ibid.* **231**, 182); in oil from the pepperwort or summer savory, *Satureia hortensis*, and the mountain savory, *S. montana* (Jahns, Ber. **15**, 816; Haller, Comp. Rend. **94**, 132; Bull. Soc. [2] **37**, 411); in oil of thyme from *Thymus serpyllum* (Jahns, Arch. Pharm. **216**, 277; Ber. **15**, 819); in oil of wild bergamot from *Monarda fistulosa* (Kremers, Ch. Centr. 1897, **2**, 41; Pharm. Rund. **13**, 207; Melzner and Kremers, Pharm. Rev. **14**, 198; Kremers and Hendricks, Pharm. Arch. **2**, 73), and in the oil from *Pycnanthemum lanceolatum* = *Thymus virginicus* (Correll, Pharm. Rev. **14**, 32; Ch. Centr. 1898, **1**, 123).

Occurs in small quantity in the ethereal oil from the fruit of the Mexican *Schinus molle* (Gildemeister and Stephan, Arch. Pharm. **235**, 582).

According to Duyk carvacrol occurs with thymol in oil of thyme from *T. vulgaris* (Ch. Centr. 1898, **1**, 783; Journ. Pharm. [6] **7**, 190). The oil of *Monarda punctata* (from Wisconsin) probably contains (with thymol) carvacrol (Kremers and Hendricks, Ch. Centr. 1899, **2**, 125; Pharm. Arch. **2**, 73). The oil from the N. American wild mint, *Mentha canadensis*, may contain carvacrol (Gage, Pharm. Rev. **16**, 412).

Carvacrol is among the phenolic con-

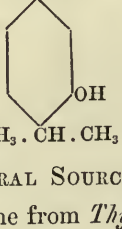
stituents of oil of camphor (Sugiyama; Schimmel's Ber. Oct. 1902; Ch. Centr. 1902, **2**, 1207).

Synthetical Processes.

[A.] From *cymene* [6] by sulphonation (Gerhardt and Cahours, Ann. Chim. [3] **1**, 106; Delalande, *Ibid.* 368; Müller, Ber. **2**, 130; Jacobsen, Ber. **11**, 1060; Claus and Cratz, Ber. **13**, 901; **14**, 2141; Spica, Ber. **14**, 653; Gazz. **11**, 201; Sieveking, Ann. **106**, 260; Beilstein, Ann. **170**, 287; Paternò, Ber. **7**, 591; Gazz. **3**, 544; Kraut, Ann. **192**, 226; Baur, Ann. **220**, 18), and potash fusion of the *a*-(2)-sulphonic acid thus formed (Pott, Ber. **2**, 121; H. Müller, *Ibid.* 130; Jacobsen, Ber. **11**, 1060). Cymene on nitration gives 2-nitrocymene ($CH_3 = 1$) (Barlow, Ann. **98**, 245; Landolph, Ber. **6**, 937; Fittica, Ann. **172**, 314; Schumoff, Journ. Russ. Soc. **19**, 119; Widman, Ber. **19**, 584; Söderbaum and Widman, Ber. **21**, 2126), and 2-aminocymene by reduction (Söderbaum and Widman, *loc. cit.* 2127). The cymidine thus formed yields carvacrol by the diazo-method (Semmler, Ber. **25**, 3353).

[B.] *Carvone* [127] on heating with acids or alkalis gives carvacrol (Völckel, Ann. **85**, 246; Kekulé and Fleischer, Ber. **6**, 1088; Lustig, Ber. **19**, 12; Reychler, Bull. Soc. [3] **7**, 32; Tiemann, Ber. **32**, 109). With formic acid the yield is quantitative (Klages, Ber. **32**, 1516).

67. Thymol; Metacymophenol; 5-Methyl-2-Isopropylphenol; 1 : 4-Methylmethoethyl-3-Phenol.



Natural Sources.

In oil of thyme from *Thymus vulgaris* (Doveri, Ann. Chim. [3] **20**, 174; Ann. **64**, 374: Lallemand, Comp. Rend. **37**, 498; Ann. Chim. [3] **49**, 148; Ann. **102**, 119) and *T. serpyllum* (Jahns, Ber. **15**, 819; Arch. Pharm. **216**, 277); in oil from the seeds of bishop's weed, *Ptychotis ajowan* (Haines, Journ. Ch. Soc. **8**, 289; Stenhouse, Ann. **93**, 269; **98**, 309; H. Müller, Ber. **2**, 130); in oil of American horse-mint, *Monarda punctata* (Arppe, Ann. **58**, 41; Schimmel's Ber. Oct. 1885; Schumann and Kremers, Ch. Centr. 1897, **2**, 42; Pharm. Rev. **1896**, 1); and in oil of Oswego tea from *Monarda didyma* (Flückiger, Arch. Pharm. **212**, 488).

Menthol [41] or peppermint camphor, which occurs in the oil of *Mentha piperita* and other species of *Mentha*, is a hexahydrothymol. The phenols present in the oil of wild bergamot from *Monarda fistulosa* contain less than 2 per cent. of thymol (Kremers, Ch. Centr. 1899, **2**, 126; Pharm. Arch. **2**, 73).

Thymol occurs in the N. American oil of *Cunila mariana* (Millemann, Am. Journ. Pharm. **38**, 495; Schimmel's Ber. Oct. 1893), and (possibly) in the oil of the N. American wild mint, *Mentha canadensis* (Gage, Pharm. Rev. **16**, 412).

The oil from the Japanese *Mosla japonica* contains 44 per cent. thymol (Shimoyama; see Gildemeister and Hoffmann, p. 861).

Oil from the Algerian *Origanum floribundum* = *O. cinereum* contains thymol (Battandier, Journ. Pharm. **16**, 536; Journ. Soc. Ch. Ind. **21**, 1551).

Synthetical Processes.

[A.] From *cumic aldehyde* [116] by nitration, conversion of the nitro-derivative into nitrocymylidene chloride ($C_6H_3 . CHCl_2 . NO_2 . C_3H_7 = 1 : 3 : 4$) by the action of phosphorus pentachloride, reduction to the corresponding 3-aminocymene by zinc and hydrochloric acid, and conversion into thymol by the diazo-method (Widman, Ber. **15**, 166).

[B.] From *menthone* [129] through the dibromo-derivative, the latter giving thymol on heating with quinoline (Beckmann and Eickelberg, Ber. **29**, 418: see also Oddo, Gazz. **27**, 112).

Or menthone gives, among the products of bromination, pentabromdehydrothymol, and this yields thymol by reduc-

tion with zinc dust and hydrochloric acid followed by sodium in alcoholic solution (v. Baeyer and Seuffert, Ber. **34**, 47).

[C.] *Cymene* [6] is brominated and then sulphonated. The bromsulphonic acid on heating with ammonia and zinc dust is debrominated, and the 3-cymenesulphonic acid thus obtained gives thymol on fusion with alkali (Dinesmann, Germ. Pat. 125097 of 1900; Ch. Centr. 1901, **2**, 1030; Eng. Pat. 13745 of 1901; Journ. Soc. Ch. Ind. **20**, 1019).

68. Anethole; Anisstearoptene; Para-anol Methyl Ether; 1^1-Propenyl-4-Anisole.

Natural Sources.

In oil of aniseed from *Pimpinella anisum* (De Saussure, Ann. Chim. [2] **13**, 280; Dumas, Ann. **6**, 245; Blanchet and Sell, *Ibid.* 287; Cahours, *Ibid.* **41**, 56; **56**, 177; Laurent, *Ibid.* **44**, 313; Gerhardt, *Ibid.* 318; **48**, 234; Journ. pr. Ch. [1] **36**, 267), and in oil of star-anise from *Illicium verum* (Cahours, Comp. Rend. **12**, 1213; Ann. **35**, 313; Persoz, Comp. Rend. **13**, 433; Ann. **44**, 311); in Chinese oil of star-anise (Tardy, Bull. Soc. [3] **27**, 990).

In oil of anise-bark from a species of *Illicium* (? *parviflorum*) from Madagascar (Schimmel's Ber. April, 1892); in oil of fennel from *Fœniculum vulgare* (Blanchet and Sell, Ann. **6**, 287; Cahours, Ann. **41**, 74; Journ. pr. Ch. **24**, 359).

In oil of French, Algerian, and Galician bitter fennel (Tardy, Bull. Soc. [3] **17**, 660; **27**, 994); in oil of Japanese fennel (Schimmel's Ber. Oct. 1893; Umney, Pharm. Journ. **57**, 91); in oil of Macedonian fennel and of Indian fennel from *F. panmorium* (Umney, *loc. cit.* **58**, 226).

Anethole has been found in the ethereal oil of *Piper peltatum* (Surie, Ch. Centr. 1899, **1**, 883), and in oil of *Osmorrhiza longistylis* from N. America (Eberhardt, Pharm. Rund. **5**, 149).

Note :—The anethole which Gerhardt believed to exist in oil of tarragon from *Artemisia dracunculus* (Comp. Rend. **19**, 489) has since been shown to be the isomeric methylchavicol = estragol (Schimmel's Ber. April, 1892; Grimaux, Comp. Rend. **117**, 1089; Hell and Gaab, Ber. **29**, 344).

Synthetical Processes.

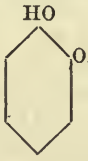
[A.] From *anisic aldehyde* [120] through methylparapropiocoumaric acid by heating the aldehyde with *propionic anhydride* and dry sodium propionate, and distilling the acid thus formed (Perkin, Journ. Ch. Soc. **31**, I, 411).

Or the anisic aldehyde may be heated with sodium propionate and propionic anhydride at 200°, when anethole is directly formed (Moureu and Chauvet, Comp. Rend. **124**, 404; Moureu, Ann. Chim. [7] **15**, 135).

Or from anisic aldehyde and *ethyl alcohol* [14]. The aldehyde and magnesium ethiodide condense to form anethole and a polymeride (Béhal and Tiffeneau, Comp. Rend. **132**, 563: see also Bougault, Bull. Soc. [3] **25**, 1160).

[B.] From *phenol* [60], *propionic acid* [Vol. II], and *methyl alcohol* [13]. Phenol is converted into anisole (see under anisic aldehyde [120; B]), and the latter into p-propionylanisole by treatment with propionyl chloride in presence of aluminium chloride (Gattermann, Ber. **22**, 1129; Klages, Ber. **35**, 2262). Propionylanisole reduces to a carbinol [1-propylol-(1^1)-4-methoxybenzene], of which the acetate gives anethole on boiling with pyridine (Klages, *loc. cit.*).

69. Catechol; Pyrocatechol; Orthodihydroxybenzene; 1 : 2-Phenediol.



Natural Sources.

Said to have been found in various parts of plants, especially in autumnal

foliage (Kraus, N. Rep. Pharm. **22**, 273; Journ. Ch. Soc. **26**, 1049 : Preusse, Bied. Centr. **1879**, 874, denies the existence of free catechol in plants).

Occurs in leaves of the Virginian creeper, *Ampelopsis hederacea* (Gorup-Besanez, Ber. **4**, 905), in sap of the kino plants, *Butea frondosa*, *Eucalyptus resinifera*, *Pterocarpus marsupium*, *P. erinaceus*, &c. (Eisfeldt, Ber. **4**, 906; Flückiger, Ber. **5**, 1; Gorup-Besanez, *Ibid.* 47), in raw beet-sugar (v. Lippmann, Ber. **20**, 3298 : see also Ber. **26**, 3061), and in the dry external scales of the onion.

Catechol has been found in Puglia olive oil (Canzoneri, Gazz. **27**, 3), in the colouring-matter of red grapes (Sostegni, Journ. Ch. Soc. **70**, II, 122), in the aqueous distillate (tar water) from bituminous shale (Germ. Pat. 68944 of 1892; Ber. **35**, 4325 note) and from coal (Börnstein, Ber. **35**, 4324). In these last cases the catechol may be a product of destructive distillation.

A glucoside contained in the tansy, *Tanacetum vulgare*, is a compound of catechol with dextrose and lævulose (Nedra, Journ. Soc. Ch. Ind. **19**, 686).

The catechol complex exists in many products of vegetable origin :—

Quercetin and isomerides from Persian berries (fruit of various species of *Rhamnus*); from the bark of *Quercus tinctoria*; from the fruit, flowers, and leaves of the horse-chestnut; from the berries of the sea-buckthorn (*Hippophaë rhamnoides*); from the flowers of *Reseda luteola*; from *Andromeda japonica*; from *Carya tomentosa*; from the bark of apple; from leaves of the tea plant, vine, and ash; from catechu, hops, and from rutin, a glucoside which is contained in the leaves of rue, *Ruta graveolens*.

Quercetin occurs also in flowers of *Capparis spinosa*, in safflower, in rose leaves, and leaves of buckwheat, *Polygonum fagopyrum*. The colouring-matter sophorin from Chinese berries, from *Sophora japonica*, may contain the quercetin complex in the form of a glucoside.

Note :—Quercetin exists in the above plants sometimes free, but more generally in the form of the glucosides quercitrin, rutin, robinin, &c. According to Schmidt and Waljaschko (Ch. Centr. 1901, 2, 121) the rutin from common rue is not identical with robinin or quercitrin, but resembles the glucoside from capers and from *Viola tricolor* (violaquercitrin ? : see below). For details of distribution of these colouring-matters and glucosides see 'Die Glykoside,' by Van Rijn, 1900, and 'Die Chemie der natürlichen Farbstoffe,' by Hans Rupe, 1900.

Quercetin occurs also as the glucoside osyritrin or myrticolorin in Cape sumach from the leaves of *Colpoon compressum* (A. G. Perkin, Trans. Ch. Soc. **71**, 1132), and in the leaves of *Eucalyptus macrorrhyncha* (Smith, Trans. Ch. Soc. **73**, 697; A. G. Perkin, Proc. Ch. Soc. **18**, 58), and in *Viola tricolor variensis* as the glucoside violaquercitrin (Mandelin, Jahresber. **1883**, 1369 : according to A. G. Perkin, Trans. Ch. Soc. **81**, 477, violaquercitrin, myrticolorin, and osyritrin are identical).

The presence of quercetin in catechu from *Uncaria* (*Nauclea*) *gambier* and *Acacia catechu* (Löwe, Zeit. anal. Ch. **12**, 134) has been confirmed by A. G. Perkin (Trans. Ch. Soc. **71**, 1135), and its existence in the colouring-matters from the yellow wallflower, *Cheiranthus cheiri*, from white hawthorn flowers, *Cratægus oxyacantha*, and from *Rumex obtusifolius*, shown by the same author (*loc. cit.* **69**, 1566; 1570; **71**, 1199).

The yellow colouring-matter of Indian and American podophyllum from *Podophyllum emodi* and *P. peltatum* is quercetin (Dunstan and Henry, *Ibid.* **73**, 221); the dyestuff from the Indian *Delphinium zalil* also contains a glucoside of quercetin (A. G. Perkin and Pilgrim, *Ibid.* 273).

A colouring-matter from the leaves and stem of *Tamaris gallica* and *T. africana* is a methylquercetin (A. G. Perkin and Wood, *Ibid.* 380); the leaves of *Ailanthus glandulosa* contain quercetin (*Ibid.* 382); an isomeride of quercetin exists in colouring-matters from the leaves of *Arctostaphylos uva-ursi* and from S. African 'broach leaves' (*Ibid.* 384; also A. G. P. Proc. Ch. Soc. **14**, 104; **16**, 45; Trans. **77**, 425).

Quercetin is contained in the leaves of *Rhus rhodanthema* from N. S. Wales (A. G. P. Trans. Ch. Soc. **73**, 1018); in common ling or heather,

Calluna vulgaris (*Ibid.* **75**, 837); in logwood, *Hæmatoxylon campeachianum*; in the leaves of *Rhus metopium* and *Coriaria myrtifolia* (*Ibid.* Proc. Ch. Soc. **16**, 45; Trans. **77**, 423); and (or an isomeride) in the New Zealand *Rhus thymifolia* (Easterfield and Aston, Trans. Ch. Soc. **79**, 122).

Quercetin is contained in the ethereal extract of the spotted knotweed, *Polygonum persicaria* (Horst, Ch. Zeit. **25**, 1055).

Rhamnetin, which occurs as a glucoside (xanthorhamnin) in Persian berries, is monomethylquercetin, and rhamnazin, existing also as a glucoside in the same berries, is a quercetin dimethyl ether containing the methylcatechol (guaiacol) complex (A. G. Perkin and Geldard, Trans. Ch. Soc. **67**, 496; A. G. P. and Martin, *Ibid.* **71**, 818; A. G. P. and Allison, *Ibid.* **81**, 469).

Isorhamnetin from the yellow wallflower (see above) is also a methylquercetin (A. G. P. and Hummel, *Ibid.* **69**, 1569). Isorhamnetin is also contained as glucoside in the colouring-matter from the flowers of *Delphinium zalil* (A. G. P. and Pilgrim, *Ibid.* **73**, 271).

The catechol complex is present in fisetin from the wood of *Querbracho colorado* and from young fustic, the wood of *Rhus cotinus*, in which it exists as the glucoside fustin. Luteolin [**141**], the colouring-matter of weld, from *Reseda luteola* and from dyer's broom, *Genista tinctoria*, contains the catechol complex (A. G. P. *Ibid.* **69**, 803; A. G. P. and Newbury, Proc. **15**, 179; 242; **16**, 181; A. G. P. and Horsfall, Trans. **77**, 1314).

A glucoside contained with apiin [**140**] in parsley is a derivative of luteolin methyl ether (Vongerichten, Ber. **33**, 2334; 2904).

Scoparin is related to luteolin (see under luteolin [**141**]: also A. G. P. Proc. Ch. Soc. **15**, 123; **16**, 45).

The catechol complex is probably contained in brazilin from Brazil wood from *Cæsalpinia crista*, *C. brasiliensis*, &c. (Gilbody and W. H. Perkin, junr., *Ibid.* **15**, 28; Feuerstein and v. Kostanecki, Ber. **33**, 1028; Schall, *Ibid.* 1046; Gilbody and W. H. Perkin, junr., Proc. Ch. Soc. **16**, 107; W. H. P., junr., and Yates, Trans. **79**, 1396; W. H. P., junr., Proc.Ch. Soc. **17**, 257; Trans. **81**, 221; 236; 1008; 1040; 1057; Herzig and Pollak, Monats. **23**, 165; v. Kostanecki and Lampe, Ber. **35**, 1667; Bollina, v. Kostanecki, and Tambor, *Ibid.* 1675); and in gossypetin from the flowers of *Gossypium herbaceum* (A. G. Perkin, Trans. Ch. Soc. **75**, 828).

Hæmatoxylin, the colouring-matter of logwood, appears to contain the catechol and pyrogallol complexes (Gilbody and W. H. Perkin, junr., Proc. Ch. Soc. **15**, 241; **16**, 108; W. H. P., junr., and Yates, Trans. **81**, 235, &c., as under brazilin).

The glucoside coniferin, found in the cambial fluid of coniferous trees, in beet and asparagus, and in the root of *Scorzonera hispanica*, contains, through coniferyl alcohol, the guaiacol complex.

The catechol complex is probably contained in maclurin from old fustic, the wood of *Morus tinctoria* = *Maclura aurantiaca* from Jamaica, Cuba, &c. (König and v. Kostanecki, Ber. **27**, 1996), and in fragarianin, a glucoside from the root of *Fragaria vesca*.

The catechol complex may exist also in some form in the catechins, compounds obtained from catechu from various sources, such as the twigs and unripe pods of *Acacia catechu*, from *Uncaria* (*Nauclea*) *gambier*, 'cortex lokri' from *Hymenæa courbaril*, &c. (see for instance A. G. Perkin and Yoshitake, Trans. Ch. Soc. **81**, 1172).

The complex may be contained in kinoïn and kino-red from gum kino from *Pterocarpus marsupium* (Malabar), and in certain resins and gum-resins, such as guaiacum from *G. officinale*, and gum-ammoniac from *Dorema ammoniacum*; also in tormentilla red from the root of *Potentilla tormentilla*, and in many tannins, such as those from horse-chestnut and from *Persea* (*Laurus*) *lingue*, and in fraxitannic acid from ash leaves.

The dimethylcatechol (veratrole) complex is contained in the opium alkaloids,

papaverine and narcotine, in pseudaconitine from the root of *Aconitum ferox*, in berberine from *Berberis vulgaris, Xanthoxylon clava, Hydrastis canadensis*, &c., in hydrastine from *Hydrastis canadensis*, and in corydaline from the roots of *Corydalis* (*Aristolochia*) *cava*.

The colouring-matter of red grapes appears to contain the catechol complex (Sostegni, Gazz. **32**, 17).

The following synthesised natural products contain the catechol, guaiacol, or veratrole complex:—*Isoeugenol* [**79**]; *methylisoeugenol* [**80**]; *methyleugenol* [**81**]; *vanillin* [**121**]; *luteolin* [**141**]; *alizarin* [**145**]; *hystazarin* [**147**]; *protocatechuic acid* [Vol. II]; *veratric acid* [Vol. II]; *piperonylic acid* [Vol. II]; *hydrocaffeïc acid* [Vol. II]; *caffeïc acid* [Vol. II]; *ferulaïc acid* [Vol. II]; *hesperetinic acid* [Vol. II]; *piperic acid* [Vol. II].

Catechol has been found (as a salt of catechol sulphate) in the urine of man and herbivorous animals (Baumann, Pflüger's Arch. **12**, 63; Baumann and Herter, Zeit. physiol. Ch. **1**, 244; Baumann and Preusse, *Ibid.* **3**, 157; Müller, Ber. **7**, 1526; Nencki and Giacosa, Zeit. physiol. Ch. **4**, 335; Schmiedeberg, *Ibid.* **6**, 189).

According to Halliburton (Journ. Physiol. **10**, 247), it is contained in the cerebrospinal fluid. A phenolic substance extracted from the kidneys has been considered to be catechol, but according to O. v. Fürth it is not this compound (Zeit. physiol. Ch. **24**, 142; **26**, 15; **29**, 105).

Synthetical Processes.

[A.] *Phenol* [**60**] by various iodising processes gives (with para-) ortho-iodophenol (Schützenberger and Sengenwald, Comp. Rend. **54**, 197; Körner, Ann. **137**, 197; Hlasiwetz and Weselsky, Sitzungsber. Wien. Akad. **60** [2] 290; Lobanoff, Ber. **6**, 1251; Schall, Ber. **16**, 1897; Willgerodt, Journ. pr. Ch. [2] **37**, 446). The latter on fusion with potash gives catechol (Körner, Zeit. [2] **4**, 322; Lautemann, Ann. **120**, 315; Noelting and Stricker, Ber. **20**, 3019).

Or phenol when chlorinated or brominated at 150–180° gives orthochlor- or bromphenol (Merck, Germ. Pat. 76597 of 1893). These derivatives give catechol on heating with caustic soda-lye under pressure (*Ibid.* Germ. Pat. 84828 of 1893).

Or phenol may be nitrated, the ortho- (separated from the para-) nitrophenol reduced, and the o-aminophenol converted into o-iodophenol by the diazomethod (Noelting and Wrzesinski, Ber. **8**, 820; Noelting and Stricker, Ber. **20**, 3018; Neumann, Ann. **241**, 68).

o-Aminophenol is also converted (partially) into catechol by heating to a high temperature with dilute mineral acids (Meyer, Ber. **30**, 2569).

Or o-nitrophenol can be converted into its methyl ether by methylation (Brunck, Zeit. [2] **3**, 204; Mühlhauser, Ann. **207**, 237; Willgerodt and Ferko, Journ. pr. Ch. [2] **33**, 153), into o-anisidine by reduction (Mühlhauser, *loc. cit.* 239), into guaiacol by the diazomethod (Kalle, Eng. Pat. 7233 of 1897; Journ. Soc. Ch. Ind. **17**, 269), and into catechol as below under **F.**

Or o-aminophenol can be converted into o-chlorphenol by the diazo-method (Schmitt and Cook, Ber. **1**, 67), and the chlorphenol sulphonated (Kramers, Ann. **173**, 331). The 2-chlorphenol-4-sulphonic acid on heating at 250° with caustic soda solution gives catecholsulphonic acid, from which catechol can be obtained by hydrolysis (Soc. Chim. d. Usines du Rhône, Germ. Pat. 97099 of 1896; Ch. Centr. 1898, **2**, 521).

Or *a*-phenoldisulphonic acid gives on fusion with alkali catecholsulphonic acid, from which catechol is obtained by heating with 50 per cent. sulphuric acid to 200° (Merck, Germ. Pat. 80817 of 1893). Or phenoltrisulphonic acid (Senhofer, Ann. **170**, 110; Arche and Eisenmann, Germ. Pat. 51321 of 1889) on fusion with alkali at 230–260° gives catecholdisulphonic acid (Tobias, Germ. Pat. 81210 of 1894), the sodium salt of which yields catechol when the concentrated aqueous solution is heated to 210–215° (*Ibid.* Germ. Pat. 81209 of 1894).

Or phenol may be sulphonated (Kekulé, Zeit. [2] **3**, 199), and the o-sul-

phonic acid fused with alkali (*Ibid.* 643; Degener, Journ. pr. Ch. [2] **20**, 308).

Catechol is among the products of the fusion of phenol with caustic soda (Barth and Schreder, Ber. **12**, 419); and also among the products of the electrolysis of a solution of phenol in presence of magnesium sulphate and acid carbonate by an alternating current (Drechsel, Journ. pr. Ch. [2] **29**, 249). Catechol is among the products of the action of hydrogen peroxide on phenol (Martinon, Bull. Soc. [2] **43**, 156).

[B.] *Salicylic acid* [Vol. II] when iodised by various methods gives, among other products, an iodosalicylic acid, which on rapid heating yields an iodophenol, from which catechol can be obtained as above (Kolbe and Lautemann, Ann. **115**, 157; Lautemann, Ann. **120**, 299; Hlasiwetz and Weselsky, Ber. **5**, 380; Ann. **174**, 99; Liechti, Ann. Suppl. **7**, 129; Demole, Ber. **7**, 1437; Fischer, Ann. **180**, 346; Birnbaum and Reinherz, Ber. **15**, 458; Miller, Trans. Ch. Soc. **41**, 406).

Or salicylic acid may be nitrated (Hübner, Ann. **195**, 6; 31; Schaumann, Ber. **12**, 1346; Deninger, Journ. pr. Ch. [2] **42**, 551; Hirsch, Ber. **33**, 3238), the 3-nitrosalicylic acid reduced, the NH_2-group replaced by iodine by the diazo-method, and the 3-iodosalicylic acid fused with potash so as to form catechol-o-carboxylic acid, which on dry distillation gives catechol (Miller, *loc. cit.*).

[C.] *Benzoic acid* [Vol. II] gives catechol among the products of its fusion with potash (Hlasiwetz and Barth, Ann. **130**, 352; **134**, 282).

[D.] *Protocatechuic acid* [Vol. II] on dry distillation gives catechol (Strecker, Ann. **118**, 285); also by fusion with alkali (Barth and Schreder, Ber. **12**, 1258).

[E.] *Piperonylic acid* [Vol. II] when heated with water at 210° gives catechol (Fittig and Remsen, Ann. **159**, 143).

[F.] *Veratric acid* [Vol. II], when heated with dilute hydrochloric acid, gives a mixture of vanillic (3-methoxy-protocatechuic) acid and the 4-methoxy isomeride (Tiemann, Ber. **8**, 514). Vanillic acid on distillation with lime yields guaiacol (catechol methyl ether) (*Ibid.* 1123), and this, on heating with aqueous hydriodic acid or by the action of aluminium chloride, gives catechol (Müller, Jahresber. **1864**, 525; Gorup, Ann. **143**, 166; Baeyer, Ber. **8**, 153; Tiemann and Koppe, Ber. **14**, 2017; W. H. Perkin, junr., Trans. Ch. Soc. **57**, 587; Hartmann and Gattermann, Ber. **25**, 3532). Or veratric acid on distilling its barium salt with baryta gives veratrole (Merck, Ann. **108**, 60; Koelle, Ann. **159**, 243; Tiemann, Ber. **14**, 2016), which by heating with alcoholic potash at 180–190° yields guaiacol (Bouveault, Bull. Soc. [3] **19**, 75). The latter can be converted into catechol as above.

[G.] *Vanillin* [**121**] on oxidation by moist air gives vanillic acid (Tiemann, Ber. **8**, 1123), which can be converted into guaiacol and catechol as above.

Or vanillin can be converted into acetferulaïc acid, oxidised by potassium permanganate to acetvanillic acid, hydrolysed to vanillic acid (Tiemann, Ber. **9**, 420), and then treated as above.

[H.] *Glycuronic acid* [Vol. II] on long boiling with potash solution gives (with oxalic acid, &c.) catechol (Thierfelder, Zeit. physiol. Ch. **13**, 280).

[I.] *Resorcinol* [**70**] gives catechol among other products when fused with caustic soda (Barth and Schreder, Ber. **12**, 504).

[J.] *Anisic acid* [Vol. II] gives anisole on distillation with baryta (Cahours, Ann. **41**, 69), and this on nitration yields (with p-) o-nitroanisole, and by reduction anisidine (Mühlhäuser, Ann. **207**, 237; 239; Brunck, Zeit. [2] **3**, 205). The latter by the diazo-reaction gives guaiacol (Kalle & Co., Germ. Pat. 95339 of 1896, and under **A** above), from which catechol can be obtained as under **F**.

[K.] *Hydrojuglone* [**90**] gives catechol among the products of its fusion with potash (Mylius, Ber. **18**, 475).

[L.] *Dextrose* [**154**] is said to give catechol among the products formed when heated with water under pressure (Munk, Zeit. physiol. Ch. **1**, 362).

[M.] *Mannose* [**156**] gives (with lactic acid) catechol on boiling with caustic

soda solution (Araki, Zeit. physiol. Ch. **19**, 460).

[N.] *Benzene* [6] when combined with chlorine gives a hexachloride which yields catechol, among other products, when heated with water at 200° (Meunier, Ann. Chim. [6] **10**, 266; Comp. Rend. **100**, 1591).

Or chlorbenzene on nitration gives (with para-) orthochlornitrobenzene (Jungfleisch, Ann. Chim. [4] **15**, 186; Laubenheimer, Ber. **7**, 1765; **8**, 1621; Sokoloff, Zeit. [2] **2**, 621; Lesimple, *Ibid.* [2] **4**, 225), and this by the action of sodium methylate in methyl alcohol yields o-nitroanisole (Lobry de Bruyn, Rec. Tr. Ch. **9**, 200), from which o-anisidine, guaiacol, and catechol can be obtained as under **A** and **F**.

Catechol is among the products of the oxidation of benzene with hydrogen peroxide in the presence of ferrous sulphate (Young, Proc. Ch. Soc. **15**, 131; Cross, Bevan, and Heiberg, Ber. **33**, 2018).

Nitrobenzene gives o-nitrophenol when warmed with finely divided potassium hydroxide. The transformation takes place slowly even at ordinary temperatures (Wohl, Ber. **32**, 3486). Subsequent steps as above under **A**.

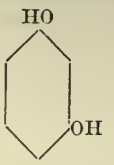
Or nitrobenzene by mild reduction gives phenylhydroxylamine, which oxidises to nitrosobenzene (Bamberger and Storch, Ber. **26**, 472; Bamberger and Landsteiner, *Ibid.* 482; Bamberger, Ber. **27**, 1182; 1273; 1347; 1548; 1555; Wohl, *Ibid.* 1432). The latter gives o-aminophenol among the products of the action of hot aqueous alkali (Bamberger, Ber. **33**, 1939).

Or aniline (by nitration of acetanilide) gives (with p-) o-nitraniline, which reduces to o-phenylenediamine. The latter yields catechol on heating with 10 per cent. hydrochloric acid to 180° (Meyer, Ber. **30**, 2569).

[O.] From *furfural* [126] through pyromucic and mucobromic acids and nitromalonic aldehyde (see under phloroglucinol [86; I]). The latter condenses with *acetoacetic ester* [Vol. II] to form 3-nitrosalicylic acid (Hill, Soch, and Oenslager, Am. Ch. Journ. **24**, 1). Subsequent steps as above under **B**.

[P.] *Caffeïc acid* [Vol. II] decomposes at 200° with the formation of 3 : 4-dihydroxystyrene = vinylcatechol (Kunz-Krause, Ber. **30**, 1618). The latter gives catechol on distillation under reduced pressure (*Ibid.* 1620).

70. Resorcinol; Metadihydroxybenzene; 1 : 3-Phenediol.



Natural Sources.

The compound itself has not yet been found as a natural product, but the complex apparently, with the catechol complex, enters into the constitution of fisetin (for sources of fisetin see under catechol), and also into the constitution of morin, the yellow colouring-matter from old fustic, the wood of *Morus* (*Maclura*) *tinctoria*, and in the Indian dyestuff from jack-fruit, *Artocarpus integrifolia* (A. G. Perkin and Cope, Trans. Ch. Soc. **67**, 937; Bablich and A. G. Perkin, *Ibid.* **69**, 798; A. G. P. and Horsfall, Proc. Ch. Soc. **16**, 182).

The complex exists in the glucoside, lotusin, of the Egyptian vetch, *Lotus arabicus*, through lotoflavin (Dunstan and Henry, Proc. Roy. Soc. **68**, 374).

The resorcinol complex may be considered to exist also in *pæonol* [133], *gentisin* [137], *purpuroxanthin* [146], *methylpurpuroxanthin* [150], *umbelliferone* and *methylumbelliferone* [Vol. II], *euxanthone* [136], and possibly in brazilin from Brazil wood (*Cæsalpinia crista*, *C. brasiliensis*, &c.) and sapan wood (*C. sapan*).

Compounds containing this complex may also exist in many resins and gum-resins, such as galbanum, gum-ammoniac, asafœtida, acaroid, sagapenum, &c. (For references to constitution of brazilin see under catechol [69]; also Herzig, Monats. **16**, 906; **19**, 738; Gilbody and W. H. Perkin, junr., Proc. Ch. Soc. **16**, 105;

Gilbody, W.H. Perkin, junr., and Yates, Trans. Ch. Soc. **79**, 1396.)

Synthetical Processes.

[**A.**] *Benzene* can be converted into resorcinol by various processes :—

By nitration and partial reduction m-dinitrobenzene and m-nitraniline can be obtained (Deville, Ann. Chim. [3] **3**, 187; Muspratt and Hofmann, Ann. **57**, 214; Beilstein and Kurbatoff, Ann. **176**, 43; Anschütz and Heusler, Ber. **19**, 2161; Wülfing, Germ. Pat. 67018 of 1891; Ber. **26**, Ref. 421). The latter gives m-iodonitrobenzene by the diazo-method (Griess, Zeit. [2] **2**, 218), m-iodaniline by reduction (*Ibid.*), and m-iodophenol by the diazo-method (Noelting and Stricker, Ber. **20**, 3020). The latter on fusion with potash gives resorcinol (Körner, Zeit. [2] **4**, 322).

Or m-nitraniline can be converted into m-nitrophenol by the diazo-method (Fittig and Bantlin, Ber. **7**, 179; **11**, 2099; Henriques, Ann. **215**, 323; Wagner, Journ. pr. Ch. [2] **32**, 70), m-aminophenol by reduction (Bantlin, Ber. **11**, 2101), and resorcinol by the diazo-method (*Ibid.*).

Or m-dinitrobenzene can be reduced to m-phenylenediamine, which, on heating with dilute acids to a high temperature, is converted (partially) into resorcinol (Meyer, Ber. **30**, 2569).

Metadinitrobenzene when boiled with potassium cyanide and methyl alcohol is converted into the nitrile of 6-nitro-2-methoxybenzoic acid (Lobry de Bruyn, Rec. Tr. Ch. **2**, 212). The latter on heating with methyl alcohol and potash is converted into the nitrile of 2 : 6-dimethoxybenzoic acid (*Ibid.* 219), which, on heating with strong hydrochloric acid at 170°, splits up into carbon dioxide, methyl chloride, ammonium chloride, and resorcinol. Or by potash fusion the nitrile is converted into 2 : 6-dihydroxybenzoic acid, which splits up into carbon dioxide and resorcinol on heating above 167°.

Or benzene may be nitrated, the mononitrobenzene converted into m-nitrosulphonic acid by fuming sulphuric acid (Limpricht and Bernthsen, Ann. **177**, 82), into m-sulphanilic acid by reduction, and m-aminophenol by fusing the latter with caustic soda (Gesell. f. Ch. Ind., Germ. Pat. 44792 of 1888; Meyer and Sundmacher, Ber. **32**, 2112).

Benzene when sulphonated under appropriate conditions gives p- and m-disulphonic acids, the proportions varying according to the conditions of sulphonation (Buckton and Hofmann, Journ. Ch. Soc. **9**, 255; Barth and Senhofer, Ber. **8**, 754; 1477; **9**, 969; Egli, Ber. **8**, 817; Limpricht, Ber. **9**, 550; Körner and Monselise, *Ibid.* 583; Binschedler and Busch, Monit. Sci. 1878, 1169). Both p- and m-benzenedisulphonic acid (the former by isomeric transformation) give resorcinol on fusion with caustic alkali, this being the technical process (Garrick, Zeit. [2] **5**, 551; Barth and Senhofer, Ber. **8**, 1483; Degener, Journ. pr. Ch. [2] **20**, 319; Genvresse, Bull. Soc. [3] **15**, 409; Fahlberg, Am. Ch. Journ. **2**, 195; Binschedler and Busch, Jahresber. **1878**, 1137 and 1184; Schoop, Zeit. ch. Ind. 1887, II, 1; Mühlhäuser, Ding. Poly. Journ. **263**, 154; Journ. Soc. Ch. Ind. **6**, 284).

[**B.**] From *toluene* (see under benzyl alcohol [**54**; **A**, &c.]) through p-nitrotoluene by nitration, 4-nitrotoluene-2-sulphonic acid by sulphonation (Beilstein and Kuhlberg, Ann. **155**, 8; Jenssen, Ann. **172**, 230), the amino-acid by reduction (B. and K. Ann. **172**, 230; Jenssen, *loc. cit.* 233; Brackett and Hayes, Am. Ch. Journ. **9**, 400), p-cresol-2-sulphonic acid by the diazo-method (Jenssen, *loc. cit.* 237), and 2 : 4-dihydroxybenzoic (2:4-phenediolcarboxylic or β-resorcylic) acid by potash fusion of the cresolsulphonic acid (Ascher, Ann. **161**, 11). β-Resorcylic acid on heating with sodium hydroxide, or *per se*, gives resorcinol (Senhofer, Ber. **12**, 1259).

Or toluene may be converted into the 2 : 4-disulphonic acid by sulphonation (Hakanson, Ber. **5**, 1085; Gnehm and Forrer, Ber. **10**, 542; Gnehm, *ibid.* 1276; Fahlberg, Ber. **12**, 1052; Klason and Berg, Ber. **13**, 1170; Senhofer, Ann. **164**, 126; Klason, Ber. **19**, 2890), the disulphonic acid oxidised to 2 : 4-disulphobenzoic acid (Blomstrand, Ber. **5**,

1088; Brunner, Jahresber. **1879**, 759; Fahlberg, Am. Ch. Journ. **2**, 188), and the latter converted by potash fusion (below 250°) into β-resorcylic acid (Blomstrand, *loc. cit.*; Fahlberg, *loc. cit.* 196), from which resorcinol can be obtained as above.

[C.] From *phenol* [60] through p-bromphenol (Hübner and Brenken, Ber. **6**, 170; Gordon, Proc. Ch. Soc. **7**, 64; Meldola and F. H. Streatfeild, Trans. Ch. Soc. **73**, 681), and fusion with potash (Fittig and Mager, Ber. **7**, 1177; **8**, 362), the resorcinol in this case being formed by isomeric transformation.

Or phenol may be converted into o- and p-nitrophenol by nitration, the latter reduced to p-aminophenol, and the NH_2-group replaced by iodine or chlorine by the diazo-method (Noelting and Stricker, Ber. **20**, 3018; Schmitt, Ber. **1**, 67: for references to direct iodising of phenol see under catechol [69; A]; for direct chlorination of phenol see Petersen and Bähr-Praderi, Ann. **157**, 123; also Dubois, Zeit. [2] **2**, 705; **3**, 205). Both p-chlor- and p-iodophenol give resorcinol (by isomeric transformation) when fused with potash, the latter above 165° (Faust, Ber. **6**, 1022; Noelting and Wrzesinsky, Ber. **8**, 820).

Resorcinol is also among the products of fusion of phenol with caustic soda (Barth and Schreder, Ber. **12**, 420). The phenolsulphonic acids (see under catechol [69; A]) also (by isomeric transformation) give resorcinol when fused with potash (Kekulé, Zeit. [2] **3**, 301).

[D.] *Benzoic acid* [Vol. II] when sulphonated with fuming sulphuric acid in the presence of phosphorus pentoxide gives 3 : 5-disulphobenzoic acid (Barth and Senhofer, Ann. **159**, 217), from which by potash fusion 3 : 5-dihydroxybenzoic (3 : 5-phenediolcarboxylic or α-resorcylic) acid is obtained (*Ibid.* 222). This acid, on heating with sodium hydroxide above 350°, yields resorcinol (Barth and Schreder, Ber. **12**, 1258).

Or benzoic acid may be converted directly or indirectly into m-brombenzoic acid (Peligot, Ann. **28**, 246; Griess, Ann. **117**, 25; Reinecke, Zeit. [2] **1**, 116; **2**, 367; **5**, 109; Hübner, Ohly, and Philipp, Ann. **143**, 233; Hübner and Petermann, Ann. **149**, 131; Angerstein, Ann. **158**, 2 and 5; Friedburg, *Ibid.* 26; Hübner, Ann. **222**, 100), the latter sulphonated by sulphuric anhydride (Hübner and Upmann, Zeit. [2] **6**, 295), the 3-brom-5-sulphobenzoic acid thus formed converted into α-resorcylic acid by potash fusion (Böttinger, Ber. **8**, 374), and then into resorcinol as above.

[E.] *Umbelliferone* [Vol. II] on fusion with potash gives β-resorcylic acid (Tiemann and Reimer, Ber. **12**, 997; Tiemann and Parrisius, Ber. **13**, 2358), and finally resorcinol (Hlasiwetz and Grabowski, Ann. **139**, 99).

[F.] *Ethyl alcohol* [14], *glycerol* [48], and *acetic acid* [Vol. II] furnish the resorcinol complex by the following processes:—

Acetic acid and alcohol give acetic ester, and the latter *acetoacetic ester*. Glycerol on oxidation with nitric acid or other oxidising agents gives glyceric acid (Debus, Phil. Mag. [4] **15**, 195; Ann. **106**, 79; **109**, 227; Sokoloff, Ann. **106**, 95; De la Rue and Müller, Ann. **109**, 122; Beilstein, Ann. **120**, 228; Barth, Ann. **124**, 341; Moldenhauer, Ann. **131**, 324; Mulder, Ber. **9**, 1902; Börnstein, Ber. **18**, 3357; Lewkowitsch, Proc. Ch. Soc. **5**, 14; Wöhlk, Journ. pr. Ch. [2] **61**, 200; Zinno, Monit. Sci. **16**, 493: see also under benzyl alcohol [54; F]). Glyceric acid by the action of phosphorus iodide yields β-iodopropionic acid (Beilstein, Ann. **120**, 226; **122**, 366; Erlenmeyer, Ann. **191**, 284; Rosenthal, Ann. **233**, 16; Meyer, Ber. **19**, 3294; **21**, 24). The ester of β-iodopropionic acid condenses with sodioacetoacetic ester to form acetoglutaric diethyl ester (Wislicenus and Limpach, Ann. **192**, 128), which on heating with hydrochloric acid gives γ-acetobutyric (5-hexanonic) acid (Fittig and Wolff, Ann. **216**, 129; Fittig and Christ, Ann. **268**, 113; W. H. Perkin, junr., Trans. Ch. Soc. **69**, 1510). γ-Acetobutyric ester condenses under the influence of sodium ethoxide to diketohexamethylene or dihydroresorcinol, from which resorcinol can be obtained

by bromination and subsequent removal of hydrogen bromide (Merling, Ann. **278**, 28; Vorländer, Ber. **28**, 2348; Ann. **294**, 269).

Or the glycerol may be converted into allyl bromide and trimethylene bromide (see under n-propyl alcohol [**15**; **E**]). The latter interacts with sodio-acetoacetic ester to form brompropylacetoacetic ester (Lipp, Ber. **18**, 3279), which gives acetylbutyl alcohol on heating with dilute hydrochloric acid (*Ibid.* 3280; Colman and W. H. Perkin, junr., Trans. Ch. Soc. **55**, 354). The alcohol yields γ-acetobutyric acid on oxidation with chromic acid mixture.

Or from ethyl alcohol through iodoform and methylene iodide [**14**; **I**, p. 55] and the action of the latter on sodio-acetoacetic ester, which gives a product (consisting of two methylketohexenylenecarboxylic esters, $C_{10}H_{14}O_3$) which, on boiling with dilute sulphuric acid, yields methyl-1-cyclohexenone-3. The latter on oxidation with alkaline permanganate gives γ-acetobutyric acid (Hagemann, Ber. **26**, 876, &c.; Harries, Ber. **35**, 1176: see also Hagemann and Knoevenagel, Ann. **297**, 138). Subsequent steps as above.

The glycerol in the above synthesis might be replaced by *lactic acid* [Vol. II], which gives acrylic acid (among other products) when the calcium salt is heated (Claus, Ann. **136**, 288: for production of acrylic acid from lactic acid *via* α-chlorpropionic acid see Michael and Garner, Ber. **34**, 4050). Ethyl acrylate condenses with sodio-acetoacetic ester to form acetoglutaric ester (Vorländer, Ber. **28**, 2349), which can be converted into γ-acetobutyric acid, &c., as above.

Or *succinic ac* [Vol. II] gives β-iodopropionic aci by electrolysing the sodium salt with potassium iodide for the negative electrolyte (v. Miller and Hofer, Ber. **28**, 2436). β-Iodopropionic acid and acetoacetic ester give γ-acetobutyric acid and resorcinol as above.

Or the glycerol may be replaced by *acetic aldehyde* [**92**], which on chlorination gives butyrochloral = 2 : 2 : 3-trichlorbutanal (Krämer and Pinner, Ber. **3**, 383; Pinner, Ann. **179**, 26). The latter on heating with potash solution gives an allylene dichloride ($C_3H_4Cl_2$), which on heating with water yields acrylic acid (Pinner, Ber. **7**, 66). Subsequent steps as above.

NOTE :—*Propionic acid* [Vol. II] gives αα- and αβ-dibromo-acid (see under benzyl alcohol [**54**; **O**]). The αβ-acid yields acrylic acid on treating the solution with zinc and sulphuric acid (Caspary and Tollens, Ann. **167**, 241; Melikoff, Journ. Russ. Soc. **13**, 156).

The *propyl alcohols* [**15**; **16**] also give acrylic acid through propylene and *acroleïn* [**101**] (see under benzyl alcohol [**54**; **E**]), and *mannitol* [**51**] gives acroleïn among the products of its oxidation by manganese dioxide and sulphuric acid (**54**; **AA**).

[**G.**] *Euxanthone* [**136**] gives resorcinol among the products of fusion with potash.

[**H.**] From *furfural* [**126**] and *acetone* [**106**] through pyromucic acid, mucobromic acid, and nitromalonic aldehyde (see under phloroglucinol [**86**; **I**]). The latter condenses with acetone in the presence of alkali to form p-nitrophenol (Hill and Torrey, Ber. **28**, 2598; Am. Ch. Journ. **22**, 89). Subsequent steps as above under **C**.

[**I.**] From *malonic* and *citric acids* [Vol. II] and *alcohol* [**14**]. Chloroform [**1**; **D**, &c.] reacts with sodium ethoxide to form orthoformic triethyl ester (Williamson and Kay, Ann. **92**, 346; Stapff, Zeit. [2] **7**, 186; Deutsch, Ber. **12**, 116; Wichelhaus and Ladenburg, Ann. **152**, 164; Arnhold, Ann. **240**, 193). This ester condenses with diethyl malonate (acetic anhydride as condensing agent) to form ethoxymethylenemalonic ester (Claisen, Ber. **26**, 2729). The latter condenses with acetonedicarboxylic ester (from *citric acid*; see under glycerol [**48**; **M**]) under the influence of sodium ethoxide to form acetonedicarboxylmethenylmalonic ester, which undergoes further condensation with the elimination of alcohol and the formation of resorcinoltricarboxylic ester (dihydroxytrimesic ester). The latter on boiling with sodium hydroxide solution gives resorcinoldicarboxylic = β-dihydroxybenzoic acid (Errera, Gazz. **31**, 139; Ch. Centr. 1901, **1**, 1092). The acid yields resorcinol on heating (Senhofer and Brunner, Ber. **13**, Ref. 930).

[J.] From *quinol* [71] through hydroxyquinol by alkaline fusion (Barth and Schreder, Monats. **4**, 176; **5**, 590). Hydroxyquinol (or its carboxylic acid) gives dihydroresorcinol on reduction with sodium amalgam (Thiele and Jaeger, Ber. **34**, 2841). Subsequent treatment as above under **F**.

71. Quinol; Hydroquinone; Paradihydroxybenzene; Pyrogentisic acid; 1 : 4-Phenediol.

Natural Sources.

Occurs to the extent of from 2 to 5 per cent. in the S. African 'sugar bush,' *Protea mellifera* (Hesse, Ann. **290**, 317), and as glucoside (arbutin) in the berries of the red whortleberry, *Vaccinium vitis-idæa*, in leaves of the red bearberry, *Arctostaphylos uva-ursi*, and *A. glauca*, and of *Pyrola umbellata*, *P. rotundifolia*, *P. chlorantha*, *P. elliptica*, *Calluna vulgaris*, *Ledum palustre*, *Epigæa repens*, *Gaultheria procumbens*, and *Chimaphila maculata* (Kawalier, Ann. **82**, 241; **84**, 356; Zwenger and Himmelmann, Ann. **129**, 203; Claassen, Jahresber. **1870**, 877; **1885**, 1761; Schiff, Ann. **206**, 165; Schunck and Marchlewski, Ann. **278**, 354; Maisch, Am. Journ. Pharm. **46**, 319).

Arbutin is decomposed by the moulds *Aspergillus niger*, *A. glaucus*, and *Penicillium glaucum* with the liberation of quinol (Puriewitsch, Ber. deutsch. bot. Gesell. **16**, 368).

The quinol complex is contained in *euxanthone* [136], *gentisin* [137], *homogentisic acid* [Vol. II], *methylarbutin* [159], and (possibly) in saponarin, a glucoside contained in *Saponaria officinalis* (Barger, Ber. **35**, 1296).

Quinol occurs as a constituent of normal urine (Platt, Am. Ch. Journ. **19**, 382).

Synthetical Processes.

[A.] From *phenol* through p-iodophenol by various iodising processes (see under catechol [69; A]), and fusion of the latter with potash at a temperature below 165° (Körner, Zeit. [2] **2**, 662; 731; **4**, 322).

Or from phenol through p-nitrophenol by nitration, p-aminophenol by reduction, and the diazo-reaction with the latter (Weselsky and Schuler, Ber. **9**, 1160).

From phenol by the action of potassium persulphate in alkaline solution (Ch. Fab. vorm. E. Schering, Germ. Pat. 81068 of 1894; Ber. **28**, Ref. 666).

Quinol is among the products of electrolysis of a solution of phenol by an alternating current in presence of magnesium sulphate and acid carbonate (Drechsel, Journ. pr. Ch. [2] **29**, 249), and also among the products of the oxidation of phenol by hydrogen peroxide (Martinon, Bull. Soc. [2] **43**, 156).

From phenol through p-nitrosophenol = quinone-oxime (Bridge, Ann. **277**, 85; Wurster, Ber. **20**, 2632), and the action of hydroxylamine on the latter (Hepp, Ber. **10**, 1654).

From phenol and *carbon tetrachloride* [1; L] through 5-nitrosalicylic and gentisic acids as under euxanthone [136; C]. From gentisic acid as under C below.

[B.] *Quinone* [142] gives quinol on reduction (Wöhler, Ann. **51**, 152). The reduction can be effected by alcohol under the influence of light (Ciamician and Silber, Ber. **33**, 2911; **35**, 3594). Also by isopropyl alcohol and formic acid under similar circumstances (*Ibid.* **34**, 1542). Quinol (and p-diethoxyquinone) is formed by heating quinone with alcohol in the presence of zinc chloride (Knoevenagel and Bückel, Ber. **34**, 3798).

[C.] *Salicylic acid* [Vol. II] can by various processes be iodised or brominated so as to form 5-iodo- or 5-bromsalicylic acid (Gerhardt, Ann. Chim. [3] **7**, 217; Cahours, *Ibid.* **10**, 341; **13**, 99; Henry, Ber. **2**, 275; Lautemann,

Ann. **120**, 302; Demole, Ber. **7**, 1437; Goldberg, Journ. pr. Ch. [2] **19**, 368; Hübner, Ber. **12**, 1347; Birnbaum and Reinherz, Ber. **15**, 458; Hübner and Heinzerling, Zeit. [2] **7**, 709; Hand, Ann. **234**, 133), which on fusion with potash gives 2 : 5-dihydroxybenzoic (5-hydroxysalicylic, gentisic, or 2 : 5-phenediolcarboxylic) acid (Lautemann, *loc. cit.* 311; Liechti, Ann. Suppl. **7**, 144; Demole, *loc. cit.*; Goldberg, *loc. cit.* 371; Miller, Ann. **220**, 124; Rakowski and Leppert, Ber. **8**, 789). The latter on dry distillation yields quinol among other products (Herrmann, Ann. **211**, 336).

Or salicylic acid may be nitrated (Hübner, Ann. **195**, 6; 31; Schiff and Masino, Ann. **198**, 258; Deninger, Journ. pr. Ch. [2] **42**, 550; Hirsch, Ber. **33**, 3238), the 5- (separated from the 3-) nitro-acid reduced to 5-aminosalicylic acid (Beilstein, Ann. **130**, 243; Hübner, Ann. **195**, 18; Schmitt, Jahresber. **1864**, 383), the latter converted into 2 : 5-dihydroxybenzoic (= gentisic) acid by the diazo-method (Goldberg, *loc. cit.* 368), and then into quinol as before.

NOTE :—5-Aminosalicylic acid is best prepared by the reduction of benzeneazosalicylic acid (Fischer and Schaar-Rosenburg, Ber. 32, 81). 5-Nitrosalicylic acid also on heating with lime gives p-nitrophenol, which can be reduced to p-aminophenol and treated as above under **A**. Salicylic acid yields gentisic acid by direct oxidation with potassium persulphate in alkaline solution (Ch. Fab. vorm. Schering, Germ. Pat. 81297 of 1894; Ber. 28, Ref. 692).

[**D.**] *Benzoic acid* [Vol. II] when nitrated gives chiefly m-nitrobenzoic acid (Mulder, Ann. **34**, 297; Gerland, Ann. **91**, 186; Griess, Ann. **166**, 129; Hübner, Ann. **222**, 72; Holleman, Zeit. physik. Ch. **31**, 79). A solution of this acid in sulphuric acid gives 5-aminosalicylic acid on electrolysis (Gattermann, Ber. **26**, 1850), and from this 2 : 5-dihydroxybenzoic acid and quinol can be obtained as above.

m-Nitrobenzoic acid also gives 5-aminosalicylic acid by reduction in strong sulphuric acid with zinc dust at a low temperature (Germ. Pat. 96,853 of 1896; Ch. Centr. 1898, **2**, 160).

Benzoic acid also gives among the products of its nitration some o-nitro-acid (Griess, *loc. cit.* and Ber. **8**, 526; **10**, 1871; Ernst, Jahresber. **1860**, 299; Liebermann, Ber. **10**, 862; Widnmann, Ann. **193**, 204; Holleman, Rec. Tr. Ch. **18**, 267), which by reduction gives *o-aminobenzoic* (*anthranilic*) *acid* [Vol. II] (Beilstein and Kuhlberg, Ann. **163**, 138). The latter by the action of *potassium cyanate* [**172**] on the hydrochloride yields o-uraminobenzoic acid (Griess, Journ. pr. Ch. [2] **5**, 371), and this on nitration gives a dinitro-uraminobenzoic acid (Griess, Ber. **11**, 1730), which on boiling with water yields 5-nitro-2-aminobenzoic acid (*Ibid.*). The latter on heating with potash solution gives 5-nitrosalicylic acid (*Ibid.*), which can be treated as under **B**.

NOTE :—Generators of *anthranilic acid* [Vol. II] thus become generators of quinol.

Or benzoic acid may be brominated (Peligot, Ann. **28**, 246; Angerstein, Ann. **158**, 2; Reinecke, Zeit. [2] **1**, 116; **5**, 109; Hübner, Ohly, and Philipp, Ann. **143**, 233; Hübner and Petermann, Ann. **149**, 131; Angerstein, Ann. **158**, 5) so as to give m-brombenzoic acid. The latter on nitration gives (with the 3-brom-2-nitro-acid) 3-brom-6-nitrobenzoic acid (Hübner, Ohly, and Philipp, *loc. cit.*; Hübner and Petermann, *loc. cit.*), which by reduction yields 6-amino-3-brom- (= 5-brom-2-amino) benzoic acid (H., O., and P. *loc. cit.* 241), from which by the diazo-method 5-bromsalicylic acid can be obtained (Hübner and Emmerling, Zeit. [2] **7**, 709). The latter can be converted into 2 : 5-dihydroxybenzoic (gentisic) acid, &c., as under **C**.

[**E.**] *Cinnamic acid* [Vol. II] on nitration gives a mixture of p- and o-nitro-acids (Beilstein and Kuhlberg, Ann. **163**, 126), from the latter of which o-nitrobenzoic acid can be obtained by oxidation with chromic acid (*Ibid.*; Widnmann, Ber. **8**, 393), o-aminobenzoic acid by reduction, and then as under **C**.

[**F.**] *Benzoic aldehyde* [114] on nitration gives chiefly m-nitro-, but also some o-nitrobenzoic aldehyde (Rudolph, Ber.

13, 310; Fittica, Ber. 10, 1630). The latter can be oxidised to o-nitrobenzoic acid, and then treated as under C.

Or from benzoic aldehyde through toluene by heating with strong hydriodic acid solution at 280° (Berthelot, Jahresber. 1867, 346), o-nitrotoluene by nitration (see under o-cresol [61; A]), o-nitrobenzoic acid by oxidation (Weith, Ber. 7, 1058; Widnmann, Ann. 193, 225; Monnet, Reverdin, and Noelting, Ber. 12, 443; Noyes, Ber. 16, 53), and then as above.

[G.] The *cresols* [61; 62; 63] by distillation with hot zinc dust (Baeyer, Ann. 140, 295; Marasse, Ann. 152, 64), or by heating with phosphorus trisulphide (Kekulé and Fleischer, Ber. 6, 1088; Geuther, Ann. 221, 55), give toluene, from which o-nitrobenzoic acid, &c., can be obtained as above.

[H.] *Benzyl alcohol* [54] heated with hydriodic acid and phosphorus at 140° is reduced to toluene (Graebe, Ber. 8, 1054), which can be treated as above.

NOTE:—All generators of *toluene* (see under benzyl alcohol [54; A, &c.]) thus become generators of quinol.

[I.] *Phenylacetic acid* [Vol. II] when nitrated gives the 2 : 4-dinitro-acid (Radziszewski, Ber. 2, 210; Gabriel and Meyer, Ber. 14, 823), and this by reduction the 2-nitro-4-amino-acid (G. and M. *loc. cit.* 824). The latter, on replacing the NH_2-group by hydrogen by the diazo-method and the simultaneous action of nitrous acid, gives the oxime of o-nitrobenzoic aldehyde (*Ibid.* 826; 15, 3057; 16, 520), from which the nitro-aldehyde can be obtained by oxidation with chromic acid mixture (*Ibid.* 14, 829), and finally o-nitrobenzoic acid by oxidation with potassium permanganate. Subsequent steps as above.

Or the 2 : 4-dinitro-acid in alkaline solution decomposes into 2 : 4-dinitrotoluene (Radziszewski, Ber. 2, 210; 3, 648; Gabriel and Meyer, Ber. 14, 824), which on reduction with ammonium sulphide gives 2-nitro-4-toluidine (Beilstein and Kuhlberg, Ann. 155, 14). The latter by the diazo-method yields o-nitrotoluene, from which o-nitrobenzoic acid can be obtained by oxidation (see above under F).

[J.] *Indigo* [Vol. II] when boiled with aqueous potash gives *o-aminobenzoic* (*anthranilic*) *acid* [Vol. II] (Fritzsche, Ann. 39, 83; Liebig, *Ibid.* 91), which can be converted into quinol as under D.

[K.] *Homogentisic acid* [Vol. II] gives quinol on fusion with potash.

[L.] *Gentisin* [137] when fused with potash gives 2 : 5-dihydroxybenzoic (gentisic) acid (Hlasiwetz and Habermann, Ann. 175, 62; 180, 345; Tiemann and Müller, Ber. 14, 1988), which can be converted into quinol as under B.

[M.] *Euxanthone* [136] gives quinol among the products of fusion with potash (Baeyer, Zeit. [2] 5, 569).

[N.] *Succinic acid* [Vol. II] gives quinol among other products by the dry distillation of its salts (v. Richter, Journ. pr. Ch. [2] 20, 207).

Or succinic acid (ester) by the action of sodium in presence of alcohol or of dry sodium ethoxide can be converted into succinylsuccinic (cyclohexanedione-2 : 5-dicarboxylic-1 : 4) ester (Fehling, Ann. 49, 186; Herrmann, Ber. 10, 107; Ann. 211, 306; Duisberg, Ber. 16, 133; Volhard, *Ibid.* 134; Piutti, Gazz. 20, 167; Vorländer, Ann. 280, 186). The latter on oxidation by air or bromine gives p-dihydroxyterephthalic (quinoldicarboxylic or 2 : 5-phenedioldicarboxylic) ester (Herrmann, *loc. cit.* 111; Ann. 211, 327), and the acid on dry distillation or on fusion with potash yields quinol (*Ibid.* Ber. 10, 112; Ann. 211, 336).

Or succinylsuccinic ester can be converted into dihydroxyterephthalic acid by the action of phosphorus pentachloride (Levy and Curchod, Ber. 22, 2108).

Or from succinic acid through lævulic acid (see under erythritol [50; C]) and then through the dibromo-acid and diacetyl as below under O.

[O.] From *acetoacetic ester* [Vol. II] and its dibromo-derivative by bromination (Duisberg, Ann. 213, 143; Schönbrodt, Ann. 253, 177; Epprecht, Ann. 278, 85). The latter when acted on in dry ethereal solution by sodium gives dihydroxyterephthalic ester (Wedel, Ann. 219, 74).

Or acetoacetic ester can be converted

into methylacetoacetic ester (Geuther, Jahresber. 1865, 303; Isbert, Ann. 234, 188; Roubleff, Ann. 259, 254; Nef, Ann. 266, 90), and the latter converted by the action of nitrous acid into isonitrosomethylethyl ketone = butadioneoxime (Meyer and Züblin, Ber. 11, 322). The latter on decomposition by heating with dilute sulphuric acid gives *diacetyl* [113] (v. Pechmann, Ber. 20, 2539; 2904; 3162; 3213; 21, 1411; 22, 2115; 24, 3954). On heating diacetyl with excess of dilute caustic soda solution it yields p-xyloquinone (*Ibid.* 21, 1420), from which dihydroxyterephthalic acid and quinol can be obtained as below under **R.**

Or diacetyl under the influence of hydrochloric acid gives a trimolecular polymeride, and this yields p-xyloquinol among other products on reduction with sodium amalgam (Diels and Jost, Ber. 35, 3292).

Note :—Generators of *diacetyl* [113] thus become generators of quinol.

Or acetoacetic ester can be converted into acetosuccinic ester by the action of ethyl chloracetate on the sodium compound (Conrad, Ann. 188, 218), and then into β-isonitrosolævulic acid by the action of nitrous acid (Thal, Ber. 25, 1718). The isonitroso-compound gives diacetyl on boiling with dilute sulphuric acid (*Ibid.* 1723), and this can be converted into p-xyloquinone, &c., as above.

Or methylacetoacetic ester can be brominated and the γ-bromo-derivative converted into tetrinic = α-methyltetronic acid by heating with alcoholic potash, or *per se* at 100° (Demarçay, Ann. Chim. [5] 20, 451; Bull. Soc. [2] 33, 518; Pawloff, Ber. 16, 486; Conrad and Kreichgauer, Ber. 29, 1047; Wolff, Ann. 288, 16). Tetrinic acid gives diacetyl on oxidation with nitric acid, potassium permanganate, or with chromic acid (Wolff, Ber. 26, 2220; Ann. 288, 27).

Or from acetoacetic ester through lævulic acid (see under erythritol [50; D]). The latter on bromination gives the β-dibromo-acid (Hell and Kehrer, Ber. 17, 1981; Wolff, Ann. 229, 266), and this on boiling with water yields diacetyl among other products (Wolff, *loc. cit.*; Ber. 26, 2216).

Or from acetoacetic acid and *glycerol* [48] *via* allylacetone (see under erythritol [50; G]), lævulic acid, and diacetyl as above.

Or from acetoacetic ester through the γ-bromo-derivative and succinylsuccinic acid (see under n-propyl alcohol [15; AA]), and then through dihydroxyterephthalic ester, &c., as above.

[P.] *Thymol* [67] can by various processes of oxidation be converted into thymoquinone (Lallemand, Jahresber. 1854, 592; Carstanjen, Journ. pr. Ch. [2] 3, 53; 15, 410; Andresen, Journ. pr. Ch. [2] 23, 172; Armstrong, Ber. 10, 297; Liebermann and Ilinski, Ber. 18, 3194), which easily reduces to *thymoquinol* [82]. The latter on heating with phosphorus oxychloride gives a diphosphoric ester, the potassium salt of which on oxidation with potassium permanganate yields dihydroxyterephthalic acid (Heymann and Königs, Ber. 20, 2393).

[Q.] *Carvacrol* [66] on oxidation also gives thymoquinone (Claus, Journ. pr. Ch. [2] 39, 356; Reychler, Bull. Soc. [3] 7, 32), which can be treated as above.

[R.] From *acetone* [106] through pseudocumene (see under o-cresol [61; B]), nitropseudocumene, and pseudocumidine (5-amino-1 : 2 : 4-trimethylbenzene) by nitration and reduction (Schaper, Zeit. [2] 3, 12). The latter on oxidation gives p-xyloquinone (Noelting and Baumann, Ber. 18, 1151; Sutkowski, Ber. 20, 977), which reduces to p-xyloquinol. The latter is converted by phosphorus oxychloride into a diphosphoric ester of which the potassium salt is oxidised by permanganate to dihydroxyterephthalic acid (Heymann and Königs, Ber. 20, 2396).

Or from acetone and *ethyl acetate* through acetylacetone and lævulic acid (see under erythritol [50; G]). From the latter through *diacetyl* [113] as above under **O.**

Note:—Xylidines derived from the *xylenes* (61, A; 62, A; 63, A) can, by heating their hydrochlorides with methyl alcohol at a high temperature (300–320°), be made to furnish pseudocumidine (Hofmann, Ber. 15, 2895; Noelting and Forel, Ber. 18, 2680).

Also amino- and diamino-p-xylene give xyloquinone on oxidation (Carstanjen, Journ. pr. Ch. [2] 23, 423; Noelting, Witt, and Forel, Ber. 18, 2667; Nietzki, Ann. 215, 168). Generators of the xylenes (see under o-cresol [61; A and B] and p-cresol [63; A and B]) thus become generators of dihydroxyterephthalic acid and quinol.

[S.] From *oxalic* and *acetic acids* [Vol. II] and *alcohol* [14] through ketipic acid (diacetyldicarboxylic or 3 : 4-hexadionediacid) by the action of ethylchloracetate on oxalic diethyl ester in the presence of zinc, and hydrolysis of the ketipic ester formed (Fittig, Daimler, and Keller, Ann. **249**, 183). Ketipic acid on dry distillation or on heating with dilute sulphuric acid gives diacetyl (*Ibid.* 200), which can be converted into p-xyloquinone, &c., as under **N** and **Q**.

Ketipic acid can also be obtained from oxalic and acetic esters in ethereal solution by the action of dry sodium ethylate (Wislicenus, Ber. **20**, 589; Ann. **246**, 328).

[T.] *Benzene* [6], irrespective of the compounds of which it is the generator under the preceding headings (phenol [A], quinone [B], &c.), can be made to furnish quinol directly by electrolysing a solution of the hydrocarbon in alcohol in presence of sulphuric acid (Gattermann and Friedrichs, Ber. **27**, 1942). Or by electrolysis in suspension in sulphuric acid (Kempf, Germ. Pat. 117251 of 1899; Ch. Centr. 1901, **1**, 348).

Quinol is among the products of the oxidation of benzene by hydrogen peroxide in presence of ferrous sulphate (Cross, Bevan, and Heiberg, Ber. **33**, 2018).

Nitrobenzene in strong sulphuric acid solution gives p-aminophenol on electrolysis (Gattermann and Koppert, Ber. **26**, 2810; Noyes and Clement, *Ibid.* 990; Gattermann, *Ibid.* 1844; **27**, 1927), and this can be converted as under **A**.

Or benzene might be converted into nitrobenzene, aniline, acetanilide, p-nitraniline, and p-phenylenediamine. The latter on heating with acids to a high temperature gives quinol (Meyer, Ber. **30**, 2569). Aniline yields quinol (16–18 per cent.) on oxidation with chromic acid mixture (Nietzki, Ber. **10**, 1934).

Nitrobenzene on mild reduction gives phenylhydroxylamine (Bamberger, Ber. **27**, 1347; 1548; Wohl, *Ibid.* 1432), and this on electrolysis in alcoholic sulphuric acid solution (Haber, Zeit. Elektroch. **4**, 506), or by heating with the same solution (Bamberger, Ber. **27**, 1349; Bamberger and Lagutt, Ber. **31**, 1500), yields, among other products, p-aminophenol, which can be converted into quinol as under **A**.

Aniline gives, among other products, p-aminophenol on oxidation with hydrogen peroxide (Prudhomme, Bull. Soc. [3] **7**, 621), or with hypochlorous acid (Bamberger and Tschirner, Ber. **31**, 1522).

Or phenylhydroxylamine can be oxidised to nitrosobenzene, and this gives p-aminophenol among the products of the action of hot aqueous alkali (see under catechol [69; M]).

Aniline on methylation gives dimethylaniline, which by the action of nitrous acid yields the p-nitroso-derivative. The latter on decomposition by alkali gives (with dimethylamine) p-nitrosophenol (Baeyer and Caro, Ber. **7**, 809; 967), which can be treated as under **A**. p-Nitrosophenol is among the products of the action of aqueous alkali at ordinary temperatures on nitrosobenzene (Bamberger, Ber. **33**, 1954).

[U.] From *furfural* [126] and *acetone* [106] through p-nitrophenol (see under resorcinol [70; H]), and then as under **A** above.

[V.] From *lævulose* [155] or *mannose* [156] through lævulic acid (see under erythritol [50; H; I]), and then through diacetyl as above under **O**.

[W.] From *isohexoic acid* [Vol. II] through lævulic acid [50; E], and then as above through diacetyl.

[X.] From *malonic* or *acetic acid* [Vol. II] and *glycerol* [48] through lævulic acid [50; F; G]. Or from glycerol through glyceric acid and pyroracemic acid (see under benzyl alcohol [54; F]), and then as below under **BB**.

[Y.] From *crotonic aldehyde* [102] through lævulic acid [50; O].

[Z.] From *methylheptenone* [111] through lævulic acid [50; Q].

[AA.] From *dimethylheptenol* [35] through lævulic acid [50; N].

[BB.] From *tartaric* or *racemic acid* [Vol. II] through pyroracemic acid (see under benzyl alcohol [54; N]). Potassium pyroracemate gives diacetyl among the products of electrolysis (Hofer and Uhl, Ber. **33**, 653).

[CC.] From *ethyl alcohol* [14] and *hydrogen cyanide* [172] through propionitrile (see under benzyl alcohol [54; I] and acetone [106; S]), αα-dichlorpropionic and pyroracemic acids, and then diacetyl as above.

[DD.] From *acetic* or *acetoacetic acid* [Vol. II] and *hydrogen cyanide* [172] through acetyl cyanide and pyroracemic acid [54; I], and then as above.

[EE.] From *citric acid* [Vol. II] through citraconic or mesaconic acid and pyroracemic acid [54; M] (see also other generators of citraconic acid, p. 63).

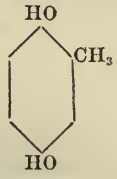
[FF.] From *propionic acid* [Vol. II] through the αα-dibromo-acid and pyroracemic acid [54; O].

[GG.] From *lactic acid* [Vol. II] through pyroracemic acid [54; P].

[HH.] From *normal* or *isopropyl alcohol* [15; 16] through propylene, *acroleïn* [101], acrylic acid, α-chlorlactic acid, glyceric acid, and pyroracemic acid [54; E].

Note:—For generators of propylene see under glycerol [48; B; C; D, &c.].

72. Toluquinol; Hydrotoluquinone; Methylquinol; Paradihydroxytoluene; Methyl-2 : 5-Phenediol.



Natural Source.

The complex is possibly contained in excoecarin, a colouring-matter obtained from green ebony, the wood of *Excoecaria glandulosa* or *Jacaranda ovalifolia* (A. G. Perkin and Briggs, Proc. Ch. Soc. **18**, 11; Trans. **81**, 210).

Synthetical Processes.

[A.] From *toluene* [54; A, &c.] through o-nitrotoluene and o-toluidine. The latter gives toluquinone on oxidation with ferric chloride (Ladenburg, Ber. **10**, 1128), or with sulphuric acid and manganese dioxide (Clark, Am. Ch. Journ. **14**, 565 : see also Schniter, Ber. **20**, 2283; Nietzki, Ann. **215**, 158). Toluquinone is reduced to the hydroquinone by sulphurous acid (Nietzki, *loc. cit.*).

o-Toluidine gives toluquinone on oxidation with chromic acid mixture (Nietzki, Ber. **10**, 1935). Or o-toluidine can be acetylated and nitrated, the nitro-derivative hydrolysed to 5-nitro-2-toluidine (Beilstein and Kuhlberg, Ann. **158**, 345), and the latter reduced to 2 : 5-toluylenediamine, which gives toluquinone on oxidation with sulphuric acid and manganese dioxide (Nietzki, Ber. **10**, 833).

Note:—Both o- and p-nitrotoluene are generators of m-nitrotoluene through the corresponding toluidines and nitrotoluidines (see under vanillin [121; J]). m-Nitrotoluene gives 5-aminocresol by electrolytic reduction in sulphuric acid solution (Gattermann, Ber. 27, 1930) and this yields toluquinol by the diazo-method as below under B. p-Nitrotoluene on mild reduction gives p-toluylhydroxylamine (Bamberger, Ber. 28, 245; 1221; Lumière and Seyewitz, Bull. Soc. [3] 11, 1040), and this on heating with dilute sulphuric acid yields toluquinol (Bamberger, *loc. cit.* 246). p-Toluidine also gives p-toluylhydroxylamine on oxidation by monopersulphuric acid (Bamberger and Tschirner, Ber. 32, 1677).

[B.] From *o-* or *m-cresol* [61; 62] through toluquinone by oxidation with sulphuric acid and manganese dioxide (Carstanjen, Journ. pr. Ch. [2] **23**, 425). Also by oxidation with alkaline potassium persulphate and hydrolysis of the sulphate formed (Ch. Fab. Schering, Germ. Pat. 81068 of 1894; Ber. **28**, Ref. 666).

Or o-cresol on nitration in acetic acid gives (with 3-nitro-) 5-nitrocresol (Hirsch, Ber. **18**, 1512), which reduces to 5-aminocresol (Nevile and Winther, Ber. **15**, 2979). The latter gives toluquinol by the diazo-method (*Ibid.*). Or

o-cresol can be converted into toluquinone-oxime (nitroso-o-cresol) by nitrosylsulphate (Noelting and Kohn, Ber. **17**, 370), and this gives 5-amino-cresol on reduction (*Ibid.*).

73. Quinol Methyl Ether; p-Hydroxyanisole; p-Methoxyphenol.

Natural Source.

Occurs with the glucoside of quinol (arbutin) as the glucoside *methylarbutin* [**159**] (see under quinol [**71**] for botanical sources).

Synthetical Process.

[**A.**] From *quinol* [**71**] and *methyl alcohol* [**13**] by heating the potassium compound of the former with potassium methyl sulphate (Hlasiwetz and Habermann, Ann. **177**, 338), or by heating the potassium compound with methyl iodide diluted with methyl alcohol (Hesse, Ann. **200**, 254).

74. Quinol Ethyl Ether; p-Hydroxyphenetole; p-Ethoxyphenol.

Natural Sources.

Occurs in small quantity in oil of star-anise from *Illicium verum* (Oswald in Beilstein's 'Handb. d. org. Chem.' 3rd ed. II, 939); in Chinese oil of star-anise (Tardy, Bull. Soc. [3] **27**, 990).

Synthetical Processes.

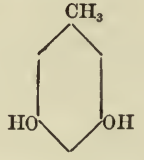
[**A.**] From *quinol* [**71**] and *alcohol* [**14**] by heating the potassium compound of the former with ethyl iodide (Wichelhaus, Ber. **12**, 1501).

[**B.**] From *phenol* [**60**] and *alcohol* [**14**] through the ethyl ether, phenetole (Cahours, Ann. **78**, 226; Kolbe, Journ. pr. Ch. [2] **27**, 424), p-nitrophenetole by nitration (Hallock, Am. Ch. Journ. **1**, 271), phenetidine by reduction (Wagner, Journ. pr. Ch. [2] **27**, 206), and the diazo-reaction with latter (Hantzsch, *Ibid.* **22**, 462). Or phenol can be nitrated, the p-nitrophenol converted into p-nitrophenetole by heating the potassium salt with potassium ethyl sulphate in alcohol (Willgerodt and Ferko, Journ. pr. Ch. [2] **33**, 153), and then into phenetidine, &c., as before.

[**C.**] From *salicylic acid* [Vol. II] and *alcohol* [**14**] through ethyl salicylate (Cahours, Ann. **52**, 332; **74**, 314; Göttig, Ber. **9**, 1473). The latter, according to Baly (Ann. **70**, 269), gives phenetole on distillation with baryta, and this can be treated as under **B**.

[**D.**] *Benzene* [**6**] can be converted into p-nitrophenetole by boiling p-chlornitrobenzene with alcoholic potash (Willgerodt, Ber. **15**, 1002), and this can be converted as under **B**.

75. Orcinol; 3 : 5-Dihydroxytoluene; Methylresorcinol; Methyl-3 : 5-Phenediol.



Natural Sources.

Orcinol does not occur in the free state in the vegetable kingdom, but the complex is contained in certain acids obtained from lichens. *Roccella tinctoria*, *R. fuciformis*, and *R. montagnei* have long been known to yield orcinol. The complex exists in the following compounds:—

Evernic acid from *Evernia prunastri*, var. *vulgaris*, *Ramalina pollinaria* (Stenhouse, Ann. **68**, 84; **155**, 55; Hesse, Ann. **117**, 297; Journ. pr. Ch. [2] **57**, 250; Zopf, Ann. **297**, 300; 306), and *Physcia* (= *Anaptychia*) *ciliaris* (Hesse, Journ. pr. Ch. [2] **58**, 465).

Erythrin = erythric acid from *Roccella montagnei*, *R. peruensis*, and other species; from *Parmelia olivetorum* and *Aspicilia calcarea* (Heeren, Berz. Jahresber. **11**, 279; Kane, Ann. **39**, 25; Schunck, Ann. **61**, 64; Stenhouse, Ann. **68**, 72; Hesse, Ann. **117**, 297; **139**, 22; Journ. pr. Ch. [2] **57**, 232; 256; **62**, 470; Zopf, Ann. **297**, 276; 303; **313**, 342: see also De Luynes, Ann. Chim. [4] **2**, 385; Menschutkin, Bull. Soc. [2] **2**, 424).

β-Erythrin from certain forms of *Roccella fuciformis* contains (through orsellic acid) the orcinol complex (Menschutkin, *loc. cit.*; Lamparter, Ann. **134**, 243).

Divaricatic acid from *Evernia divaricata*, *E. prunastri*, var. *thamnodes*, and *Hæmatomma ventosum* (Zopf, Ann. **297**, 298; **300**, 352; **317**, 137; Hesse, Ber. **30**, 364; Journ. pr. Ch. [2] **57**, 246; **58**, 465; **62**, 439; **65**, 537).

Diffusin from *Platysma diffusum* and *Parmelia sorediata* (Zopf, Ann. **306**, 282; **313**, 317; **317**, 110).

Gyrophoric acid from *Umbilicaria* (*Gyrophora*) *pustulata*, *G. proboscidea*, *G. hirsuta*, *G. deusta*, *G. vellea*, *G. polyphylla*, *G. spodochroa*, var. *depressa*, *Lecanora tartarea* (?), *Blastenia arenaria*, var. *teicholytum*, *Parmelia locarnensis*, and *Lecidea grisella* (Stenhouse, Ann. **70**, 218; Zopf, Ann. **300**, 332; **313**, 322; 326; **317**, 110; Hesse, Journ. pr. Ch. [2] **58**, 475; **62**, 462; 466; 472; **63**, 522).

Glomelliferin from *Parmelia glomellifera* (Zopf, Ann. **306**, 282; **321**, 37).

Lecanoric (= parmelic) acid from *Lecanora parella*, *Evernia prunastri*, *Roccella tinctoria*, *Psora ostreata*, *Parmelia fuliginosa*, var. *ferruginascens*, *P. verruculifera*, *P. borreri*, *P. tiliacea*, var. *scortea*, *P. sorediata*, *P. tinctorum*, *P. perlata* (trace), *P. perforata* (trace), *P. olivetorum*, *P. tinctorum* = *coralloïdes*, *P. glabra* (= *P. olivacea* and *P. glabra*), *P. sordida*, *Urceolaria cretacea*, *U. scruposa*, var. *arenaria*, *Pachnolepia decussata*, and *Pertusaria lactea* (Schunck, Ann. **41**, 158; **54**, 264; Rochleder and Heldt, Ann. **48**, 2; Stenhouse, Ann. **68**, 59; Zopf, Ann. **295**, 278; **306**, 304; 317; 318; 319; **313**, 331; **317**, 110; **321**, 37; Hesse, Journ. pr. Ch. [2] **57**, 264; 409; 411; **58**, 473; 499; 556; **62**, 451; 452; 453; 472; **63**, 533; 550; **65**, 553: Hesse was unable to find this acid in *Lecanora parella*, Schaer = *Ochrolechia pallescens-γ-parella*, and suggests that Schunck must have had some other species in hand).

Patellaric acid from *Urceolaria* (*Patellaria*) *scruposa* (Weigelt, Jahresber. **1869**, 768: see also Hesse, Journ. pr. Ch. [2] **58**, 558; Zopf, Ann. **324**, 39).

Ramalic acid from *Ramalina pollinaria* and many species of *Evernia* (Hesse, Journ. pr. Ch. [2] **57**, 232; 253; Ber. **30**, 364; Zopf, Ann. **297**, 306).

Usnetic = stereocaulic (= lobaric acid) acid from *Usnea barbata*, *Stereocaulon alpinum*, *S. coralloïdes*, *S. pileatum*, *Lepra cholerina*, *Lecanora badia*, *Parmelia saxatilis*, var. *panniformis*, var. *phæotropa*, *P. aleurites*, *P. omphalodes* (Hesse, Ber. **10**, 1326; Journ. pr. Ch. [2] **62**, 445; 459; Zopf, Ann. **288**, 57; **295**, 271; 297; **306**, 300; 314: see also Salkowski, Ann. **319**, 391).

Umbilicaric acid from *Gyrophora polyphylla*, *G. deusta*, *G. hyperborea* (Zopf, Ann. **300**, 337; **317**, 139; Hesse, Journ. pr. Ch. [2] **63**, 545).

Orcinol can be liberated from the lichen acids which contain the complex by the action of micro-organisms (Czapek, Ch. Centr. 1898, **1**, 684, from Centr. Bakter. II, **4**, 49).

The dimethylorcinol complex may be contained in podophyllotoxin from the Indian *Podophyllum emodi* and the American *P. peltatum* (Dunstan and Henry, Trans. Ch. Soc. **73**, 223).

Synthetical Processes.

[A.] From *toluene* [**54**; **A**, &c.] through p-chlortoluene. The latter on sulphonation gives (with the 2-sulphonic acid) p-chlor-3-sulphonic acid (Vogt and Henninger, Ann. **165**, 362; Wynne, Trans. Ch. Soc. **61**, 1078), which on fusion with potash yields orcinol among other products (V. and H. *loc. cit.* 366; Bull. Soc. [2] **21**, 373). There must be isomeric transformation in this case.

Or toluene may be nitrated, the o-nitrotoluene reduced to o-toluidine, the latter sulphonated (Gerver, Ann. **169**, 374; Pagel, Ann. **176**, 292; Nevile and Winther, Trans. Ch. Soc. **37**, 626; Ber. **13**, 1941), the 2-toluidine-5-sulphonic acid brominated, and thus converted into 3-brom-2-toluidine-5-sulphonic acid (N. and W. Ber. **13**, 1942). The latter on replacing the NH_2-group by hydrogen by the diazo-method gives 3-bromtoluene-5-sulphonic acid (*Ibid.* 1944), from which orcinol can be obtained by potash fusion (*Ibid.* Ber. **15**, 2990).

Or 2-toluidine-5-sulphonic acid may be converted into 2-toluidine-3 : 5-disulphonic acid by further sulphonation (*Ibid.* 2992; Hasse, Ann. **230**, 288), the disulphonic acid into toluene-3 : 5-disulphonic acid by replacing the NH_2-group by hydrogen (Limpricht and Hasse, Ber. **18**, 2177; Ann. **230**, 295; Nevile and Winther, Ber. **15**, 2992), and the disulphonic acid into orcinol by potash fusion (N. and W. *loc. cit.* 2993).

Or o-toluidine may be converted into 3 : 5-dibrom-2-toluidine by bromination (Wroblewski, Ann. **168**, 162), into 3 : 5-dibromtoluene by replacing the NH_2-group by hydrogen (N. and W. Ber. **13**, 966), and the dibromtoluene into orcinol by potash fusion (*Ibid.* **15**, 2992).

Toluene may also be nitrated, the p-nitrotoluene reduced, the p-toluidine converted into 3 : 5-dibrom-4-toluidine by bromination (Wroblewski, Ann. **168**, 188), the NH_2-group replaced by hydrogen (*Ibid.*), and the 3 : 5-dibromtoluene converted into orcinol as above.

Or p-toluidine may be converted into 3 : 5-dinitro-4-toluidine by nitration and hydrolysis of the acetyl- or benzoyl-derivative (Beilstein and Kuhlberg, Ann. **158**, 341; Hübner, Ann. **208**, 312; **222**, 74), the NH_2-group replaced by hydrogen (Städel, Ber. **14**, 901; Ann. **217**, 189; Hübner, Ann. **222**, 74; Nevile and Winther, Ber. **15**, 2984; Hönig, Ber. **20**, 2418), the 3 : 5-dinitrotoluene reduced by ammonium sulphide to 5-nitro-3-toluidine (Städel, Ann. **217**, 189; N. and W. *loc. cit.* 2985), and the latter converted into 5-nitro-3-cresol by the diazo-method (N. and W. *loc. cit.* 2986). The nitrocresol on reduction and replacement of the NH_2-group by hydroxyl by the diazo-method gives orcinol (*Ibid.* 2987).

p-Acettoluide may also be brominated and then nitrated, or nitrated and then brominated so as to give on hydrolysis 3-brom-5-nitro-4-toluidine (Wroblewski, Ann. **192**, 202; N. and W. Ber. **13**, 968). The latter on replacement of the NH_2-group by hydrogen gives 3-brom-5-nitrotoluene, and by reduction 5-brom-3-toluidine, from which, by the diazo-method, 5-brom-3-cresol can be obtained, and this also gives orcinol on fusion with potash (N. and W. Ber. **15**, 2991 : see also Nevile, Eng. Pat. 4389 of 1881).

[B.] *Paracresol* [**63**] when the ethyl ether is nitrated is converted into the 3 : 5-dinitro-p-cresol ether (Städel, Ann. **217**, 161). Or p-cresol may be nitrated (Frische, Ann. **224**, 139 : see also Armstrong and Field, Ber. **6**, 974), and converted into the dinitro-ether by the action of ethyl iodide on the silver salt (Noelting and Salis, Ber. **15**, 1859). The dinitro-ether on treatment with alcoholic ammonia is converted into 3 : 5-dinitro-4-toluidine (Städel, *loc. cit.* 186), from which 3 : 5-dinitrotoluene, 5-nitro-3-toluidine, 5-nitro-3-cresol, 5-amino-3-cresol and orcinol can be obtained as under **A.**

[C.] *Citric acid* [Vol. II] when heated with sulphuric acid gives acetonedicarboxylic (β-ketoglutaric or 3-pentanonedicarboxylic) acid (v. Pechmann, Ber. **17**, 2543; **18**, 2289; **19**, 1446, 2465; 2694; **20**, 145; **24**, 857; 3250; 4095; Ann. **261**, 151; v. P. and Neger, Ann. **273**, 186; Henry and v. P. Ber. **26**, 997; also Germ. Pat. 32245 of 1884). The diethyl ester of this acid by the action of sodium gives dihydroxyphenyltricarboxylic triethyl ester (Cornelius and v. P. Ber. **19**, 1448; v. P. and Wolman, Ber. **31**, 2014), and the latter on hydrolysis by alcoholic potash gives s-dihydroxyphenylacetic (3 : 5-phenediolethylic) acid (C. and v. P. *loc. cit.* 1449), the silver salt of which yields orcinol on dry distillation (*Ibid.* 1451).

The dihydroxyphenyltricarboxylic ester (ethyl orcinoltricarboxylate) is also obtained (with a 'lactone') by the action of sodium ethoxide on an alcoholic solution of acetonedicarboxylic ester (Jerdan, Proc. Ch. Soc. **15**, 151; Trans. **75**, 808). Methyl acetonedicarboxylate undergoes condensation to an orcinol derivative more readily than the ethyl ester (Dootson, Trans. Ch. Soc. **77**, 1196).

NOTE :—Citric acid gives acetonedicarboxylic acid when oxidised by potassium permanganate at 30–35° (Denigès, Comp. Rend. **130**, 32; Ann. Chim. [7] **18**, 413).

Citric acid can also be converted into dehydracetic acid by the action of acetic anhydride on acetonedicarboxylic acid (v. Pechmann, Ber. **24**, 3600). Dehydracetic acid can be converted into orcinol as below under **D**.

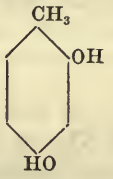
[**D.**] *Acetoacetic ester* [Vol. II] on chlorination gives (with α-) γ-chloroacetoacetic ester (Haller and Held, Comp. Rend. **108**, 516; **111**, 647; **114**, 400, 452; Ann. Chim. [6] **23**, 157: see also Genvresse, Comp. Rend. **107**, 687; Ann. Chim. [6] **24**, 46; Hantzsch, Ber. **23**, 2339; Hantzsch and Schiffer, Ber. **25**, 728); the corresponding γ-cyanacetoacetic ester obtained by the action of *potassium cyanide* [**172**] on the chloro-ester gives, on hydrolysis with hydrochloric acid and alcohol, acetonedicarboxylic ester (Haller and Held, Comp. Rend. **111**, 682), which can be converted into orcinol as above under **C**.

Or acetoacetic ester can, by the action of heat, be converted into dehydracetic acid (Geuther, Zeit. [2] **4**, 655; Oppenheim and Precht, Ber. **9**, 324; W. H. Perkin, junr., Trans. Ch. Soc. **51**, 489), and the latter gives orcinol on heating with baryta water or (better) with syrupy caustic soda solution at 150° (Oppenheim and Precht, *loc. cit.*; Collie, Trans. Ch. Soc. **59**, 183; Collie and Myers, *Ibid.* **63**, 124).

Dehydracetic acid is formed also by the action of pyridine on acetyl chloride (Dennstedt and Zimmermann, Ber. **19**, 76), or of triethylamine or ferric chloride on acetyl chloride (Wedekind, Ch. Centr. 1900, **2**, 561; Ann. **323**, 246).

[**E.**] From *malonic acid* [Vol. II] through acetonetricarboxylic and dicarboxylic acid (see under phloroglucinol [**86**; **E**]), and then as above under **C**.

76. Cresorcinol; 2 : 4-Dihydroxytoluene; Methyl-2 : 4-Phenediol.



NATURAL SOURCE.

The cresorcinol complex probably exists in cyanomaclurin, which occurs with morin in the wood of *Artocarpus integrifolia* from India and Java (A. G. Perkin and Cope, Trans. Ch. Soc. **67**, 939).

SYNTHETICAL PROCESSES.

[**A.**] From *toluene* [**54**; **A**, &c.] through p-toluidine, 2-nitro-4-toluidine by nitration (Noelting and Collin, Ber. **17**, 263), 2-nitro-4-cresol by the diazo-method (Neville and Winther, Ber. **15**, 2980; Knecht, Ann. **215**, 87), 2-amino-4-cresol by reduction (Knecht, *loc. cit.* 91; Wallach, Ber. **15**, 2833), and the diazo-reaction with the latter (Knecht, *loc. cit.* 92).

Or directly from toluene through the 2 : 4-disulphonic acid (Hakanson, Ber. **5**, 1085; Gnehm and Forrer, Ber. **10**, 542; 1276; Claesson and Berg, Ber. **13**, 1170; Fahlberg, Ber. **12**, 1052; Senhofer, Ann. **164**, 126; Klason, Ber. **19**, 2890), and fusion with potash (Hakanson, *loc. cit.* 1087; Noelting, Ber. **19**, 136).

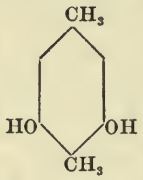
Or from o-toluidine through 4-nitro-2-toluidine by nitration (Noelting and Collin, *loc. cit.* 265), 4-nitro-2-cresol by the diazo-method (nitroindazole is simultaneously formed: Noelting and Collin, *loc. cit.* 269; Witt, Noelting, and Grandmougin, Ber. **23**, 3636; Michel and Grandmougin, Ber. **26**, 2351), 4-amino-2-cresol by reduction (Noelting and Collin, Ber. **17**, 270), and the diazo-reaction with the latter (Wallach, Ber. **15**, 2835).

The two nitrotoluidines required for

this synthesis are also obtainable from 2 : 4-dinitrotoluene by partial reduction (Beilstein and Kuhlberg, Ann. **155**, 14; Graeff, Ann. **229**, 343; Anschütz and Heusler, Ber. **19**, 2161); or the 2 : 4-toluylenediamine may be monacetylated, converted into 4-acetamino-2-cresol by the diazo-method, hydrolysed, and the 4-amino-2-cresol converted into cresorcinol as before (Wallach, Ber. **15**, 2832 and 2835).

[B.] From *resorcinol* [70] and *carbon disulphide* [160]. A mixture of these compounds on heating in presence of potassium sulphide solution gives resorcinoldithiocarbonic acid. The latter on reduction with zinc dust and acetic acid gives cresorcinol (Schall, Journ. pr. Ch. [2] **54**, 415).

77. β-Orcinol; 3 : 5-Dihydroxy-p-xylene; p-Xylorcin; 1 : 4-Dimethyl-3 : 5-Phenediol.



Natural Sources.

The β-orcinol complex is contained in β-erythrin from the lichen *Roccella fuciformis*, in barbatic acid from the lichen *Usnea barbata*, and in β-usnic or cladonic acid from the lichen *Cladonia rangiferina*. (For occurrence of β-erythrin, which yields β-orcinol through picroerythrin, see under orcinol [75]; for barbatic acid, Stenhouse and Groves, Ann. **203**, 302; for β-usnic = cladonic acid, Stenhouse, Ann. **68**, 98; **155**, 58; Hesse, Ann. **117**, 346: cladonic acid may be a mixture of usnic and barbatic acids, Paternò, Gazz. **6**, 113; **12**, 231; Stenhouse, *loc. cit.* 285: for barbatic acid in various species of *Usnea* see Hesse, Ber. **30**, 357: according to the latter author cladonic acid is a mixture of usnic and atronoric acids: for barbatic acid in *Usnea longissima* see Zopf, Ann. **297**, 293; Hesse, Journ. pr. Ch. [2] **57**, 239; in *Alectoria ochroleuca*, Zopf, Ann. **306**, 298; in *Usnea barbata* β-*hirta*, Hesse, *loc. cit.* **65**, 537; in *Usnea ceratina* and *U. dasypoga* (?), Zopf, Ann. **324**, 39).

Atranorin = atranoric acid, which is contained in a large number of lichens (for occurrence see under methyl alcohol [13]); and ceratophyllin = atraric acid = physcianin, which is a decomposition product of atranorin, also contain the β-orcinol complex (Hesse, Ber. **30**, 1988).

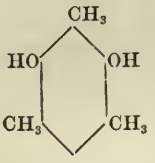
The complex is contained in rhizonic and rhizoninic acids from *Rhizocarpon geographicum*, var. *contiguum* (*Ibid.* **31**, 664; Journ. pr. Ch. [2] **58**, 527).

Coccellic acid from *Cladonia coccifera*, *C. amauracræa*, and *C. floerkeana* = *C. bacillaris*, contains the rhizoninic and therefore the β-orcinol complex (*Ibid.* Ann. **284**, 107; Journ. pr. Ch. [2] **57**, 274; **58**, 472; **62**, 447; Zopf, Ann. **300**, 330).

Synthetical Process.

[A.] From *toluene* [54; A, &c.] and *p-xylene* (see under metacresol [62; A]). The xylene on nitration gives (with other isomerides) 3 : 5-dinitro-p-xylene, which by reduction with nascent ammonium sulphide yields 5-nitro-3-amino-p-xylene = m-nitro-p-xylidine (Fittig, Ahrens, and Mattheides, Ann. **147**, 22). The latter by the diazo-method gives 5-nitro-p-xylenol-3 (Kostanecki, Ber. **19**, 2320), the corresponding amino-xylenol by reduction with tin and hydrochloric acid, and β-orcinol by the diazo-method (*Ibid.* 2321).

78. Mesorcinol; 1 : 3 : 5-Trimethyl-2 : 6-Phenediol.



Natural Source.

Coccellic acid from the lichens *Cladonia coccifera*, &c. (see under β-orcinol [77]), hydrolyses to rhizonic and coccel-

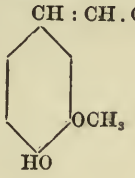
linic acids. The latter may be a mesorcinol derivative (Hesse, Journ. pr. Ch. [2] **62**, 447).

Synthetical Process.

[A.] From *mesitylene* (see under benzyl alcohol [**54**; **D**; **E**; **F**; **G**; **H**, &c.]), which on nitration gives a dinitro-derivative, and this by mild reduction nitromesidine (Fittig, Ann. **141**, 133; Maule, Ann. **71**, 137; Knecht, Ann. **215**, 98; Klobbie, Rec. Tr. Ch. **6**, 32; Küster and Stallberg, Ann. **278**, 214). Nitromesidine gives by the diazo-method nitromesitol, and the latter aminomesitol by reduction (Knecht, *loc. cit.*). Aminomesitol by the diazo-method gives mesorcinol (Knecht, Ann. **215**, 100).

Note:—For production of nitromesidine from mononitromesitylene and mesidine see papers by Fittig, Ann. **141**, 132; Fittig and Storer, Ann. **147**, 2; Schultz, Ber. **17**, 477; Ladenburg, Ann. **179**, 165; Biedermann and Ledoux, Ber. **8**, 58; Noelting and Stoeckling, Ber. **24**, 570).

79. Isoeugenol; 1[1]-Propenyl-3 : 4-Phenediol 3-Methyl Ether.



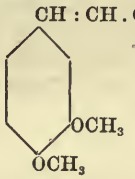
Natural Source.

In ylang-ylang oil (Schimmel's Ber. Oct. 1901; Ch. Centr. 1901, **2**, 1007).

Synthetical Process.

[A.] From *vanillin* [**121**] and *propionic acid* [Vol. II]. Vanillin is converted into propionylhomoferulaïc acid by heating with propionic anhydride and sodium propionate (Tiemann and Kraaz, Ber. **15**, 2060). Homoferulaïc acid obtained from the propionyl compound by hydrolysis gives isoeugenol on heating with lime (*Ibid.* 2063). Or from vanillin and *ethyl alcohol* [**14**] by the interaction of the aldehyde and magnesium ethiodide (Béhal and Tiffeneau, Comp. Rend. **132**, 563).

80. Methylisoeugenol; Isoeugenol Methyl Ether; 1[1]-Propenyl-3 : 4-Phenediol Dimethyl Ether.



Natural Source.

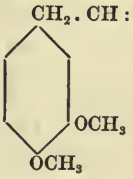
A constituent of the oil of *Asarum arifolium* (Miller, Arch. Pharm. **240**, 371; Ch. Centr. 1902, **2**, 642).

Synthetical Process.

[A.] From *isoeugenol* [**79**] and *methyl alcohol* [**13**] by methylation of the phenol with methyl iodide and alcoholic potash (Ciamician and Silber, Ber. **23**, 1164).

Note:—The synthetical product was obtained from eugenol, but this undergoes isomeric transformation into isoeugenol under the influence of the alcoholic potash.

81. Methyleugenol; 3 : 4-Dimethoxyallylbenzene; 1[2]-Propenyl-3 : 4-Phenediol Dimethyl Ether.



Natural Sources.

In oil of paracoto bark, Bolivia (Wallach and Rheindorff, Ann. **271**, 300); in oil from the root of *Asarum europæum* (Petersen, Arch. Pharm. **226**, 89; Ber. **21**, 1057 : compare Mittmann, Arch. Pharm. **227**, 543, who suggests methylisoeugenol), and *A. canadense* (Power, Pharm. Rund. **6**, 101; Proc. Am. Pharm. Assoc. **28**, 464; Power and Lees, Proc. Ch. Soc. **17**, 210; Trans. **81**, 67). Also in oil of bay

from *Myrcia* (*Eugenia*) *acris*, W. Indies (Mittmann, Arch. Pharm. **227**, 529).

Occurs also in the oil from the 'clove bark' of Amboyna from *Cinnamomum culilawan* (Gildemeister and Stephan, Arch. Pharm. **235**, 582), and in certain oils of lemon poor in geraniol (Schimmel's Ber. Oct. 1898; Ch. Centr. 1898, **2**, 985). Methyleugenol probably occurs in matico oil from the leaves of *Piper angustifolium* (*Ibid.*).

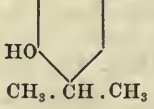
The betelphenol or chavibetol of the ethereal oil of *Piper betle* (Bertram and Gildemeister, Journ. pr. Ch. [2] **39**, 349) is possibly identical with this methyleugenol. Occurs in Ceylon 'Lana Batu' and in Java citronella oils (Schimmel's Ber. Oct. 1899; Ch. Centr. 1899, **2**, 880; Journ. Soc. Ch. Ind. **19**, 556).

Methyleugenol is a constituent of the oil of *Asarum arifolium* (Miller, Arch. Pharm. **240**, 371; Ch. Centr. 1902, **2**, 642).

Synthetical Process.

[A.] From *catechol* [69], *glycerol* [48], and *methyl alcohol* [13]. Catechol is by methylation converted into veratrole (Béhal and Choay, Bull. Soc. [3] **9**, 142; Gorup, Ann. **147**, 248; Marasse, Ann. **152**, 74). Glycerol is converted into allyl iodide by distilling with iodine and phosphorus (for references see under isobutyl alcohol [18; D]), and veratrole when heated with allyl iodide and zinc gives methyleugenol (Moureu, Comp. Rend. **121**, 721).

82. Thymoquinol; Hydrothymoquinone; 1 : 4-Methylmethoethyl-2 : 5-Phenediol.



Natural Sources.

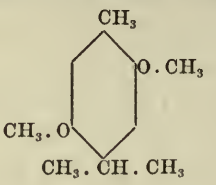
In oil of wild bergamot from *Monarda fistulosa* (Brandel and Kremers, Pharm. Rev. **19**, 200; 244), and probably in Algerian oil of bitter fennel (Tardy, Bull. Soc. [3] **27**, 994).

Synthetical Processes.

[A.] From *thymol* [67] through thymoquinone and reduction of latter (see below under the dimethyl ether [83; A]).

[B.] From *carvacrol* [66] through thymoquinone, &c. [83; B].

83. Dimethylthymoquinol; Thymoquinol Dimethyl Ether; 1 : 4-Methylmethoethyl-2 : 5-Phenediol Dimethyl Ether.



Natural Source.

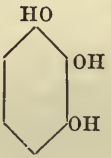
Occurs with phloryl isobutyrate in oil of arnica root from *Arnica montana* (Sigel, Ann. **170**, 363).

Synthetical Processes.

[A.] *Thymol* and derivatives [67] on oxidation give thymoquinone (Lallemand, Jahresber. **1854**, 592; Paternò, Ber. **8**, 440; Steiner, Ber. **11**, 289; Andresen, Journ. pr. Ch. [2] **23**, 172; Bayrac, Bull. Soc. [3] **7**, 99; Armstrong, Ber. **10**, 297; Liebermann and Ilinski, Ber. **18**, 3194), and this on reduction gives thymoquinol (Carstanjen, Journ. pr. Ch. [2] **3**, 54; Lallemand, Comp. Rend. **37**, 498; Ann. **101**, 121). The dimethyl ether should be obtainable by methylation, but the identity of the natural product with the synthetical ether remains to be established.

[B.] *Carvacrol* [66] on oxidation also gives thymoquinone (Carstanjen, *loc. cit.* **15**, 410; Claus, Journ. pr. Ch. [2] **39**, 356; Reychler, Bull. Soc. [3] **7**, 32). Subsequent steps as above.

84. Pyrogallol; Pyrogallic Acid; 1 : 2 : 3-Phenetriol.



Natural Sources.

The pyrogallol complex exists in *gallic acid* [Vol. II], and in myricetin from the bark of the box-myrtle, *Myrica nagi* = *M. sapida* = *M. integrifolia* = *M. rubra*, &c., from India, China, Singapore, and Japan (A. G. Perkin and Hummel, Trans. Ch. Soc. **69**, 1293; A. G. P. and Clifford, *Ibid.* **81**, 203).

Myricetin is contained also in Sicilian sumach from *Rhus coriaria* (A. G. P. and Allen, *Ibid.* 1302), in the colouring-matter from the leaves of *Pistacia lentiscus*, in 'gambruzzo' from the stalk of *Rhus coriaria*, and in the galls of *Pistacia terebinthus* (A. G. P. and Wood, Proc. Ch. Soc. **14**, 104; Trans. **73**, 374 *et seq.*). Myricetin is present in Venetian sumach from the leaves of *Rhus cotinus* (A. G. P. Trans. Ch. Soc. **73**, 1017), in the leaves of *Rhus metopium*, *Myrica gale*, and (probably) of logwood, *Hæmatoxylon campeachianum* (*Ibid.* Proc. **16**, 45; Trans. **77**, 426). A rhamnoside of myricetin is contained in the bark of *Myrica nagi* (*Ibid.* Proc. **18**, 11).

The pyrogallol complex is probably contained in hæmatoxylin from logwood (see under catechol [69]).

Mezcalin, one of the cactus alkaloids from *Echinocactus lewinii*, probably contains the pyrogallol complex (Heffter, Ber. **34**, 3009).

The dimethyl- (methyl) pyrocatechol complex exists in iridin, a glucoside found in the orris-root from *Iris florentina* from Macedonia, coasts of Black Sea, and Asia Minor (G. de Laire and Tiemann, Ber. **26**, 2011).

Sinalbin, a glucoside which occurs in the seed of white mustard [171], contains the sinapic acid complex, and the latter is a derivative of dimethylpyrogallol (Gadamer, Arch. Pharm. **235**, 570; Ch. Centr. 1898, **1**, 500; Ber. **30**, 2330).

Syringin, a glucoside found in the bark of *Syringa vulgaris*, *Ligustrum vulgare*, and *Robinia pseudacacia*, also contains (through syringenin) the same complex.

The alkaloid narcotine from opium contains the methyl-methylene-pyrogallol complex. Anthragallol [148] dimethyl ether contains the dimethyl-pyrogallol complex. The pyrogallol complex is possibly contained in kinoïn from Malabar kino from *Pterocarpus marsupium*.

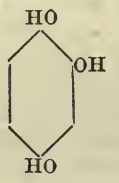
Synthetical Processes.

[A.] From *phenol* [60] through p-chlorphenol by various chlorinating processes (Dubois, Zeit. [2] **2**, 705; **3**, 205; Schmitt and Cook, Ber. **1**, 67; Petersen and Bähr-Praderi, Ann. **157**, 123), α- and β-p-chlorphenolsulphonic acid by sulphonation (Petersen and Bähr-Praderi, *loc. cit.* 128), and potash fusion of either sulphonic acid (*Ibid.* 136).

[B.] *Salicylic acid* [Vol. II] can by various iodising processes be converted into 3 : 5-diiodosalicylic acid (Lautemann, Ann. **120**, 304; Liechti, Ann. Suppl. **7**, 141; Demole, Ber. **7**, 1439; Weselsky, Ann. **174**, 103; Birnbaum and Reinherz, Ber. **15**, 459). According to Lautemann (*loc. cit.* 317), this diiodosalicylic acid when heated with aqueous potash gives pyrogallol (? by isomeric change).

[C.] *Gallic acid* [Vol. II] gives pyrogallol when heated (Braconnot, Ann. **1**, 26; Pelouze, Ann. **10**, 159; Liebig, Ann. **101**, 47; De Luynes and Esperandieu, Zeit. [2] **1**, 702; Thorpe, Pharm. Journ. [3] **11**, 990; Cazeneuve, Bull. Soc. [3] **7**, 549).

85. Hydroxyquinol; Hydroxyhydroquinone; 1 : 2 : 4-Phenetriol.



Natural Source.

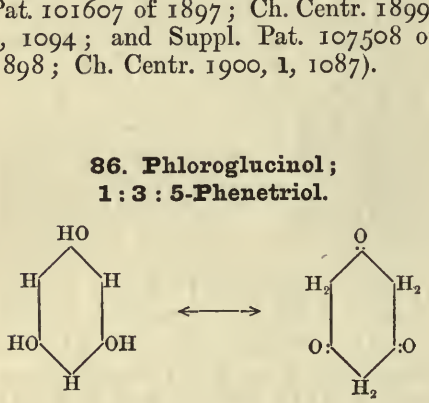
The complex is probably contained in the colouring-matter of red grapes (Sostegni, Gazz. **32**, 17).

Synthetical Processes.

[A.] From *quinol* [71] by fusion with caustic soda (Barth and Schreder, Monats. **4**, 176; **5**, 590).

[B.] *Quinone* [142] on treatment with acetic anhydride and strong sulphuric or phosphoric acid gives hydroxyquinol-triacetate, from which the phenol is liberated by acid hydrolysis (Thiele, Ber. **31**, 1247; Bayer & Co., Germ. Pat. 101607 of 1897; Ch. Centr. 1899, **1**, 1094; and Suppl. Pat. 107508 of 1898; Ch. Centr. 1900, **1**, 1087).

86. Phloroglucinol; 1 : 3 : 5-Phenetriol.



Natural Sources.

Phloroglucinol has been said to occur in the free state in many plants (Weinzierl, Lindt, and Waage, Ber. deutsch. bot. Gesell. **8**, 250), but according to Möller (Ch. Centr. 1897, **2**, 1151) this observation is erroneous. Occurs in the colouring-matter of red grapes (Sostegni, Journ. Ch. Soc. **70**, II, 122). Said to have been found in the bark of *Styrax benzoïn* and (as dibutyrate) in the root of *Aspidium filix mas*.

The phloroglucinol complex is contained in the glucosides:—

Hesperidin; widely distributed in fruit of the genus *Citrus*, such as *C. aurantium*, *C. limonum*, *C. limetta*, *C. medica*, &c. In fruit of *Diosma alba* and other species. Hesperidin is decomposed by certain moulds, such as *Aspergillus niger*, &c. (Puriewitsch, Ber. deutsch. bot. Gesell. **16**, 368).

Glycyphyllin (through phloretin); from leaves of *Smilax glycyphylla* from Australia.

Phloridzin (through phloretin); from root-bark of apple, cherry, plum, pear, &c.

Naringin or aurantiin; from all parts, and especially from the full-blown flowers, of *Citrus decumana* from Java.

Lokaïn; the colouring-matter of Chinese green from the berries of the buckthorns *Rhamnus utilis* and *R. chlorophorus*.

The phloroglucinol complex exists in quercetin, rhamnetin, isorhamnetin, rhamnazin, *luteolin* [141], and consequently in glucosides such as xanthorhamnin, quercitrin, rutin, osyritrin, violaquercitrin, and robinin. (For occurrence see under catechol [69].)

Also in maclurin [69], morin (see under resorcinol [70]), and myricetin (see under pyrogallol [84]); in *chrysin* [138], the yellow colouring-matter of poplar buds from *Populus nigra*, *P. balsamifera*, and *P. pyramidalis* (Kostanecki, Ber. **26**, 2901); in apiin (through *apigenin* [140]), a glucoside found in the stem, seeds, and leaves of parsley, *Apium petroselium* (A. G. Perkin, Trans. Ch. Soc. **71**, 817). Apigenin has been found also (with luteolin) in weld (A. G. Perkin and Horsfall, Proc. Ch. Soc. **16**, 182).

Cyanomaclurin, obtained from *Artocarpus integrifolia* (A. G. P. and Cope, Trans. Ch. Soc. **67**, 939), contains the phloroglucinol group, and is related to the catechins of Gambir and *Acacia* catechu, which also contain this complex (A. G. P. and Yoshitake, Proc. Ch. Soc. **18**, 139; Trans. **81**, 1172).

Lotusin, a glucoside contained in *Lotus arabicus* from Egypt and N. Africa, gives on hydrolysis lotoflavin,

a yellow colouring-matter related to luteolin and fisetin, and which contains the phloroglucinol complex (Dunstan and Henry, Proc. Roy. Soc. **67**, 225; **68**, 374).

A glucoside occurring with apiin in parsley is a derivative of luteolin methyl ether (Vongerichten, Ber. **33**, 2334; 2904; Ann. **318**, 121).

Acacetin, a colouring-matter contained in leaves of *Robinia pseudacacia*, is probably apigenin methyl ether (A. G. Perkin, Trans. Ch. Soc. **77**, 430).

Kampheride from the root of Chinese galangal (*Alpinia officinarum*) contains the phloroglucinol complex (Gordin, Dissert. Bern, 1897; Testoni, Gazz. **30**, 327). The same root contains galangin and its methyl ether, which also probably contain the phloroglucinol complex (*Ibid.*: see also A. G. Perkin and Allison, Trans. Ch. Soc. **81**, 472). A colouring-matter related to kampheride occurs as glucoside in the flowers of *Delphinium consolida* (A. G. Perkin, Trans. Ch. Soc. **73**, 275; A. G. P. and Wilkinson, Proc. Ch. Soc. **16**, 182). The colouring-matter from the glucoside of *Delphinium consolida* is kampherol (A. G. P. and Wilkinson, Trans. Ch. Soc. **81**, 589). Kampheride is the methyl ether of kampherol, and the latter is identical with the colouring-matter contained in the glucoside robinin from the flowers of *Robinia pseudacacia* (A. G. Perkin, Proc. Ch. Soc. **17**, 87; Trans. **81**, 473).

Scutellarin from *Scutellaria altissima* and other Labiates contains (through scutellareïn) the phloroglucinol complex (Molisch and Goldschmiedt, Monats. **22**, 679).

Cotoïn from coto bark contains the methylphloroglucinol complex (Ciamician and Silber, Ber. **27**, 409); hydrocotoïn [**134**] from the same source, the dimethylphloroglucinol complex, and methylhydrocotoïn [**135**] from paracoto bark contains the trimethylphloroglucinol complex.

The phloroglucinol complex is contained in gentisin [**137**], and exists possibly in catechin, kino, and in dragon's blood, a resin from the W. Indian *Pterocarpus* (*Dæmonorops*) *draco*; in gummigutt resin from *Garcinia morella* from Siam, Singapore, and Ceylon; in tormentilla red from the root of *Potentilla tormentilla*; possibly also in the tannin from *Persea lingue*, in the tannins from horse-chestnut, from the root-bark of apple, from the needles of *Abies pectinata*, from *Epacris* leaves, from *Ledum palustre*, and from other sources.

Vitexin and homovitexin, colouring-matters existing as glucosides in the New Zealand dyewood, 'puriri,' from *Vitex littoralis* probably contain the phloroglucinol complex (A. G. Perkin, Trans. Ch. Soc. **73**, 1029). Vitexin is probably a stable glucoside of apigenin (*Ibid.* Proc. Ch. Soc. **16**, 45; Trans. **77**, 422).

Scoparin, the colouring-matter of broom, *Spartium scoparium*, which may be a stable glucoside of luteolin methyl ether, contains this complex (*Ibid.* Proc. Ch. Soc. **15**, 123; **16**, 45; Trans. **77**, 423).

The complex is probably contained in gossypetin, a colouring-matter which occurs, as glucoside, in the cotton flowers of *Gossypium herbaceum* (*Ibid.* Trans. Ch. Soc. **75**, 828), and in genisteïn, a colouring-matter contained in dyer's broom, *Genista tinctoria* (A. G. P. and Newbury, Trans. **75**, 837; A. G. P. and Horsfall, *Ibid.* **77**, 1310).

The complex is contained in filixic and flavaspidic acids, in aspidinol and albaspidin, compounds obtained from the rhizome of *Aspidium filix mas*, *A. spinulosum*, and *Athyrium filix fœmina* (Boehm, Ann. **302**, 181; **307**, 249; **318**, 230; 245; 253: see also Herzig and Wenzel, Monats. **23**, 81 *et seq.*). Filixic acid may contain the complexes of homologues of phloroglucinol, such as dimethyl- and trimethylphloroglucinol.

Note:—For synthesis of dimethylphloroglucinol from trinitro-m-xylene see Weidel and Wenzel, Monats. **19**, 237; of trimethylphloroglucinol from trinitromesitylene, *Ibid.*, and Cassella & Co., Germ. Pats. 102358 of 1897; Ch. Centr. 1899, 1, 1263, and 103683 of 1898; Ch. Centr. 1899, 2, 503.

Synthetical Processes.

[A.] From *acetylene* [1; A], acetylene dibromide by bromination (Sabanejeff, Ann. **178**, 116), bromacetylene by the action of alcoholic soda on the dibromide (*Ibid.* Journ. Russ. Soc. **17**, 175). Bromacetylene undergoes (partial) photochemical polymerisation to 1 : 3 : 5-tribrombenzene (*Ibid.* 176), and this on treatment with sodium methylate in methyl alcohol gives 3 : 5-dibromphenol methyl ether, which on treatment with sulphuric acid yields 3 : 5-dibromphenol (Blau, Monats. **7**, 630). The latter gives phloroglucinol on fusion with potash (*Ibid.* 632).

Bromacetylene can also be obtained from ethylene through various bromine derivatives (Sawitsch, Ann. **119**, 183; Reboul, Ann. **124**, 267; **125**, 81), so that generators of ethylene [1; A; D, &c.] become generators of phloroglucinol.

[B.] From *phenol* [60], being among the products of fusion with caustic soda (Barth and Schreder, Ber. **12**, 417).

Or from phenol through picric acid (2 : 4 : 6-trinitrophenol) by nitration of the phenol or (better) its sulphonic acids (Laurent, Ann. **43**, 219; Schmitt and Glutz, Ber. **2**, 52; Vidal, Fr. Pat. 315696 of 1901; Journ. Soc. Ch. Ind. **21**, 544), 2 : 4 : 6-chlortrinitrobenzene (picryl chloride) by the action of phosphorus pentachloride (Pisani, Ann. **92**, 326; Clemm, Journ. pr. Ch. [2] **1**, 145), and 1 : 3 : 5-triaminobenzene by reduction of picryl chloride by tin and hydrochloric acid. By the action of boiling water on the hydrochloride of the triamine in an atmosphere of hydrogen phloroglucinol is produced (Flesch, Monats. **18**, 755; also Eng. Pat. 445 of 1898: see further Weidel and Pollak, Monats. **21**, 20).

Note:—The following synthesised products give picric acid by the action of nitric acid and thus become generators of phloroglucinol:—*salicylic aldehyde* [117]; *saligenin* [55]; *salicylic acid*, *coumarin*, and *indigo* [Vol. II].

[C.] From *resorcinol* [70] by fusion with caustic soda (Barth and Schreder, Ber. **12**, 503; Tiemann and Will, Ber. **14**, 954; **18**, 1323).

[D.] From *orcinol* [75] by fusion with caustic soda (Barth and Schreder, Monats. **3**, 649).

[E.] From *malonic acid* [Vol. II] and *alcohol* [14]; the diethyl ester of the acid on heating with sodium gives phloroglucinoltricarboxylic ethyl ester (Baeyer, Ber. **18**, 3457; Bally, Ber. **21**, 1767), and this by fusion with potash yields phloroglucinol (Baeyer, *loc. cit.* 3458: see also Willstätter, Ber. **32**, 1272).

Note:—According to Moore (Trans. Ch. Soc. **85**, 165) the ester formed as the first product of condensation of ethyl malonate is ethyl phloroglucinoldicarboxylate.

The tricarboxylic ester can also be obtained by the action of zinc methyl or ethyl on malonic ester (Lang, Ber. **19**, 2038).

Or from malonic ester through acetonetricarboxylic ester by the action of sodium and the distillation of the monosodium compound of the latter under reduced pressure, which gives acetonedicarboxylic ester (Willstätter, Ber. **32**, 1274). The latter can be converted into phloroglucinol as under **F** below. Acetonetricarboxylic ester is directly convertible into phloroglucinoltricarboxylic ester by the action of malonic ester and dry sodium ethylate in ethereal solution (*Ibid.* 1285).

[F.] From *citric acid* [Vol. II] and *ethyl alcohol* [14] through acetonedicarboxylic diethyl ester (see under orcinol [75; C]). The latter, on treatment with sodium in benzene solution, gives a 'lactone,' which on boiling with baryta water splits up into ethyl alcohol, malonic acid, and phloroglucinol (Jerdan, Trans. Ch. Soc. **71**, 1106). The lactone is also produced by the action of sodium ethylate on acetonedicarboxylic ester in alcoholic solution (*Ibid.* Proc. Ch. Soc. **15**, 151).

Acetonedicarboxylic ester and malonic ester condense under the influence of sodium ethylate with the formation of phloroglucinoldicarboxylic ester (Rimini, Gazz. **26**, 374).

[G.] From *acetoacetic ester* [Vol. II] through acetonedicarboxylic ester (see under orcinol [75; D]), and then as above under **F**.

[H.] *Benzene* [6] can, by processes other than those comprised under **B**, **C**, and **D**, be converted into phloroglucinol:—

1:3:5-Benzenetrisulphonic acid (Senhofer, Ann. **174**, 243; Jackson and Wing, Am. Ch. Journ. **9**, 329) gives phloroglucinol when fused with caustic soda (Barth and Schreder, Ber. **12**, 417).

Or benzene can be converted into nitrobenzene and aniline, the latter into 2:4:6-tribromaniline by bromination (Fritzsche, Ann. **44**, 291; Hofmann, Ann. **53**, 50; Silberstein, Journ. pr. Ch. [2] **27**, 101), the NH_2-group replaced by hydrogen by the diazo-method (Meyer and Stüber, Ann. **165**, 173; Baessmann, Ann. **191**, 206; Jackson and Moore, Am. Ch. Journ. **12**, 167; **14**, 335). The 1:3:5-tribrombenzene thus formed can be converted into 3:5-dibromphenol and phloroglucinol as under **A**.

Or from aniline through sulphanilic acid and benzenediazosulphonic acid, the latter giving picric acid by the action of nitric acid (Wenghöfer, Germ. Pat. 125096 of 1900; Ch. Centr. 1901, **2**, 1105).

Or benzene can be converted into 1:3:5-trinitrobenzene by extreme nitration (Hepp, Ann. **215**, 345), the latter reduced to the corresponding triamine, and then converted into phloroglucinol as under **B**.

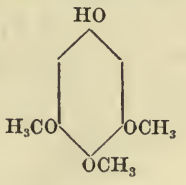
Or *toluene* on nitration gives 2:4:6-trinitrotoluene (Wilbrand, Ann. **128**, 178), and this on oxidation with nitric acid yields 2:4:6-trinitrobenzoic acid (Tiemann and Judson, Ber. **3**, 224). The 2:4:6-triaminobenzoic acid gives phloroglucinol on heating with water (Cassella & Co., Germ. Pat. 102358 of 1897; Ch. Centr. 1899, **1**, 1263).

Note:—Generators of toluene (see under benzyl alcohol [54; **A**; &c.]) thus become generators of phloroglucinol.

[I.] *Furfural* [126] on oxidation with silver oxide or alkaline permanganate, or on treatment with alcoholic potash, gives pyromucic acid (Schwanert, Ann. **114**, 63; **116**, 257; Ulrich, Jahresber. **1860**, 269; Beilstein and Schmelz, Ann. Suppl. **3**, 275; Limpricht, Ann. **165**, 279; Bieler and Tollens, Ann. **258**, 120; Schiff, Ann. **239**, 374; **261**, 255). This acid, by the action of bromine in water, yields mucobromic acid (Beilstein and Schmelz, *loc. cit.* 276; Jackson and Hill, Am. Ch. Journ. **3**, 105), and this, by the action of nitrites, gives nitromalonic aldehyde (Hill and Sanger, Ber. **15**, 1906; Hill and Torrey, Ber. **28**, 2597; Am. Ch. Journ. **22**, 89). The latter, on decomposition by aqueous hydrochloric acid, yields (with formic acid) 1:3:5-trinitrobenzene (*Ibid.*), which can be converted into phloroglucinol as above under **B**.

[J.] *Iretol* [88] is reduced to phloroglucinol by sodium amalgam (Tiemann and G. de Laire, Ber. **26**, 2026).

87. Antiarol; 1-Hydroxy-3:4:5-trimethoxybenzene; 1:3:4:5-Phenetetrol 3:4:5-Trimethyl Ether.



Natural Source.

The sap of the upas tree, *Antiaris toxicaria* (Kiliani, Arch. Pharm. **234**, 438).

Synthetical Processes.

[A.] From *pyrogallol* [84] through the trimethyl ether by methylation, 3:5-dimethoxyquinone by oxidation with nitric acid, 3:5-dimethoxyquinol by reduction, and methylation of the latter by the usual method (Will, Ber. **21**, 612; 2020).

[B.] From *catechol* [69] through guaiacol. The latter, on sulphonation at a low temperature, gives a consecutive monosulphonic acid which yields pyrogallol methyl ether on fusion with alkali (Hoffmann, La Roche & Co.,

Germ. Pat. 109789 of 1898; Ch. Centr. 1900, **2**, 460). The monomethyl ether might be converted into the trimethyl ether by further methylation, and then treated as above.

[C.] From *phloroglucinol* [86] through the trimethyl ether by methylation (Will, Ber. **21**, 603; Pollak, Monats. **18**, 736), 3 : 5-dimethoxyquinone by oxidation with chromic acid (Ciamician and Silber, Ber. **26**, 786), and then as under **A**.

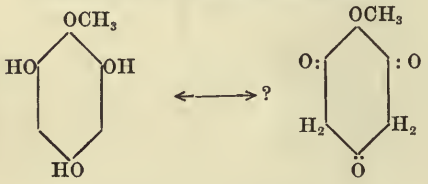
[D.] From *benzene* [6] through 1 : 3 : 5-trinitrobenzene (see under phloroglucinol [86; H]), which, on heating with sodium methoxide, gives 3 : 5-dinitroanisole (Lobry de Bruyn, Rec. Tr. Ch. **9**, 209). The latter on reduction yields diaminoanisole, and this, on heating with water, gives phloroglucinol methyl ether (Herzig and Aigner, Monats. **21**, 433).

Or from phenol through picric acid (see under phloroglucinol [86; B]) and the methyl ether of the latter by methylation. Subsequent steps as above.

Note :—Generators of picric acid, viz. *salicylic aldehyde* [117], *saligenin* [55], *salicylic acid*, *coumarin*, and *indigo* [Vol. II], thus become generators of iretol (see under phloroglucinol [86; B]).

[B.] *Anisic acid* [Vol. II] gives trinitroanisole on nitration as under **A** (Cahours, *loc. cit.*). Subsequent steps as above.

88. Iretol; 1-Methoxy-2 : 4 : 6-trihydroxybenzene; 2 : 4 : 6-Trihydroxyanisole; 1 : 2 : 4 : 6-Phenetetrol 1-Methyl Ether.



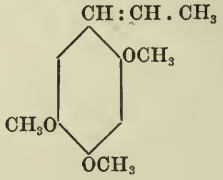
Natural Source.

The complex is possibly contained in orris root from *Iris florentina*, which contains a glucoside, iridin, which is decomposed, on heating with dilute sulphuric acid and alcohol, into glucose and irigenin. The latter gives iretol among other products (iridic and formic acids) on heating with strong potash solution (G. de Laire and Tiemann, Ber. **26**, 2015).

Synthetical Processes.

[A.] From *phenol* [60] and *methyl alcohol* [13] through anisole (see under anisic aldehyde [120; B]). The latter is nitrated with nitric and sulphuric acids (Cahours, Ann. **69**, 238), the 2 : 4 : 6-trinitroanisole reduced by tin and hydrochloric acid to diaminohydroxyanisole and the latter (hydrochloride) heated with dilute stannous chloride in an atmosphere of carbon dioxide (Kohner, Monats. **20**, 933).

89. Asarone; 1[1]-Propenyl-2 : 4 : 5-trimethoxybenzene.



Natural Sources.

In the root of *Asarum europæum* (Petersen, Ber. **21**, 1057). Also in certain matico oils from the leaves of *Piper angustifolium* (Schimmel's Ber. Oct. 1898; Ch. Centr. 1898, **2**, 985), in sweet flag oil from the root of *Acorus calamus* (Thoms and Beckstroem, Ber. **34**, 1021; Thoms, Zeit. angew. Ch. **14**, 1019; T. and B. Ber. **35**, 3190), and in the oil of *Asarum arifolium* (Miller, Arch. Pharm. **240**, 371).

Synthetical Processes.

[A.] From *phenol* [60], *propionic acid* [Vol. II], *methyl alcohol* [13], and *hydrogen cyanide* [172]. Phenol is nitrated, the o-nitrophenol converted

into its methyl ether, and then reduced to o-anisidine (Mülhäuser, Ann. **207**, 239). The latter, on oxidation with sulphuric acid and potassium dichromate, gives methoxyquinone (*Ibid.* 251; Will, Ber. **21**, 605), and this by reduction methoxyquinol (Will, *loc. cit.* 606). The latter, on further methylation with methyl iodide and potassium hydroxide, yields the 1 : 2 : 4-trimethoxybenzene (Will). By the action of hydrogen cyanide on the latter in conjunction with hydrogen chloride in presence of aluminium chloride the 2 : 4 : 5-trimethoxybenzaldehyde = *asaryl aldehyde* [125] is formed (Gattermann and Eggers, Ber. **32**, 289), and this, on heating with propionic anhydride and sodium propionate at 150°, gives asarone (*Ibid.* 290).

[B.] *Resorcinol* [70] may replace phenol in the above synthesis. Diazotised aniline is combined with resorcinol, the azo-compound methylated by heating with potassium hydroxide and methyl iodide (Bechold, Ber. **22**, 2375), and the dimethyl ether reduced to 1 : 3-methoxy-4-aminobenzene. The latter, on oxidation with sulphuric acid and sodium dichromate, gives methoxyquinone (*Ibid.* 2381), which can be reduced, methylated, and treated as under **A**.

[C.] *Quinol* [71] may replace phenol in this synthesis since, on fusion with sodium hydroxide, it gives 1 : 2 : 4-trihydroxybenzene (*hydroxyquinol* [85]) (Barth and Schreder, Monats. **4**, 176; **5**, 590), and this can be converted into the trimethyl ether by methylation, and then treated as above under **A**.

[D.] *Quinone* [142] gives hydroxyquinol triacetate on treatment with acetic anhydride and a little sulphuric acid (Thiele, Ber. **31**, 1247: see also [85]). The triacetate hydrolyses to the trihydroxy-compound, which can be treated as above.

[E.] From *asaryl aldehyde* [125] and *propionic acid* [Vol. II] by heating the aldehyde with propionic anhydride and sodium propionate (Gattermann and Eggers, as under **A** above).

90. α-Hydrojuglone; 1 : 4 : 5-Trihydroxynaphthalene; 1 : 4 : 8-Naphthalenetriol.

Natural Source.

In all green parts of the walnut tree, *Juglans regia* (Mylius, Ber. **17**, 2411; **18**, 475; 2567).

Synthetical Processes.

Syntheses of Naphthalene.

[A.] From *benzene* through *toluene* and *benzyl chloride* (see under benzyl alcohol [54; **A**, &c.]). The latter, when mixed with allyl iodide (see under isobutyl alcohol [18; **D**]) and treated in ethereal solution with sodium, gives phenylbutylene (Aronheim, Ann. **171**, 225), the dibromide (*Ibid.* 229) of which yields naphthalene on passing the vapour over hot lime (*Ibid.* 233).

From *benzyl chloride* and *isopropyl alcohol* [16] by acting with sodium on a mixture of isopropyl iodide and benzyl chloride in ether so as to form isobutylbenzene (Kohler and Aronheim, Ber. **8**, 509). The latter gives naphthalene on passing the vapour over heated lead oxide (Wreden and Snatowicz, Ber. **9**, 1606).

Benzene and *isobutyl alcohol* [18] also give isobutylbenzene by the action of sodium on brombenzene and isobutyl bromide or iodide in ether or benzene, (Riess, Ber. **3**, 779; Wredin and Snatowicz, *loc. cit.*), or directly by heating benzene with the alcohol and zinc chloride at 300° (Goldschmidt, Ber. **15**, 1066; 1425). Also by the action of aluminium chloride on a mixture of benzene and isobutyl chloride (Gossin, Bull. Soc. [2] **41**, 446).

From *toluene*, *malonic acid* [Vol. II], and *alcohol* [14]. Malonic acid is converted into its diethyl ester and the

latter into chlormalonic ester by chlorination (Conrad and Bischoff, Ann. **209**, 219). By the action of chlormalonic ester on sodiomalonic ester in alcoholic solution the tetra-ethyl ester of s-ethanetetracarboxylic (butanediacid-2 : 3-dimethylic or acetylenetetracarboxylic) acid is formed (*Ibid.* **214**, 68; Ber. **13**, 601; **21**, 2087; Bischoff and Rach, Ber. **17**, 2785).

The same tetracarboxylic ester is also formed by the action of iodine on malonic ester in presence of sodium ethoxide (Bischoff, Ber. **16**, 1046; Bischoff and Rach, Ber. **17**, 2781), by the electrolysis of an alcoholic solution of sodiomalonic diethyl ester (Mulliken, Am. Ch. Journ. **15**, 523; Weems, *Ibid.* **16**, 569), by the interaction of acetylene tetrabromide, malonic ester, and sodium ethoxide (Crossley, Proc. Ch. Soc. **14**, 248), and also from nitromalonic ester (see under hydrogen cyanide [**172**; **AA**]) through ethanedinitro-tetracarboxylic ester by electrolysis: the dinitro-ester gives the tetracarboxylic ester by reduction (Ulpiani and Gasparini, Gazz. **32**, 235).

Toluene can be converted into o-xylene (see under m-cresol [**62**; **A**]) by methylation, and the latter into o-xylylene dibromide ($1^1 : 2^1$-dibromxylene) by bromination (Radziszewski and Wispek, Ber. **18**, 1281; Schramm, *Ibid.* 1279; W. H. Perkin, junr., Trans. Ch. Soc. **53**, 5). The xylylene dibromide and ethanetetracarboxylic ester react when heated in alcoholic solution in the presence of sodium ethoxide with the formation of 1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2 : 3 : 3-tetracarboxylic tetra-ethyl ester (Baeyer and W. H. Perkin, junr., Ber. **17**, 450; W. H. P., junr., Trans. Ch. Soc. **53**, 12), and this on hydrolysis yields the free acid which, on heating at 185°, gives the anhydride of tetrahydronaphthalene-dicarboxylic acid (B. and P. *loc. cit.*). The latter, when passed through a red-hot tube, or when the silver salt of the free acid is heated, yields naphthalene (*Ibid.* 451).

Or sodio-chlormalonic ester and o-xylylene dibromide may be heated in alcoholic solution so as to form o-xylylenedichlordimalonic tetra-ethyl ester (*Ibid.* 452), and this, by treatment with zinc dust and acetic acid, gives o-xylylenedimalonic tetra-ethyl ester (*Ibid.* and W. H. Perkin, junr., Trans. Ch. Soc. **53**, 16). By the action of iodine (ethereal solution) on the sodium derivative of the latter ester the tetrahydronaphthalene derivative is formed, and can be treated as above (Baeyer and W. H. Perkin, junr., Ber. **17**, 452).

Note :—The ethanetetracarboxylic ester required for this synthesis of naphthalene can also be obtained from the *amyl alcohol* of fusel oil [**22**] by converting the latter into amylene (see under acetone [**106**; **E**]) and its dibromide. The latter on heating with sodiomalonic ester gives (with trimethylethylene) ethanetetracarboxylic ester (Ipatieff, Journ. Russ. Soc. **30**, 391). Alkylene dibromides of the general form $R_2CBr.CH_2.CH_2Br$ give the tetracarboxylic acid as a by-product by the action of sodiomalonic ester (*Ibid.* **31**, 349; also Ipatieff and Swiderski, *Ibid.* **33**, 532; Ipatieff, *Ibid.* **34**, 351).

The conversion (partial) of benzene into naphthalene may also be effected through nitrobenzene, aniline, dimethylaniline by methylation, and the action of bromine on the latter at 110–120° (Brunner and Brandenburg, Ber. **11**, 698).

Naphthalene is among the aromatic hydrocarbons formed when the copper compound of *acetylene* [**1**; **A**] is distilled with zinc dust (Erdmann and Köthner, Zeit. anorg. Ch. **18**, 48). Naphthalene is formed with other products by pyrogenic synthesis from :—

Alcohol (Reichenbach, Berz. Jahresber. **12**, 307); methane; acetic acid; toluene; xylene; pseudocumene; ethylene and benzene; ethylene and styrene; ethylene and anthracene (Berthelot, Bull. Soc. [2] **6**, 272; 279; Ferko, Ber. **20**, 660); ethylene (Norton and Noyes, Am. Ch. Journ. **8**, 362); acetylene or acetylene and benzene (Berthelot, Comp. Rend. **62**, 905; **93**, 613; Bull. Soc. [2] **6**, 268; **7**, 218; 274; 303; **9**, 456); ethylene and diphenyl (Barbier, Comp. Rend. **79**, 121); heptane; octane; n-hexyl alcohol (Worstall and Burwell, Am. Ch. Journ. **19**, 815); isobutylene (Noyes; Beilstein, I, 115).

Naphthalene is formed from certain metallic carbides, e. g. of barium, by

heating to 600–800° with the metallic hydroxide (Bradley and Jacobs, Germ. Pat. 125936 of 1898; Ch. Centr. 1902, **1**, 77).

Conversion of Naphthalene into Hydrojuglone.

By oxidation with chromic acid in acetic acid naphthalene is converted into α-naphthaquinone (Groves, Journ. Ch. Soc. **26**, 209; Plimpton, Trans. **37**, 634; Japp and Miller, *Ibid.* **39**, 220; by electrolytic oxidation, De Bottens, Zeit. Elektroch. **8**, 673). The latter on standing in dilute sodium hydroxide solution in presence of air gives the 5-α-hydroxyquinone = juglone (Kowalski, Ber. **25**, 1659), and this on reduction yields hydrojuglone (Mylius, Ber. **17**, 2412; **18**, 463; 2567).

Naphthalene on sulphonation under appropriate conditions gives (with 1 : 6-) the 1 : 5-disulphonic acid (Armstrong, Ber. **15**, 200; Armstrong and Wynne, Proc. Ch. Soc. **2**, 231; **3**, 42 and 146; Bernthsen and Semper, Ber. **20**, 934; Bernthsen, Ber. **22**, 3327). The latter on fusion with alkali yields 1 : 5-dihydroxynaphthalene (Armstrong and Wynne, Proc. Ch. Soc. **3**, 43; Bernthsen and Semper, *loc. cit.*; Erdmann, Ann. **247**, 306), and this on oxidation with chromic acid mixture gives 5-hydroxy-α-naphthaquinone, which can be treated as above.

Or naphthalene may be nitrated and the α-nitronaphthalene sulphonated, when the 1 : 5-nitrosulphonic acid is formed (with other isomerides) (Laurent, Ann. **72**, 298; Comp. Rend. **31**, 537; Schmidt and Schaal, Ber. **7**, 1367; Palmaer, Ber. **21**, 3260; Erdmann, *loc. cit.*; Cleve, Bull. Soc. [2] **24**, 506). The latter gives 1 : 5-naphthylaminesulphonic acid by reduction (references as before, and Schoellkopf Anilin Co., Germ. Pat. 40571 of 1885; Ekbom, Ber. **23**, 1118; Bernthsen, *Ibid.* 3088; Schultz, Ber. **20**, 3158; Erdmann, *Ibid.* 3185; Ann. **247**, 306; **275**, 192; 262). This aminosulphonic acid by the diazo-method is converted into 1 : 5-naphtholsulphonic acid (Cleve, *loc. cit.*; Schultz, Ber. **20**, 3161; Erdmann, *loc. cit.*), which on fusion with potash gives 1 : 5-dihydroxynaphthalene (Cleve, *loc. cit.*; Ewer and Pick, Germ. Pat. 41934 of 1887). The latter can be converted into juglone, &c., as above.

Or naphthalene-α-sulphonic acid can be nitrated and the 1 : 5-nitrosulphonic acid (which is formed with the 1 : 4 and 1 : 8 isomerides) reduced and converted as above (Cleve, *loc. cit.*; Schoellkopf Co., *loc. cit.*; Cleve, Ber. **23**, 958; Bernthsen, *Ibid.* 3088; Erdmann and Süvern, Ann. **275**, 230).

Or naphthalene can be converted into α-nitronaphthalene and α-naphthylamine. The latter (or its acetyl-derivative) gives (with other isomerides) the 1 : 5-aminosulphonic acid on sulphonation (Witt, Ber. **19**, 578; Lange, Ber. **20**, 2940; Schultz, *Ibid.* 3158; Erdmann, *Ibid.* 3185; Ann. **247**, 306; **275**, 192; 262; Mauzelius, Ber. **20**, 3401; Ewer and Pick, Germ. Pat. 42874 of 1887), and this sulpho-acid can be treated as above.

The 1 : 8-nitrosulphonic acid obtained by the nitration of naphthalene-α-sulphonic acid as above gives the 1 : 8-aminosulphonic acid on reduction (Schoellkopf Co., *loc. cit.*; Schultz, Ber. **20**, 3158; Erdmann, Ann. **247**, 306; **275**, 262; Bernthsen, Ber. **23**, 3088), and this by the diazo-reaction gives the 1 : 8-sultone (references as before). The latter on fusion with potash yields 1 : 8-dihydroxynaphthalene (Erdmann, *loc. cit.*), and this on oxidation with chromic acid mixture gives juglone (Bernthsen and Semper, Ber. **20**, 939).

Or the 1 : 8-aminosulphonic acid on fusion with alkali gives 1 : 8-aminonaphthol (Bad. An. Sod. Fab., Germ. Pat. 55404 of 1889; Ber. **24**, Ref. 481). The latter on combination with diazosulphanilic acid gives an azo-compound which on reduction yields 1 : 4-diamino-8-naphthol, and this gives juglone on oxidation with ferric chloride (Friedländer and Silberstern, Monats. **23**, 513).

Note:—Further references to processes for obtaining 1 : 8-aminonaphthol or its generators are given in Germ. Pats. 54662; 62289; 77937; 84951 and 112778 of the Bad. An. Sod. Fab.; Germ. Pats. 71836; 75055; 75317; 80668 and

109102 of Bayer & Co.; Germ. Pats. 73381 and 73607 of Cassella & Co. See also Dressel and Kothe, Ber. 27, 2139.

The conversion of naphthalene into the α-quinone, and thence (as above) into juglone, can also be effected through α-naphthylamine, α-acetnaphthalide, 1 : 4-nitroacetnaphthalide, 1 : 4-nitronaphthylamine, 1 : 4-naphthylenediamine, and oxidation of the latter by chromic acid mixture (Liebermann, Ann. **183**, 242: all azo-derivatives of α-naphthylamine give the 1 : 4-diamine on reduction; Perkin, Ann. **137**, 359; Griess, Ber. **15**, 2183).

1 : 4-Nitronaphthylamine is also obtained by the action of hydroxylamine on α-nitronaphthalene in the presence of sodium ethoxide (Angeli and Angelico, Atti Real. Accad. [5] **8**, II, 28; Ch. Centr. 1899, **2**, 371).

Or α-acetnaphthalide can be converted into 1 : 4-nitronaphthol by boiling the 1 : 4-nitro-derivative with potash solution (Andreoni and Biedermann, Ber. **6**, 342; Liebermann and Dittler, Ber. **7**, 240; Hübner and Ebell, Ber. **8**, 562; Ann. **208**, 324). The nitronaphthol on reduction gives 1 : 4-aminonaphthol, and this also oxidises to α-naphthaquinone (Liebermann, Ann. **183**, 242; Ber. **14**, 1796; Zincke, Ann. **286**, 70).

α-Naphthylamine can also be directly oxidised to the α-quinone by chromic acid mixture (Monnet, Reverdin, and Noelting, Ber. **12**, 2306).

[B.] From *benzoic aldehyde* [114] and *succinic acid* [Vol. II] by heating the aldehyde with succinic anhydride and sodium succinate so as to form phenylisocrotonic (β-benzalpropionic = phene-1[1]-butenylic) acid (Perkin, Journ. Ch. Soc. **31**, 394; Jayne, Ann. **216**, 100; Erdmann, Ann. **227**, 258; Leoni, Ann. **256**, 64). The latter on boiling with water gives α-naphthol (Fittig and Erdmann, Ann. **227**, 242), from which α-naphthaquinone, and thence juglone and hydrojuglone, can be obtained by converting the naphthol into 1 : 4-nitrosonaphthol (α-naphthaquinoneoxime) by the action of nitrous acid (2-nitroso-1-naphthol is formed simultaneously) (Fuchs, Ber. **8**, 626; Ilinsky, Ber. **17**, 2590; Henriques and Ilinsky, Ber. **18**, 706). The nitrosonaphthol reduces to 1 : 4-aminonaphthol (Grandmougin and Michel, Ber. **25**, 972), and this can be oxidised to α-naphthaquinone as under **A**.

The azo-derivatives of α-naphthol also give 1 : 4-aminonaphthol on reduction (Liebermann and Jacobson, Ann. **211**, 36; Seidel, Ber. **25**, 423; Grandmougin and Michel, *loc. cit.*). α-Naphthyl acetate gives some α-quinone on oxidation (Miller, Ber. **14**, 1600).

[C.] From *cinnamic* and *malonic acids* [Vol. II], and *methyl alcohol* [13]. Cinnamic acid is converted into its methyl ester and brominated so as to form the dibromide. The latter, when heated with sodio-malonic methyl ester in methyl alcohol solution, gives Γα1-phenyltrimethylene-2 : 2 : 3-tricarboxylic trimethyl ester, from which the free acid can be obtained by hydrolysis (Buchner and Dessauer, Ber. **25**, 1153). The acid on heating (in CO_2) at 180–200°, and finally by distillation in a vacuum, yields phenylisocrotonic acid (*Ibid.* 1155), which can be converted into α-naphthol, &c., as under **B**.

[D.] *Furfural* [126] and *benzene* [6] give α-naphthylamine by heating pyromucic acid (see under erythritol [50; N]) with aniline, zinc chloride, and lime at 300° (Canzoneri and Oliveri, Gazz. **16**, 493). The naphthylamine can be converted into α-naphthaquinone, &c., as under **A**.

[E.] *Mannitol* [51] and *benzene* [6] can be made to give a small quantity of α-naphthylamine by heating the alcohol with aniline hydrochloride at 200–240° (Effront, Jahresber. **1885**, 1210; Ber. **18**, Ref. 383).

[F.] From *cinnamic aldehyde* [123] and *hippuric acid* [Vol. II], which condense to form an anhydride which, by the action of sodium hydroxide, gives cinnamylidenehippuric acid [$C_6H_5.CH:CH.CH:C(COOH)NH.CO.C_6H_5$], and this on heating with hydrochloric acid to 110–120° yields (with α-naphthoic acid) naphthalene (Erlenmeyer, junr., and Kunlin, Ber. **35**, 384).

[G.] *Pyrogallol* [84] on oxidation gives a product (purpurogallin) which yields naphthalene on distillation with zinc dust (Nietzki and Steinmann, Ber. **20**, 1278).

ALDEHYDES AND KETONES: FATTY GROUP.

91. Formic Aldehyde; Formaldehyde; Methanal.

H . CHO

Natural Sources.

The aldehyde may possibly exist in plant cells containing chlorophyll (Reinke, Ber. **14**, 2148; Mori, Jahresber. **1882**, 1143), but this observation requires confirmation. The distilled extract of witch-hazel, *Hamamelis virginica*, N. America, is said to contain formic aldehyde (Gunn, Ch. Drug. **59**, 796). Polacci claims to have obtained distinct evidence of the presence of the aldehyde in the distillate from the leaves of plants which have been exposed to light (Ch. Centr. 1899, **2**, 881, from Boll. Chim. Pharm. **38**, 601; also Ch. Centr. 1900, **1**, 822; 1901, **2**, 938).

Synthetical Processes.

[A.] From *carbon dioxide* and hydrogen by the silent electric discharge (Brodie, Proc. Roy. Soc. **22**, 172); from carbon dioxide and water under the influence of sunlight in presence of uranium acetate (Bach, Comp. Rend. **116**, 1145; 1389). From *carbon monoxide* and hydrogen by the silent electric discharge (Losanitsch and Jovitschitsch, Ber. **30**, 136; De Hemptinne, Bull. Acad. Roy. Belg. **34**, 269; Solvay and Slosse, *Ibid.* **35**, 547), or by passing over hot spongy platinum (Jahn, Ber. **22**, 989).

From carbonic acid (carbon dioxide in water) by reduction with hydrogen-palladium or by electrolytic reduction (Bach, Comp. Rend. **126**, 479), or by the action of violet light in presence of uranium acetate (*Ibid.* Arch. Soc. Phys. Nat. Genève [4] **5**, 401; Ch. Centr. 1898, **2**, 42).

From *acetylene* [1; A, &c.], the silver, mercury, or cuprous compounds of which, as well as the sulphuric acid solution, all yield iodoform on treatment with iodine and alkali (Le Comte, Journ. Pharm. **16**, 297). From iodoform, as below under D.

[B.] *Methane* [1] and oxygen give formic aldehyde by the action of the silent electric discharge (Maquenne, Bull. Soc. [2] **37**, 298).

Or from methane and air by passing over heated catalytic surfaces of copper, asbestos, &c. (Glock, Germ. Pat. 109014 of 1898; Ch. Centr. 1900, **2**, 304), or by slow combustion at low temperatures with oxygen (Bone and Wheeler, Proc. Ch. Soc. **19**, 191; Trans. **83**, 1074).

[C.] From *methyl alcohol* [13] by incomplete combustion in air (Hofmann, Proc. Roy. Soc. **16**, 156; Ber. **2**, 152; **11**, 1685; Ann. **145**, 357; Volhard, Ann. **176**, 128; Kablukoff, Journ. Russ. Soc. **14**, 194; Tollens, Ber. **15**, 1629; **16**, 917; **19**, 2133; Loew, Journ. pr. Ch. [2] **33**, 321; Ber. **20**, 144; Klar and Schulze, Germ. Pat. 106495 of 1898; Ch. Centr. 1900, **1**, 1082). From methyl alcohol (trace only) by oxidation with air in a solution containing colloidal platinum (Glaessner, Ch. Centr. 1902, **2**, 731).

Also from methyl alcohol by electrolytic oxidation in sulphuric acid solution (Elbs and Brunner, Zeit. Elektroch. **6**, 604) or by pyrogenic decomposition (Ipatieff, Ber. **34**, 598; **35**, 1055).

Or from methyl alcohol through methyl ether (Dumas and Peligot, Ann. **15**, 12; Kane, Ann. **19**, 166; Ebelmen, Ann. **57**, 328; Erlenmeyer and Kriechbaumer, Ber. **7**, 699; Tellier, Jahresber. **1877**, 1157). The latter gives formic aldehyde by pyrogenic decomposition (Tistschenko, Journ. Russ. Soc. **31**, 784; Ch. Centr. 1900, **1**, 586).

Or from methyl alcohol through methylal by oxidation with sulphuric acid and manganese dioxide (Kane, Ann. **19**, 175; Malaguti, Ann. **32**, 55), or by electrolysis of the alcohol in dilute sulphuric acid (Renard, Ann. Chim. [5] **17**, 291). Methylal gives formic aldehyde when heated with sulphuric acid, the aldehyde rapidly polymerising (Wohl, Ber. **19**, 1841).

NOTE:—Methylal can be obtained from methyl alcohol by converting the alcohol into methyl chloride and the latter into methylene chloride by chlorination (Regnault, Ann. Chim. [2] 70, 377; Ann. 33, 328). Methylene chloride interacts with sodium methylate to form methylal (Arnhold, Ann. 240, 190).

Methyl alcohol gives formic aldehyde among the products of the action of chlorine or bromine (Lobry de Bruyn, Ber. 26, 271; Brochet, Comp. Rend. 121, 130).

By the action of fuming sulphuric acid on methyl alcohol there is formed an 'oxymethanesulphonic acid,' the sodium salt of which gives formic aldehyde on decomposition by water (Müller, Ber. 6, 1032).

Or from methyl alcohol and *acetic acid* [Vol. II] through methyl acetate, chlormethyl acetate by chlorination (Henry, Ber. 6, 740), and the action of water at 100° on the latter (Michael, Am. Ch. Journ. 1, 419).

[D.] From *ethyl alcohol* [14] by incomplete combustion (Mulliken, Brown, and French, Am. Ch. Journ. 25, 111), or by the incomplete combustion of ethyl nitrate (Pratesi, Gazz. 14, 221).

Or from ethyl ether, the vapour giving a trace of formic aldehyde when passed through a hot tube (Tistschenko, Journ. Russ. Soc. 31, 784; Ch. Centr. 1900, 1, 586).

Or from ethyl alcohol through chloroform (see under methane [1; D]), methylene chloride by reduction (Perkin, Ch. News, 18, 106; Greene, Comp. Rend. 89, 1077; Jahresber. 1879, 490; Ch. News, 50, 75; Journ. Am. Ch. Soc. 1, 522), and methylal as above under C.

NOTE:—The generators of chloroform referred to under methane [1; M; P; R, &c.] thus become, with methyl alcohol, generators of formic aldehyde through methylal.

Or from ethyl alcohol through ethylene, the latter giving formic aldehyde when heated to 400° with an insufficient quantity of oxygen for complete combustion (Schutzenberger, Bull. Soc. [2] 31, 482).

NOTE:—All generators of ethylene thus become generators of formic aldehyde.

Or from ethyl alcohol through *ethylene glycol* [45] (see under isopropyl alcohol [16; C]). The latter, on electrolysis in presence of dilute sulphuric acid, gives 'trioxymethylene' (Renard, Ann. Chim. [5] 17, 303), a polymeride of formic aldehyde which is resolved by heat, by hot water, or by combination with acid sodium sulphite into the monomolecular aldehyde (Hofmann, Ber. 2, 152; Tollens and Mayer, Ber. 21, 1571; Kraut, Ann. 258, 105; Harries, Ber. 34, 635: see also Kekulé, Ber. 25, 2435). Or trioxymethylene gives formic aldehyde when passed with air through a hot tube (Wolkoff and Menschutkin, Ber. 31, 3067).

Or from glycol through glycollic aldehyde (see under furfural [126; G]), and then as below under O.

Or from ethyl alcohol through iodoform (see under methane [1; D]), methylene iodide by heating the latter with hydriodic acid and phosphorus, &c. (Butleroff, Ann. Chim. [3] 53, 313; Hofmann, Ann. 115, 267; Baeyer, Ber. 5, 1095). Methylene iodide gives methylene chloride by chlorination (Butleroff, Ann. 107, 110; 111, 251), and this, with methyl alcohol, is a generator of methylal and of formic aldehyde as above under C.

Or iodoform and sodium ethylate give acrylic acid (Butleroff, Ann. 114, 204). From the latter through α-chlorlactic and glyceric acid [54; I] or through oxyacrylic (glycidic) acid [92; J]. The latter gives glyceric acid in contact with water (Melikoff, Ber. 13, 272). Subsequent steps as below under M.

Or from iodoform through methylene iodide and trioxymethylene by the action of silver oxide (or oxalate) on the iodide (Butleroff, Ann. 111, 242).

[E.] From *acetic aldehyde* [92] through iodoform by the action of iodine and alkali [1; I], and then as above under D. Or from aldehyde through *crotonic aldehyde* [102] and crotonic acid (see under n-butyl alcohol [17; G] and under benzyl alcohol [54; H]). From crotonic acid through β-methylglyceric acid to formic aldehyde as below under J.

[F.] From *acetone* [106], formic aldehyde being among the products formed by passing the vapour over a heated platinum spiral (Trillat, Comp. Rend.

132, 1495), or by incomplete combustion (Mulliken, Brown, and French, Am. Ch. Journ. 25, 111).

Or from acetone through diacetonamine (see under aldehyde [92; S]), the latter giving trioxymethylene (among other products) when the sulphate is oxidised by chromic acid mixture (Heintz, Ann. 198, 45).

Or from acetone through chloroform by the action of bleaching powder (see under methane [1; J]), and then, with sodium methylate, through methylal as above under D and C. Or from acetone through iodoform (see under methane [1; J]), and then as above under D.

[G.] From *formic acid* [Vol. II], the aldehyde being among the products obtained by the dry distillation of the calcium salt (Mulder, Zeit. [2] 4, 265; Ann. 159, 366; Linnemann, Ann. 157, 119; Lieben and Rossi, Ann. 158, 107).

[H.] From *acetic acid* [Vol. II] by incomplete combustion (Mulliken, Brown, and French, Am. Ch. Journ. 25, 111). Or from acetic and *glycollic acid* [Vol. II]; formic aldehyde is produced when an electric current is passed through a solution of potassium acetate (positive electrode) and potassium glycollate (negative electrode) (v. Miller and Hofer, Ber. 27, 467; 28, 2437). Or by the electrolysis of sodium acetate in presence of sodium perchlorate (Hofer and Moest, Ann. 323, 284).

Also from acetic acid through acetyl cyanide and pyroracemic acid (see under benzyl alcohol [54; I]). The latter, on heating with acetic anhydride and sodium acetate at 160–180°, gives α-crotonic acid (Homolka, Ber. 18, 987), which can be converted into β-methylglyceric acid and formic aldehyde as below under J.

Or from acetic acid and *methyl alcohol* [13] through methylglycollic acid by the action of chloracetic acid on sodium methylate (Heintz, Jahresber. 1859, 358). The methylglycollic acid gives formic aldehyde among the products of electrolysis of the sodium salt (v. Miller and Hofer, Ber. 27, 469).

Calcium glycollate on heating with dilute sulphuric acid at 170–180°, or the acid itself on heating to 220–240°, gives 'trioxymethylene' (Heintz, Ann. 138, 43; Jahresber. 1861, 444), which is related to formic aldehyde as under D.

Silver glycollate gives formic aldehyde when decomposed by iodine (Herzog and Leiser, Monats. 22, 357). Or glycollic ester interacts with hydrazine to form a hydrazide, which by the action of nitrous acid gives glycolazide ($CH_2[OH]CO.N_3$) (Curtius and Heidenreich, Journ. pr. Ch. [2] 52, 225). The azide on heating with alcohol gives glycolurethane, and this by the action of mineral acid is resolved into formic aldehyde and other products (Curtius and Müller, Ber. 34, 2795).

Or from acetic acid through monochloracetic acid and 'trioxymethylene,' the latter being among the products formed by passing the vapour of the chloro-acid through a hot tube (Grassi-Cristaldi, Gazz. 27, 502).

[I.] *Lactic acid* [Vol. II] gives iodoform by the action of iodine and alkali (Lieben, Ann. Suppl. 7, 218; 377), and this can be converted into methylene iodide, chloride, methylal, &c., as under D.

Or from lactic acid through pyroracemic acid (see under benzyl alcohol [54; P]), α-crotonic acid, &c., as above under H, and then as below under J.

Potassium lactate gives *crotonic aldehyde* [102] on electrolysis, the positive electrode being kept alkaline (v. Miller and Hofer, Ber. 27, 468). *Sarcolactic acid* [Vol. II] also yields crotonic aldehyde under these conditions (*Ibid.*).

[J.] From *normal butyric acid* [Vol. II] through α-crotonic acid [54; K], αβ-dibrombutyric acid by bromination (Körner, Ann. 137, 234; Michael and Norton, Am. Ch. Journ. 2, 12; Ber. 14, 1202: see also Kolbe, Journ. pr. Ch. [2] 25, 396), and β-methylglyceric (αβ-dihydroxybutyric = 2 : 3 - butanediol-carboxylic) acid by boiling the latter with water (Kolbe, *loc. cit.* 390). Formic aldehyde is among the products of the electrolysis of potassium β-methylglycerate (Pisarjevsky, Journ. Russ. Soc. 29, 289).

Crotonic acid also gives β-methylglyceric acid by oxidation in alkaline solution with barium permanganate (Fittig and Kochs, Ann. 268, 8).

Or crotonic acid combines with hypobromous acid to form (with α-) some β-brom-α-hydroxybutyric acid, which on heating with water gives β-methylglyceric acid (Melikoff, Ann. **266**, 425; Journ. pr. Ch. [2] **61**, 554).

Or crotonic acid combines with hypochlorous acid to give α-chlor-β-hydroxybutyric acid (Erlenmeyer and Müller, Ber. **15**, 49; Melikoff, Ann. 234, 198), which by the action of alcoholic potash is converted into β-methylglycidic acid (Melikoff, *loc. cit.* 204). The latter on heating with water at 100° gives β-methylglyceric acid (*Ibid.* 208; and Ber. **21**, 2055), from which formic aldehyde can be obtained as above.

Or β-methylglycidic acid (potassium salt) itself can be electrolysed (Pisarjevsky, *loc. cit.*).

[**K.**] From *β-hydroxybutyric acid* [Vol. II] through α-crotonic acid [**54**; **L**], and then as under **J**. *Crotonic aldehyde* is among the products of electrolysis of β-hydroxybutyric acid (v. Miller and Hofer, Ber. **27**, 469).

[**L.**] From *acetoacetic ester* [Vol. II] through α-crotonic acid [**54**; **I**], and then as above.

[**M.**] From *glycerol* [**48**] and *hydrogen cyanide* [**172**] through allyl cyanide [**54**; **F**], αβ-dibrombutyronitrile by bromination, and the acid by hydrolysis (Palmer, Am. Ch. Journ. **11**, 92). Subsequent steps as above under **J**.

Or from glycerol through glyceric acid and pyroracemic acid [**54**; **F**], and then as under **H** and **J**. Formic aldehyde is among the products of electrolysis of potassium glycerate (v. Miller and Hofer, Ber. **27**, 469). Silver glycerate gives formic aldehyde on decomposition by iodine (Herzog and Leiser, Monats. **22**, 357).

Glycerol on electrolysis in dilute sulphuric acid solution gives 'trioxymethylene' among other products (Renard, Ann. Chim. [5] **17**, 321: see also Bartoli and Papasogli, Gazz. **13**, 287), and then as under **D**.

Or from glycerol through trimethylene (see under n-propyl alcohol [**15**; **E**]), which gives formic aldehyde when passed with air through a red-hot tube (Wolkoff and Menschutkin, Ber. **31**, 3067).

Or from glycerol through allyl alcohol (see under ethyl alcohol [**14**; **G**]), the latter giving *acroleïn* [**101**] and then formic aldehyde by 'contact' oxidation over heated platinum (Trillat, Comp. Rend. **123**, 822).

[**N.**] From *propionic acid* [Vol. II] through pyroracemic acid [**54**; **O**], and then as under **H**, &c.

Or from propionyl chloride and zinc methyl through tertiary amyl alcohol (see under aldehyde [**92**; **E**]). The latter gives formic aldehyde among the products formed by passing the vapour mixed with air over a heated platinum spiral (Trillat, Comp. Rend. **132**, 1495).

[**O.**] From *tartaric* or *racemic* acid [Vol. II] through pyroracemic acid [**54**; **N**], and then as above. Formic aldehyde is among the products of electrolysis of potassium tartrate (v. Miller and Hofer, Ber. **27**, 468).

Or from tartaric acid through dihydroxymaleïc acid and glycollic aldehyde (see under furfural [**126**; **E**]). The oxime of the latter on treatment with acetic anhydride and sodium acetate gives the acetyl derivative of the nitrile, and this, on treatment with ammoniacal silver oxide and distillation of the product with dilute sulphuric acid, yields formic aldehyde (Fenton, Proc. Ch. Soc., **16**, 148).

[**P.**] From *allyl isothiocyanate* [**166**] through allyl cyanide [**54**; **J**], and then through αβ-dibrombutyric acid, &c., as under **M**.

[**Q.**] From *malonic acid* [Vol. II] by electrolysis of a solution of the potassium salt (Petersen, Zeit. physik. Ch. **33**, 714).

Or from malonic and *acetic acids* [Vol. II], and *aldehyde* [**92**: paraldehyde] through α-crotonic acid [**54**; **G**], and then as under **J**.

[**R.**] From *erythritol* [**50**] and *formic acid* [Vol. II] through *crotonic aldehyde* [**102**] (see under normal butyl alcohol [**17**; **I**]), and crotonic acid (see also under benzyl alcohol [**54**; **H**]), and then as under **J**.

[**S.**] From *mannitol* [**51**], 'trioxymethylene' being among the products of its electrolysis in dilute sulphuric acid solution (Renard, Ann. Chim. [5]

17, 321). Or from mannitol through n-hexane (n-hexyl alcohol [23; B]), and then as below under V.

NOTE:—Generators of n-hexane given under n-hexyl alcohol thus become generators of formic aldehyde.

[T.] From *malic acid* [Vol. II]. Crotonic aldehyde is among the products of electrolysis of sodium malate (v. Miller and Hofer, Ber. 27, 470), and can be converted into crotonic acid, &c., as under F and J.

[U.] *Dextrose* [154] gives 'trioxymethylene' among the products of its electrolysis in presence of dilute sulphuric acid (Renard, Ann. Chim. [5] 17, 321), and this is resolved into formic aldehyde as under D.

[V.] From *n-propyl alcohol* [15] through propyl ether (Chancel, Ann. 151, 304; Linnemann, Ann. 161, 37; Norton and Prescott, Am. Ch. Journ. 6, 243). The latter gives formic aldehyde (trace) by pyrogenic decomposition (Tistschenko, Journ. Russ. Soc. 31, 784; Ch. Centr. 1900, 1, 586).

Or the alcohol gives formic aldehyde (2·72 per cent.) by incomplete combustion (Mulliken, Brown, and French, Am. Ch. Journ. 25, 111).

Or from n-propyl alcohol through n-hexane (n-hexyl alcohol [23; A]). The latter when mixed with air and passed over heated platinum gives formic aldehyde (v. Stepski, Monats. 23, 773).

Or from normal or *isopropyl alcohol* [16] through propylene, *acroleïn* [101] (see under benzyl alcohol [54; E]), acrylic, α-chlorlactic, and glyceric acids, &c., as above under M.

NOTE:—All generators of propylene thus become generators of formic aldehyde (see under isopropyl alcohol [16] and under glycerol [48] for generators of propylene).

[W.] From *acetal* [93] through glycollic aldehyde (see under furfural [126; F]), and then as above under O.

[X.] From *isobutyl alcohol* [18], being among the products of slow combustion of the vapour in contact with heated platinum (v. Stepski, Monats. 23, 773).

Or from *tertiary butyl alcohol* [19] by incomplete combustion (5·17 per cent.: Mulliken, Brown, and French, Am. Ch. Journ. 25, 111), or by passing the vapour mixed with air over a heated platinum spiral, acetone being simultaneously formed (Trillat, Comp. Rend. 132, 1495).

Or from this last alcohol and *potassium cyanide* [172], the alcohol being converted into tertiary butyl iodide and cyanide, and the latter reduced to trimethylethylamine, the hydrochloride of which gives tertiary amyl alcohol by the action of silver nitrite (Tissier, Ann. Chim. [6] 29, 335; Freund and Lenze, Ber. 24, 2150). From tertiary amyl alcohol as above under N.

[Y.] From *amyl alcohol* [22] through amylene (trimethylethylene) and tertiary amyl alcohol (see under acetone [106; E]), and then as above under N. Formic aldehyde (2·01 per cent.) is also formed by the incomplete combustion of amylene (Mulliken, Brown, and French, *loc. cit.*).

[Z.] From *choline* [Vol. II] through *glycol* [45] and glycollic aldehyde (as under furfural [126; H; K]), and then as above under O.

[AA.] From *trimethylamine* [Vol. II] through methyl chloride (see under methane [1; Z]). From the latter through methylene chloride, methylal, &c., as above under C.

[BB.] From *acroleïn* [101] through acrylic acid by oxidation, and from the latter through α-chlorlactic, oxyacrylic (glycidic), and glyceric acids to pyroracemic, crotonic, and β-methylglyceric acids as above under D and M.

[CC.] From *crotonic aldehyde* [102] through crotonic to β-methylglyceric acid as above under M, H, and J.

[DD.] From *isobutyric* and *acetic aldehydes* [94; 92] through the aldol, $C_6H_{12}O_2$, trimethylethylene-lactic acid, and tertiary amyl alcohol (see under acetone [106; DD]). From the latter as above under N.

[EE.] From *isobutyric acid* [Vol. II] and *acetic aldehyde* [92] through trimethylethylene-lactic acid (see under acetone [106; K]), and then through tertiary amyl alcohol, &c., as above.

[FF.] *Pentane* gives formic aldehyde (0·88 per cent.) among the products of

its incomplete combustion (Mulliken, Brown, and French, Am. Ch. Journ. **25**, 111).

NOTE :—Generators of pentane as given under n-amyl alcohol [20, B ; C ; D, &c.] are : *acetic acid* ; *acetone* [106], *acetic acid* and *ethyl alcohol* [14] ; *pyridine* ; *piperidine* ; *methyl* and *n-butyl alcohols* [13 ; 17] ; *ethyl* and *n-propyl alcohols* [14 ; 15].

Generators of hexane are also generators of pentane (see under n-amyl alcohol [20 ; G ; H ; I ; J]). For similar production from isopentane see v. Stepski, Monats. 23, 773.

[GG.] From *citric acid* [Vol. II] through acetonedicarboxylic, β-oxyglutaric, vinylacetic, and crotonic acid (see under n-propyl alcohol [15 ; W]). From crotonic acid as above under J.

[HH.] *Methylamine* [Vol. II] gives the oxime of formic aldehyde among the products of its oxidation by monopersulphuric acid (Bamberger and Seligman, Ber. **35**, 4299).

92. Acetic Aldehyde; Acetaldehyde; Ethanal.

$$\begin{matrix} CH_3 \\ | \\ H.C:O \end{matrix}$$

Natural Sources.

A product of the anaerobic fermentation of sugar (Schutzenberger and Destrem, Jahresber. **1879**, 1007 : see also Roeser, Ann. Inst. Past. **7**, 41). The production of aldehyde from sugar by *Mucor racemosus* was first observed by Fitz (Ber. **6**, 48 : the mould is erroneously named *M. mucedo* in this paper) and by *M. circellinoïdes* by Gayon (Ann. Chim. [5] **14**, 285 ; Comp. Rend. **86**, 52 ; Bull. Soc. [2] **31**, 139).

Among the products of the methane fermentation of cellulose by bacteria from intestine of oxen (see under methane [1]). A product of the alcoholic fermentation of dextrose and lævulose by *Oïdium albicans* (Linossier and Roux, Comp. Rend. **110**, 355; 868 ; Bull. Soc. [3] **4**, 704).

Aldehyde (trace) was found among the products of fermentation of saccharose by an ellipsoidal yeast (Claudon and Morin, Comp. Rend. **104**, 1109 ; Bull. Soc. [2] **49**, 178).

Aldehyde is a product of fermentation by the mould-fungus, *Eurotiopsis gayoni* (Duclaux, Journ. Fed. Inst. **6**, 412). This mould can produce aldehyde from lactic acid when grown in a nutrient solution containing the acid (Mazé, Comp. Rend. **134**, 240 : see also Ann. Inst. Past. **16**, 433) and probably from dextrose through alcohol (*Ibid.* Ann. Inst. Past. **16**, 346).

According to Böttinger, aldehyde is invariably present in fermentation acetic acid (Ch. Zeit. **24**, 793).

Aldehyde is among the products of fermentation of dextrose by Dunbar's and other *Vibrios* (Gosio : quoted by Emmerling, 'Die Zersetzung stickstoffreier organischer Substanzen durch Bakterien,' pp. 47 and 56), and of starch by *Bacillus suaveolens* (Sclavo and Gosio, Bied. Centr. **20**, 419 ; Journ. Ch. Soc. **60**, abst. 1284).

Aldehyde occurs in certain brandies, in the first runnings from the rectification of crude spirit, and in certain fusel oils (see, for instance, Pierre and Puchot, Ann. **163**, 253 ; Krämer and Pinner, Ber. **2**, 403 ; **4**, 787 ; Kekulé, Ber. **4**, 718 ; Rabuteau, Comp. Rend. **87**, 501 ; Ordonneau, Comp. Rend. **102**, 217 ; Allen, Journ. Fed. Inst. **3**, 38 and 43). It is doubtful whether the aldehyde in these cases is of biochemical origin or due to secondary oxidation.

Acetic aldehyde occurs in American oil of peppermint (Power and Kleber, Pharm. Rund. **12**, 157 ; Arch. Pharm. **232**, 639 ; Zeit. anal. Ch. **33**, 762) and in the first (aqueous) distillates from oil of camphor from *Laurus camphora* (Gildemeister and Hoffmann, p. 485), and from oil of aniseed from *Pimpinella anisum* (*Ibid.* 734).

Synthetical Processes.

[A.] From *acetylene* (see under methane [1 ; A]), by absorption of this gas by 1·35 sp. gr. sulphuric acid, and distillation of the product with water (Lagermark and Eltekoff, Ber. **10**, 637 : see also Zeisel, Ann. **191**, 372 ;

Erdmann and Köthner, Zeit. anorg. Ch. **18**, 48), or by the action of mercuric bromide on acetylene and water (Kutscheroff, Ber. **14**, 1540); also by combining acetylene with mercuric chloride and decomposing the compound with dilute hydrochloric acid (*Ibid.* **17**, 13; Krüger and Pückert, Ch. Ind. 1895, p. 454: see also Travers and Plimpton, Trans. Ch. Soc. **65**, 265).

Acetylene also combines with mercuric nitrate to form a compound which readily gives aldehyde on decomposition (Köthner, Inaug. Diss. Halle, 1896; Erdmann and Köthner, *loc. cit.*; Ber. **31**, 2475; K. A. Hofmann, Ber. **31**, 2212; 2783). Acetylene forms a compound with mercuric acetate which decomposes on heating with acids with the formation of aldehyde (Burkard and Travers, Trans. Ch. Soc. **81**, 1271).

Aldehyde is formed when acetylene is passed through boiling phosphoric acid (1·15 sp. gr.) or sulphuric acid (30 per cent.) containing mercuric oxide in suspension (Erdmann and Köthner, *loc. cit.*).

Aldehyde is among the products of oxidation of acetylene by hydrogen peroxide in presence of ferrous sulphate (Cross, Bevan, and Heiberg, Ber. **33**, 2015).

Acetylene combines with water to form aldehyde above 300° (Desgrez, Ann. Chim. [7] **3**, 216).

Or from *ethylene* by heating with carbon dioxide at 400° (Schützenberger, Bull. Soc. [2] **31**, 482); or from ethylene dibromide and water at 150–160° (Carius, Ann. **131**, 172), or from the dibromide through vinyl bromide and the action of mercuric acetate on the latter (Saytzeff, Zeit. [2] **3**, 675; Linnemann, Ann. **143**, 347).

Also from ethylene through *glycol* [45]. The latter gives aldehyde when heated with water to 210° (Nevolé, Bull. Soc. [2] **25**, 289), or with zinc chloride (Wurtz, Ann. **108**, 915: see also Lieben, Monats. **23**, 60).

Or ethylene can be combined with hypochlorous acid to form chlorethyl alcohol = glycol chlorhydrin (Carius, Ann. **126**, 197), which on treatment with potassium iodide gives glycol iodhydrin (Butleroff and Ossokin, Ann. **144**, 42). The latter, on heating with lead hydroxide, gives aldehyde quantitatively (Charon and Paix-Séailles, Comp. Rend. **130**, 1407).

Glycol chlorhydrin gives aldehyde among the products of decomposition by heating in contact with lead or zinc oxide. (Kaschirsky, Ber. **10**, 1104), or (in small quantity) by heating with water (Krassusky, Journ. Russ. Soc. **34**, 287). Or the chlorhydrin, on treatment with potash, gives ethylene oxide (Wurtz, Ann. Chim. [3] **69**, 317; Ann. **110**, 125; Demole, Ann. **173**, 125). The latter yields aldehyde more readily than the glycol when heated with zinc chloride (Krassusky, *loc. cit.* 537).

According to Berthelot, aldehyde is formed by the oxidation of ethylene with chromic acid (Comp. Rend. **68**, 334).

The 'ethylenic nitrate' formed by the combination of ethylene with nitric anhydride gives aldehyde on reduction (Demjanoff, Ch. Centr. 1899, **1**, 1064).

[B.] *Methane* [1] and carbon monoxide give aldehyde under the influence of the silent electric discharge (Losanitsch and Jovitschitsch, Ber. **30**, 137).

Ethane and carbon monoxide also give aldehyde by this method (De Hemptinne, Bull. Acad. Roy. Belg. [3] **34**, 269).

Or from ethane and air by passing over hot copper or asbestos, &c. (Glock, Germ. Pat. 109015 of 1899; Ch. Centr. 1900, **2**, 304).

Note:—All generators of ethane (see under ethyl alcohol [14; A; D, &c.]) thus become generators of aldehyde.

[C.] From *ethyl alcohol* [14] by oxidation (Döbereiner, Gmelin's 'Handbuch d. org. Ch.' IV, 556; 585; 611; Liebig, Ann. **14**, 133; W. and R. Rodgers, Journ. pr. Ch. **40**, 240; Städeler, *Ibid.* **76**, 54: for conditions determining the electrolytic oxidation of alcohol to aldehyde see Dony-Hénault, Zeit. Elektroch. **6**, 533).

Or from ethyl alcohol through its

ether, the latter giving acetaldehyde among the products of its photochemical oxidation (Berthelot, Comp. Rend. **129**, 627), or by passing through a hot tube (Liebig, Ann. **14**, 134; Tistschenko, Journ. Russ. Soc. **31**, 784; Ch. Centr. 1900, **1**, 586).

From alcohol by chemical, aided by electrolytic, oxidation (Darmstädter, Germ. Pat. 109012 of 1897; Ch. Centr. 1900, **2**, 151); or by electrolysis in presence of sulphuric acid (Elbs and Brunner, Zeit. Elektroch. **6**, 604). Among the products of photo-oxidation of alcohol by ferric chloride (De Coninck, Comp. Rend. **131**, 275), and among the products of pyrogenic decomposition (Ipatieff, Ber. **34**, 598): the yield is increased by the pyrogenic 'contact' influence of certain metals, such as iron or zinc, &c., or certain metallic oxides (*Ibid.* **34**, 3579; **35**, 1047).

Ethyl alcohol is oxidised to aldehyde by quinones, ketones, benzaldehyde, and anisaldehyde in presence of light (Ciamician and Silber, Ber. **34**, 1530).

Magnesium ethylate gives aldehyde when acted upon by dry chlorine (Meunier, Comp. Rend. **134**, 472).

Ethyl hypochlorite decomposes spontaneously into aldehyde and hydrogen chloride (Schmitt and Goldberg, Journ. pr. Ch. [2] **19**, 393; **24**, 106).

[D.] From *formic* and *acetic* acids [Vol. II] by distilling a mixture of the dry calcium salts (Ritter, Ann. **97**, 369).

Or from acetic acid through acetyl cyanide and pyroracemic acid (see under benzyl alcohol [**54**; **I**]), and then as below under **E**.

Formylacetic ethyl ester (see under cymene [**6**; IX]), when boiled with dilute sulphuric acid, gives aldehyde among other products (Wislicenus and Bindemann, Ann. **316**, 18).

[E.] From *propionic acid* [Vol. II], being among the products of electrolysis of sodium propionate in presence of sodium perchlorate (Hofer and Moest, Ann. **323**, 284).

Or from propionic acid through ethane by photochemical decomposition in presence of uranium salts, or through ethylene by electrolysis (see under ethyl alcohol [**14**; **H**]). Ethane yields aldehyde as under **B**, and ethylene as under **A**.

Or from propionic acid and *methyl alcohol* [**13**] through tertiary amyl alcohol by the interaction of propionyl chloride and zinc methyl (Popoff, Ann. **145**, 293; Jermolajeff, Zeit. [2] **7**, 275; Wischnegradsky, Ann. **190**, 336), the corresponding iodide, and amylene (trimethylethylene) by the action of alcoholic potash on the latter. According to Wagner (Ber. **21**, 1235), acetic aldehyde is among the products of oxidation of this amylene.

Or from propionic acid through the α-bromo-acid by bromination (Friedel and Machuca, Comp. Rend. **53**, 408; Ann. **120**, 286; Bischoff, Ann. **206**, 319; Zelinsky, Ber. **20**, 2026; Michael and Graves, Ber. **34**, 4044), the α-cyano-acid by the action of *potassium cyanide* [**172**], and hydrolysis of the latter to isosuccinic (methylmalonic) acid (Wichelhaus, Zeit. [2] **3**, 247; Byk, Journ. pr. Ch. [2] **1**, 19; Cohn, Ann. **251**, 335; Pusch, Arch. Pharm. **232**, 188). Acetic aldehyde (trace) is among the products of electrolysis of the potassium salt of this latter acid (Petersen, Ch. Centr. 1897, **2**, 519; Zeit. physik. Ch. **33**, 702).

Or from propionic acid through pyroracemic acid (see under benzyl alcohol [**54**; **O**]). The latter, on heating with dilute sulphuric acid at 150°, gives aldehyde (Beilstein and Wiegand, Ber. **17**, 840). Pyroracemic acid also yields aldehyde among the products of its electrolytic oxidation (Rockwell, Journ. Am. Ch. Soc. **24**, 719).

Or $\alpha\beta$-dibrompropionic acid can be converted into acrylic acid by treatment with zinc and sulphuric acid (Caspary and Tollens, Ann. **167**, 241; Melikoff, Journ. Russ. Soc. **13**, 156), and the latter into β-chlorlactic acid by the addition of hypochlorous acid (Melikoff *loc. cit.* 157). β-Chlorlactic acid gives aldehyde on heating with water, or by boiling a strong solution of the sodium salt (Erlenmeyer, Ber. **13**, 309; Reisse, Ann. **257**, 337).

[F.] From *malonic acid* [Vol. II], *methyl* and *ethyl alcohols* [**13**; **14**],

through isosuccinic (methylmalonic) acid by the action of methyl iodide on sodiomalonic ester (Züblin, Ber. **12**, 1112), and then as above under **E**.

Or from malonic acid through ethylene by electrolysis (see under ethyl alcohol [**14**; **W**]), and then as above under **A**.

[**G**.] From *succinic acid* [Vol. II] through ethylene by electrolysis [**14**; **X**], and then as under **A**.

Or through dibromsuccinic acid by bromination (Kekulé, Ann. **117**, 123; Suppl. **1**, 131: see also under methane [**1**; **T**]), and the action of boiling water on the dibromo-acid or its salts (Lossen and Riebensahm, Ann. **292**, 295; Lossen, Ann. **300**, 1; Lossen and Reisch, *Ibid.* 5).

Aldehyde is among the products of electrolysis of potassium succinate (Petersen, Zeit. physik. Ch. **33**, 711).

Or from succinic acid through acetylenedicarboxylic acid (see under methane [**1**; **T**]). The latter gives aldehyde (and paraldehyde) on heating with water to 300° (Desgrez, Ann. Chim. [7] **3**, 219).

[**H**.] From *lactic acid* [Vol. II] by oxidation with various oxidising compounds (Liebig; Städeler, Ann. **69**, 332), or by heating with dilute sulphuric acid at 130° (Erlenmeyer, Zeit. [2] **4**, 343). Also by electrolysis of a strong solution of the potassium salt (Kolbe, Ann. **113**, 244; Brester, Zeit. [2] **2**, 680; v. Miller and Hofer, Ber. **27**, 468), or by the action of iodine on the silver salt (Herzog and Leiser, Monats. **22**, 357).

Also from lactic acid through pyroracemic acid (see under benzyl alcohol [**54**; **P**]), and then as under **E**.

Or lactic ester can be converted into lactic hydrazide by the action of hydrazine, and the hydrazide into the azide by nitrous acid. The azide hydrolyses to acetic aldehyde, &c. (Curtius and Aufhäuser, Ber. **34**, 2796).

Sarcolactic acid [Vol. II] gives acetic aldehyde under similar conditions to those which give rise to this aldehyde from ordinary lactic acid (for electrolysis see v. Miller and Hofer, *loc. cit.*).

[**I**.] From *tartaric* or *racemic* acid [Vol. II] through pyroracemic acid [**54**; **N**], and then as under **E**. Aldehyde is among the products of the distillation of tartaric acid (Völckel, Ann. **89**, 57).

[**J**.] From *glycerol* [**48**] through glyceric acid and pyroracemic acid [**54**; **F**], and then as under **E**.

Or from glycerol and *potassium cyanide* [**172**] through allyl cyanide [**54**; **F**] and β-methylglyceric acid (see under formic aldehyde [**91**; **M** and **J**]). Acetic aldehyde is among the products of electrolysis of potassium β-methylglycerate (Pisarjevsky, Journ. Russ. Soc. **29**, 289).

Or glycerol may be converted into *acroleïn* [**101**] by dehydration (Redtenbacher, Ann. **47**, 120; Geuther and Cartmell, Ann. **112**, 2; Hübner, Ann. **114**, 35; Van Romburgh, Bull. Soc. [2] **36**, 549; Wagner, Journ. Russ. Soc. **16**, 317; Griner, Ann. Chim. [6] **26**, 367; Aronstein, Ann. Suppl. **3**, 180; Fischer, Ber. **20**, 3388; Wohl and Neuberg, Ber. **32**, 1352; Wöhlk, Journ. pr. Ch. [2] **61**, 200), acrylic acid by oxidation of the latter (Redtenbacher, *loc. cit.* 125; Claus, Ann. Suppl. **2**, 123), and β-chlorlactic acid by the addition of hypochlorous acid to acrylic acid (Melikoff, Journ. Russ. Soc. **13**, 157). β-Chlorlactic acid gives aldehyde as above under **E**.

Or acroleïn and *ethyl alcohol* [**14**] combine under the influence of hydrogen chloride to form β-chlorpropionacetal (Wohl, Ber. **21**, 618; **31**, 1796). The latter is converted by the action of alkali into the β-hydroxy-acetal, and this by oxidation with potassium permanganate gives β-diethoxypropionic acid. The latter, on heating with dilute sulphuric acid at 50°, yields the semi-aldehyde of malonic acid, which is resolved above 50° into carbon dioxide and acetic aldehyde (Wohl and Emmerich, Ber. **33**, 2760).

Or from glycerol through glyceric acid, α-chlorlactic acid by the action of hydrochloric acid on the latter (Werigo and Melikoff, Ber. **12**, 178), oxyacrylic (glycidic) acid by the action of alcoholic potash (Melikoff, Ber. **13**, 271; Journ. Russ. Soc. **13**, 211), β-chlorlactic acid

by addition of hydrogen chloride (*Ibid.* Journ. Russ. Soc. **13**, 157), and then as above.

Glycerol may also be converted into α-chlorlactic acid through αβ-dichlorpropyl alcohol by the action of chlorine on allyl alcohol (Tollens, Ann. **156**, 164; Hübner and Müller, Ann. **159**, 168), by the addition of hypochlorous acid to allyl chloride (v. Gegerfeldt, Ann. **154**, 247; Ber. **6**, 720; Henry, Ber. **3**, 352; **7**, 414), or by the direct action of dry hydrogen chloride (Fauconnier and Sanson, Bull. Soc. [2] **48**, 236). The αβ-dichlorpropyl alcohol gives αβ-dichlorpropionic acid on oxidation (Henry, Ber. **7**, 414; Werigo and Melikoff, Ber. **10**, 1500), and the latter yields α-chlorlactic acid by the action of water (Melikoff, Ber. **12**, 2227).

Or glyceric acid may be converted into β-iodopropionic acid by the action of phosphorus iodide (Beilstein, Ann. **120**, 226; **122**, 366; Erlenmeyer, Ann. **191**, 284; Meyer, Ber. **19**, 3294; **21**, 24). The iodo-acid gives acrylic acid by the action of alcoholic potash, or by heating with lead oxide (Schneider and Erlenmeyer, Ber. **3**, 339; Wislicenus, Ann. **166**, 2), and this can be converted into β-chlorlactic acid and aldehyde as above.

Or from glycerol through α-epichlorhydrin by the action of phosphorus pentachloride, or by the action of hydrochloric acid or alkali on dichlorhydrin (Berthelot, Ann. Chim. [3] **41**, 299; Reboul, Ann. Suppl. **1**, 221; Prevost, Journ. pr. Ch. [2] **12**, 160; Fauconnier, Bull. Soc. [2] **50**, 213). Epichlorhydrin on oxidation with nitric acid gives β-chlorlactic acid (Richter, Journ. pr. Ch. [2] **20**, 193), from which aldehyde can be obtained as above.

Acetic aldehyde is among the products of the dry distillation of the calcium derivative of glycerol (Destrem, Ann. Chim. [5] **27**, 20).

[**K.**] From *normal butyric acid* [Vol. II] through α-crotonic acid (see under benzyl alcohol [**54**; **K**]), and β-methylglyceric = αβ-dihydroxybutyric acid (see under formic aldehyde [**91**; **J**]), and then as above under **J**.

Or α-crotonic acid gives aldehyde directly by oxidation with chromic acid mixture (Kekulé, Ann. **162**, 315).

Or from *isobutyric acid* [Vol. II] through α-hydroxyisobutyric = 2-methyl-2-propanolic acid by oxidation with potassium permanganate (Meyer, Ann. **219**, 240). The acid gives aldehyde among other products by the action of heat or dehydrating agents (Scholtz, 'Der Einfluss der Raumerfüllung der Atomgruppen auf den Verlauf chemischer Reaktionen,' 1899, p. 363; Bischoff and Walden, Ann. **279**, 111).

Or isobutyric acid can be brominated (Markownikoff, Ann. **153**, 229; Hell and Waldbauer, Ber. **10**, 448), the α-bromo-acid converted into the hydroxy-acid by treatment with barium hydroxide or sodium carbonate solution (Markownikoff, *loc. cit.*; Fittig, Ann. **200**, 70), and then as above.

Or isobutyric acid (or chloride) on chlorination gives, with other products, α-chlorisobutyric acid (Balbiano, Ber. **11**, 1693; Michael and Garner, Ber. **34**, 4054), and this yields the hydroxy-acid on heating with water at 180° (Ostropjatoff, Journ. Russ. Soc. **28**, 51).

[**L.**] From *acetoacetic ester* [Vol. II] through α-crotonic acid (see under benzyl alcohol [**54**; **I**]), or through β-methylglyceric acid (see under formic aldehyde [**91**; **L** and **J**]), and then as above under **J** and **K**.

Or acetoacetic ester may be converted into its methylpropyl-derivative by the alternate introduction of methyl and propyl by the action of the alkyl iodides on sodio-acetoacetic ester (Liebermann and Kleemann, Ber. **17**, 918; Jones, Ann. **226**, 287). Methylpropyl-acetoacetic ester on reduction with sodium amalgam gives α-methylpropyl-β-hydroxybutyric (3-methyl-2-hexanol-3-carboxylic) acid (Jones, *loc. cit.* 288), and this on dry distillation breaks down into acetic aldehyde and methylpropyl-acetic acid.

Or instead of methyl and propyl two other alkyls may be introduced into acetoacetic ester, such as two ethyls, giving rise to α-diethyl-β-hydroxybutyric (3-ethyl-2-pentanol-3-carboxylic) acid by reduction with sodium amalgam as above (Schnapp, Ann. **201**, 65).

This acid on dry distillation also breaks down into acetaldehyde and diethylacetic acid.

NOTE :—This synthesis of aldehyde from dialkyl-β-hydroxybutyric acids is general whatever the alkyls may be (Reformatsky, Journ. pr. Ch. [2] 54, 477).

Or from acetoacetic ester through 'oxymesitenedicarbonic' acid and its anhydride (lactone) which is formed by the action of hydrochloric or sulphuric acid on the ester (Duisberg, Ann. 213, 177; Polonowska, Ber. 19, 2402; Anschütz, Bendix, and Kerp, Ann. 259, 153). The lactone on distillation with lime gives mesityl oxide (Hantzsch, Ann. 222, 21), and this can be converted into hydroxyisobutyric acid as below under S, and aldehyde as above under K.

[M.] From *β-hydroxybutyric acid* [Vol. II] through *α*-crotonic acid (see under benzyl alcohol [54; L]), or through β-methylglyceric acid (see under formic aldehyde [91; K]), and then as under J and K.

[N.] From *erythritol* [50] and *formic acid* [Vol. II] through *α-crotonic aldehyde* [102] and acid, or through β-methylglyceric acid (see under formic aldehyde [91; R]), and then as under J and K.

[O.] From *allyl isothiocyanate* [166] through β-methylglyceric acid [91; P], and then as under J.

[P.] From *fumaric* or *maleïc acids* [Vol. II] through acetylene (see under methane [1; U]), and then as above under A.

Or from fumaric acid through dibromsuccinic acid by the addition of bromine (Kekulé, Ann. 117, 123; Suppl. 1, 131; Baeyer, Ber. 18, 676), and then as under G.

Or from maleïc acid through isodibromsuccinic acid by the addition of bromine (Kekulé, Ann. Suppl. 2, 89), and decomposition of the isodibromsuccinates by boiling with water (Lossen and Reisch, Ann. 300, 5).

[Q.] From *malic acid* [Vol. II], being formed in small quantity by the electrolysis of a strong solution of the potassium or sodium salt (Bourgoin, Bull. Soc. [2] 9, 427; v. Miller and Hofer, Ber. 27, 470).

Also by boiling the aqueous solution of the acid with manganese dioxide (Liebig, Ann. 113, 14), by heating with dilute sulphuric acid at 135° (Weith, Ber. 10, 1744), or by oxidation with potassium permanganate (Denigès, Comp. Rend. 130, 32).

[R.] *Tiglic acid* [Vol. II] gives aldehyde on oxidation with potassium permanganate (Beilstein and Wiegand, Ber. 17, 2262).

[S.] From *acetone* [106] through the dibromide or diiodo-derivative (see under glycerol [48; E]), *acroleïn* [101], acrylic acid, β-chlorlactic acid, &c., as above under J.

Or from acetone and *hydrogen cyanide* [172], which condense in the presence of hydrochloric acid to form hydroxyisobutyric acid (Staedeler, Ann. 111, 320; Markownikoff, Ann. 146, 339). The latter gives aldehyde as above under K.

Or from acetone and *chloroform* [1; D], which condense in the presence of caustic alkali to form 'acetone-chloroform' (see under tertiary butyl alcohol [19; D]). The latter gives hydroxyisobutyric acid on heating with water or dilute alkali (Willgerodt, Ber. 15, 2307; Willgerodt and Schiff, Journ. pr. Ch. [2] 41, 519).

Acetone by the action of sulphuric acid, of lime, or of hydrogen chloride followed by caustic alkali or water gives mesityl oxide = 2-methyl-2-pentenone-4 (Kane, Phil. Trans. 44, 475; Fittig, Ann. 110, 32; Kasanzeff, Journ. Russ. Soc. 7, 173; Baeyer, Ann. 140, 297; Claisen, Ann. 180, 4; Freer and Lachman, Am. Ch. Journ. 19, 887, note). Or mesityl oxide results from the action of *zinc methyl* or *ethyl* (Pawloff, Ber. 9, 1311; Ann. 188, 130), or of *acetyl chloride* on acetone (Beilstein and Wiegand, Bull. Soc. [2] 38, 167). Mesityl oxide gives hydroxyisobutyric acid on oxidation with potassium permanganate (Pinner, Ber. 15, 591).

Acetone and ammonia condense in the presence of acids to form diacetonamine (Heintz, Ann. 174, 154; 189, 214). The latter (or its salts) gives mesityl oxide on dry distillation (Soko-

loff and Latschinoff, Ber. 7, 1387; 1777; Heintz, Ann. 174, 156; 175, 252; 181, 70).

Diacetonamine salts also give mesityl oxide (with diacetone alcohol) on treatment with potassium nitrite (Sokoloff and Latschinoff, *loc. cit.*; Heintz, Ann. 178, 342). Diacetone alcohol also gives mesityl oxide on treatment with strong sulphuric acid (Heintz, Ann. 178, 351).

Or diacetonamine on oxidation with chromic acid mixture gives α-aminoisobutyric acid (Heintz, Ann. 198, 46), and this yields hydroxyisobutyric acid by the action of nitrous acid (Tiemann and Friedländer, Ber. 14, 1973), from which aldehyde can be obtained as under **K**.

[**T.**] *Dextrose* [154] gives acetic aldehyde among other products on oxidation with sulphuric acid and manganese dioxide (Liebig, Ann. 113, 16).

'Invert sugar' (dextrose and lævulose) gives this aldehyde on electrolysis of the aqueous solution in presence of sulphuric acid (H. T. Brown, Journ. Ch. Soc. 25, 578).

[**U.**] *Ethylamine* [Vol. II] gives aldehyde among other products on oxidation with chromic acid mixture (Wanklyn and Chapman, Journ. Ch. Soc. 20, 328), and the oxime of the aldehyde among the products of oxidation by monopersulphuric acid (Bamberger, Ber. 35, 4293).

[**V.**] *Alanine* [Vol. II] gives aldehyde on boiling its aqueous solution with lead peroxide, on heating *per se*, or on heating with strong phosphoric acid solution at 220° (Drechsel, Ber. 25, 3503).

[**W.**] *Choline* [Vol. II] on boiling in concentrated aqueous solution gives *glycol* [45] and trimethylamine. From the former aldehyde can be obtained as under **A**.

[**X.**] *Furfural* [126] on oxidation gives pyromucic acid (Schwanert, Ann. 114, 63; 116, 257; Volhard, Ann. 261, 379), which on heating with bromine at 100° yields δ-brompyromucic acid (Hill and Sanger, Ann. 232, 46; Ber. 16, 1130). The latter on heating with bromine and water gives isodibromsuccinic acid (H. and S. Ann. 232, 53), which yields aldehyde as under **P**.

[**Y.**] *Citral* [104] on boiling with dilute alkali gives (with methylheptenone) acetaldehyde (Verley, Bull. Soc. [3] 17, 175).

[**Z.**] From *citric acid* [Vol. II] through acetonedicarboxylic acid (see under orcinol [75; **C**]). The latter by the action of strong sulphuric acid yields citracoumalic acid (Nieme and v. Pechmann, Ann. 261, 199), and this on heating at 200° gives the lactone of mesitenecarbonic acid (*Ibid.* 202), from which mesityl oxide can be obtained as under **L**, hydroxyisobutyric acid as under **S**, and aldehyde as under **K**.

Or from acetonedicarboxylic acid through β-oxyglutaric, vinylacetic, and crotonic acid (see under n-propyl alcohol [15; **W**]), and then as above under **K**.

[**AA.**] From *amyl alcohol* from fusel oil [22] through amylene = trimethylethylene (Balard, Ann. Chim. [3] 12, 320; Frankland, Journ. Ch. Soc. 3, 35; Wurtz, Bull. Soc. 5, 301), trimethylethylene bromide, and glycol (see under acetone [106; **E**]). The latter gives hydroxyisobutyric acid on oxidation with nitric acid (Wurtz, Ann. 107, 197). Subsequent treatment as under **K**.

Aldehyde is among the products of oxidation of this amylene by potassium permanganate, the glycol being formed as an intermediate product (Wagner, Ber. 21, 1235).

Or from isoamyl alcohol through the iodide, which gives secondary pentane (4-methylbutane) on heating with zinc and water (Frankland, Ann. 74, 53). The pentane gives hydroxyisobutyric acid among the products of the action of nitric acid (Poni, Ch. Centr. 1902, 2, 16).

[**BB.**] From *oxalic acid* [Vol. II] and *methyl alcohol* [13] through hydroxyisobutyric acid (see under acetone [106; **O**]), and then as above under **K**.

[**CC.**] From *methyl alcohol* [13], acetic aldehyde being among the products obtained by heating aluminium methylate (Tistschenko, Journ. Russ. Soc. 31, 784; Ch. Centr. 1900, 1, 585).

Or from methyl alcohol through ethane (see under ethyl alcohol [14; D]), and then as above under B.

[DD.] *Isobutylene glycol* [47] on treatment with hydrochloric acid gives a chlorhydrin which, on oxidation with nitric acid, yields α-chlorisobutyric acid (Henry, Bull. Soc. [2] 26, 24). From the latter through α-hydroxyisobutyric acid as above under K.

[EE.] *Methylisoeugenol* [80] gives aldehyde among the products of oxidation by potassium permanganate (Kolokoloff, Journ. Russ. Soc. 29, 23; Ch. Centr. 1897, 1, 915).

[FF.] From *isobutyl alcohol* [18], or *tertiary butyl alcohol* [19], through isobutylene [18; A; 19; B] and *acetic acid* [Vol. II]. Isobutylene and acetyl chloride or acetic anhydride condense in presence of zinc chloride to form mesityl oxide (Kondakoff, Journ. Russ. Soc. 26, 12; 232). Subsequent treatment as above under S, &c.

Note :—Generators of isobutylene are given under isobutyl alcohol [18; B; C] and under butyric aldehyde below [94].

93. Acetal; Ethylidenediethyl Ether.

$CH_3 . CH (O . C_2H_5)_2$

Natural Sources.

Occurs in raw spirit after filtration through animal charcoal (Geuther, Ann. 126, 63); also in fusel oil of whisky (Allen, Journ. Fed. Inst. 3, 38). Has been found in forerunnings from spirit rectification (Krämer and Pinner, Ber. 2, 402; 4, 788; Kekulé, Ber. 4, 719).

It is doubtful whether the acetal is a biochemical product or due to secondary reactions.

Synthetical Processes.

[A.] From *ethyl alcohol* [14] by oxidation (Döbereiner, Gmelin's Handb. d. org. Ch. IV, 805; Liebig, Ann. 5, 25; 14, 156; Stas, Ann. Chim. [3] 19, 146; Wurtz, *Ibid.* 48, 370; Ann. 108, 84). By electrolysis (Renard, Ber. 8, 132).

[B.] From *aldehyde* [92] and *ethyl alcohol* [14] by passing hydrogen chloride into a mixture, and acting on the monochlorethyl ether ($CH_3 . CHCl . OC_2H_5$) thus formed with sodium ethylate (Wurtz and Frapolli, Comp. Rend. 47, 418; Ann. 108, 223). Or by passing hydrogen chloride into a mixture of alcohol and aldehyde, and allowing to interact at ordinary temperatures (Fischer and Giebe, Ber. 30, 3053).

Also by converting aldehyde into ethylidene dibromide by the action of phosphorus pentabromide, and the interaction of the dibromide with sodium ethylate (W. and F., *loc. cit.*).

Or from aldehyde by heating with alcohol and acetic acid at 100° (Geuther, Ann. 126, 63), or by passing hydrogen phosphide into a cold mixture of aldehyde and absolute alcohol (Engel and Girard, Comp. Rend. 91, 692; Jahresber. 1880, 694).

Also from aldehyde through α-chlorethyl acetate (Wurtz, Ann. 102, 94), or by the action of acetyl chloride on aldehyde (Simpson, Ann. 109, 156). By the action of bromine at 100–103° α-chlorethyl acetate gives bromethyl bromacetate (Kessel, Ber. 10, 1994; 11, 1916), and the latter ($CH_2Br . CO . O . CHBr . CH_3$), when heated with alcohol, yields acetal among other products (*Ibid.* 11, 1918).

Hydrogen chloride passed into a cooled mixture of alcohol and *hydrogen cyanide* [172] gives formimino-ethyl ether (Pinner, Ber. 16, 354, 1644). The hydrochloride of the latter interacts with acetic aldehyde to form acetal (Claisen, Ber. 31, 1014).

Acetal is best prepared by acting on aldehyde with a 1 per cent. solution of hydrogen chloride in alcohol (Fischer and Giebe, *loc. cit.*).

94. Butyric Aldehyde; Butanal.

$C_3H_7 . CHO$

Natural Sources.

A butyric aldehyde is said to occur in the oil of *Eucalyptus globulus* and in oil of cajeput from *Melaleuca leucaden-*

dron (Voiry, Bull. Soc. [2] **40**, 106; **50**, 108; Comp. Rend. **106**, 1419; 1538). A butyric aldehyde occurs in rancid fat, probably a bacterial product (Nagel, Am. Ch. Journ. **23**, 173).

Synthetical Processes.

The constitution of the natural product has not been determined, so the synthetical methods for both normal and iso-aldehydes are given :—

[A.] *Butyric* and *formic acids* [Vol. II] give the n-aldehyde on distilling a mixture of the dry calcium salts (Lieben and Rossi, Ann. **158**, 146; Linnemann, Ann. **161**, 186; Lipp, Ann. **211**, 355; Kahn, Ber. **18**, 3364).

Or n-butyric acid can be converted into the chloride, and the latter reduced in moist ethereal solution with sodium amalgam (W. H. Perkin, junr., and Sudborough, Proc. Ch. Soc. **10**, 216).

[B.] *Isobutyric acid* [Vol. II] gives the iso-aldehyde by distilling the calcium salt *per se*, or with *calcium formate* [Vol. II] (Popoff, Ber. **6**, 1255; Barbaglia and Gucci, Ber. **13**, 1572; Linnemann and Zotta, Ann. **162**, 7).

[C.] *Isobutyl alcohol* [18] gives the iso-aldehyde on oxidation with chromic acid mixture (Pfeiffer, Ber. **5**, 699; Michaelson, Ann. **133**, 182; Pierre and Puchot, Comp. Rend. **70**, 434; Lipp, Ann. **205**, 2; Fossek, Monats. **2**, 614; W. H. Perkin, junr., Trans. Ch. Soc. **43**, 91). Also by pyrogenic decomposition (Ipatieff, Ber. **34**, 598); especially by the contact action of certain heated metals (*Ibid.* **35**, 1052), or by passing the vapour mixed with air over heated platinum (v. Stepski, Monats. **23**, 773).

Isobutyl hypochlorite is decomposed by hydrochloric acid with the formation of isobutyric aldehyde (Tiesenhold : Krassusky, Journ. Russ. Soc. **34**, 556).

[D.] *Tertiary butyl alcohol* [19] can be converted into isobutylene by acting on the iodide with alcoholic potash, or on the alcohol with sulphuric acid or zinc chloride (Wurtz, Ann. **93**, 107; De Luynes, Comp. Rend. **56**, 1175; Butleroff, Ann. **144**, 19; Zeit. [2] **6**, 236; Konowaloff, Bull. Soc. [2] **34**, 333; Nevolé, Bull. Soc. [2] **24**, 122; Lermontoff, Ann. **196**, 117; Puchot, Ann. Chim. [5] **28**, 508; Scheschukoff, Bull. Soc. [2] **45**, 181). Isobutylene bromide, when heated with water at 160°, gives isobutyric aldehyde (Linnemann and Zotta, Ann. **162**, 36).

Or from isobutylene through the chlorhydrin, which gives isobutyric aldehyde on heating with water or by passing over heated zinc oxide (Krassusky, Journ. Russ. Soc. **34**, 287). Isobutylene oxide (from the chlorhydrin) gives the aldehyde when heated with zinc chloride (*Ibid.* 537).

Or isobutylene by chlorination gives (with an isomeride) isobutenylchloride = 2-methyl-3-chlorpropylene (Scheschukoff, Journ. Russ. Soc. **16**, 495), which, by potassium carbonate and water, is converted into isopropenyl carbinol = 1-hydroxy-2-methylpropylene (*Ibid.* 499). The latter, on heating with water acidified with sulphuric acid, gives isobutyric aldehyde (*Ibid.* 502).

[E.] *Isovaleric acid* [Vol. II] gives isobutylene among the products of the electrolysis of a strong solution of the potassium salt (Kolbe, Ann. **69**, 259), and this can be converted into isobutyric aldehyde as above under **D**.

Or from isovaleric acid through β-dimethylacrylic acid and isobutylene (see under isobutyl alcohol [18; C]).

Or β-dimethylacrylic ester on nitration gives an α-nitro-derivative (Bouveault and Wahl, Comp. Rend. **131**, 687), which, on reduction by sodium in moist ether, or by heating with sodium hydroxide solution, yields nitroisobutylene (*Ibid.* 1211). The latter, on reduction with aluminium amalgam or zinc dust and acetic acid, gives the oxime of isobutyric aldehyde, from which the aldehyde can be obtained by hydrolysis (*Ibid.* **134**, 1145).

Note:—Other generators of β-dimethylacrylic acid given under isobutyl alcohol are *acetone* [106] and *glycerol* [48], or *acetone*, *malonic acid*, and *acetic anhydride*.

Or isovaleric acid can be brominated or chlorinated (Cahours, Ann. Suppl. **2**, 78; Borodin, Ann. **119**, 121; Fittig and Clark, Ann. **139**, 199; Ley and Popoff, Ann. **174**, 63; Schmidt, Ann.

193, 104; Schlebusch, Ann. **141**, 322), and the α-halo-acid converted into α-hydroxyisovaleric acid = 2-methyl-3-butanolic-4-acid (Fittig and Clark, Ann. **139**, 206; Schmidt and Sachtleben, Ann. **193**, 106; Schlebusch, *loc. cit.*). The latter gives isobutyric aldehyde on heating with acids, or by oxidation with chromic acid mixture (Ley and Popoff, *loc. cit.*; Ley, Journ. Russ. Soc. **9**, 131), or with lead peroxide and phosphoric acid (v. Baeyer and H. v. Liebig, Ber. **31**, 2110).

[F.] *Leucine* [Vol. II], on distillation with water and lead peroxide, gives butyric aldehyde (? normal: Liebig, Ann. **70**, 313).

[G.] From *glycerol* [**48**] and *acetone* [**106**] through dimethylallyl carbinol, β-hydroxyisovaleric acid, β-dimethylacrylic acid, and isobutylene or nitroisobutylene (see under isobutyl alcohol [**18**; **D**]), and then as above under **D** or **E**.

[H.] From *isoamyl alcohol* [**22**]. Isobutylene is among the products formed when the vapour of fusel oil is passed through a hot tube (Wurtz, Ann. **104**, 249; Butleroff, Ann. **145**, 277; Ipatieff, Ber. **35**, 1053).

Or from amyl alcohol through amylene (isopropylethylene) (Eltekoff, Ber. **10**, 1904; Wischnegradsky, Ann. **190**, 358). Isobutyric aldehyde is among the products of oxidation of this amylene by potassium permanganate (Wagner, Ber. **21**, 1233).

[I.] From *oxalic acid* [Vol. II], *ethyl alcohol* [**14**], and *isopropyl alcohol* [**16**], through α-hydroxyisovaleric acid by the action of zinc on a mixture of oxalic diethylester and isopropyl iodide, and hydrolysis of the ester thus formed (Markownikoff, Zeit. [2] **6**, 517). Subsequent steps as under **E** above.

[J.] From *crotonic aldehyde* [**102**], n-butyric aldehyde being among the products of reduction (Lieben and Zeisel, Monats. **1**, 825; Charon, Ann. Chim. [7] **17**, 223).

[K.] *Isobutylene glycol* [**47**] gives isobutyric aldehyde on heating with water to 180–200° (Nevolé, Ber. **9**, 448).

95. Valeric Aldehyde; Valeral.

$C_4H_9.CHO$

Natural Sources.

A valeric aldehyde is said to occur in the oils of *Eucalyptus globulus* and of cajeput from *Melaleuca leucadendron* (Voiry: see under butyric aldehyde [**94**]) and (isovaleric aldehyde) in American peppermint oil (Power and Kleber, Zeit. anal. Ch. **33**, 762; Pharm. Rund. **12**, 157; Arch. Pharm. **232**, 639).

A valeric aldehyde probably occurs in the Japanese 'kesso' oil from the root of *Valeriana officinalis* var. *angustifolia* (Bertram and Gildemeister, Arch. Pharm. **228**, 483).

The oil of *Eucalyptus rostrata* contains a valeric aldehyde (Schimmel's Ber. Oct. 1891).

Synthetical Processes.

I. Normal Valeric Aldehyde; Pentanal.

$CH_3.CH_2.CH_2.CH_2.CHO$

[A.] From *normal valeric* and *formic acids* [Vol. II] by distilling a mixture of the calcium salts (Lieben and Rossi, Ann. **159**, 70; Zander, Ann. **224**, 81).

[B.] *Succinic acid* [Vol. II] is converted into the dibromo-acid by bromination (Kekulé, Ann. **117**, 123; Suppl. **1**, 131; Bourgoin, Bull. Soc. [2] **19**, 148; Gorodetzky and Hell, Ber. **21**, 1731; Lassar-Cohn, Ann. **251**, 346). The dibromo-acid, on heating with alcoholic potash, gives acetylenedicarboxylic acid (Bandrowski, Ber. **10**, 838; **12**, 2212; **13**, 2340; **15**, 2694; Baeyer, Ber. **18**, 677; 2269), and the latter (or its acid potassium salt), on heating with water, yields propiolic (propargylic = propinic) acid (Bandrowski, Ber. **13**, 2340), which, by oxidation with cupric hydroxide, is converted into diacetylenedicarboxylic = hexanediinedicarboxylic acid (Baeyer, *loc. cit.* 678; 2270). The acid sodium salt of the latter acid on heating in aqueous solution and subsequent oxidation of the copper salt with potassium ferricyanide, gives tetraacetylenedicarboxylic acid (*Ibid.* 2271),

which, on reduction with zinc and sulphuric acid and finally with sodium amalgam, yields an acid apparently identical with sebacic acid (*Ibid.* 2272). Sebacic acid on heating with lime is said to give, among other products, valeric aldehyde (Calvi, Ann. **91**, 110; Petersen, Ann. **103**, 184; Dale and Schorlemmer, Ann. **199**, 149).

[C.] *Fumaric acid* [Vol. II] gives dibromsuccinic acid on heating with bromine and water (Kekulé, Ann. Suppl. **1**, 131; Baeyer, Ber. **18**, 676), and this can be converted into sebacic acid as above.

[D.] From *adipic acid* [Vol. II], which gives sebacic acid (ester) on electrolysis of a solution of the potassium salt of the monoethyl ester (Crum Brown and Walker, Ann. **261**, 121).

[E.] *Stearic acid* [Vol. II] gives sebacic acid when heated with nitric acid (Arppe, Zeit. [2] **1**, 296).

[F.] *Normal hexoic acid* [Vol. II], on bromination and boiling with sodium carbonate solution, gives α-hydroxyhexoic = 2-hexanolic acid (Jelisafoff, Journ. Russ. Soc. **12**, 367), and this, on oxidation with chromic acid mixture, yields valeric aldehyde among other products (Ley, *Ibid.* **9**, 139).

II. Isovaleric Aldehyde; 2-Methyl-4-butanal.

$CH_3 . CH(CH_3) . CH_2 . CHO$

[A.] From *isoamyl alcohol* [22] by oxidation (Dumas and Stas, Ann. Chim. [2] **73**, 145; Parkinson, Ann. **90**, 114; Kolbe and Guthrie, Ann. **109**, 296; Bouveault and Rousset, Bull. Soc. [3] **11**, 300).

An amylene from fusel oil (isopropylethylene: see above under butyric aldehyde [94; H]) gives isopropylethylene glycol (Flawitzky, Ann. **179**, 351; Wagner, Ber. **21**, 1232), and this on heating with phosphorus pentoxide or zinc chloride yields isovaleric aldehyde (Flawitzky, Ber. **10**, 2240: see also Michailenko, Journ. Russ. Soc. **27**, 57).

Isoamyl alcohol gives 30–40 per cent. isovaleric aldehyde by pyrogenic decomposition (Ipatieff, Ber. **34**, 598).

[B.] From *isovaleric acid* [Vol. II] by the dry distillation of its salts or by distilling the calcium salt with calcium *formate* [Vol. II] (Chancel, Ann. **60**, 318; Ebersbach, Ann. **106**, 262; Wurtz, Ann. **134**, 302; Schmidt, Ber. **5**, 600; Limpricht, Ann. **97**, 370; Dilthey, Ber. **34**, 2115). Or isovaleric acid can be converted into isovaleryl chloride, and the latter reduced in moist ethereal solution with sodium amalgam (W. H. Perkin, junr., and Sudborough, Proc. Ch. Soc. **10**, 216).

[C.] *Leucine* [Vol. II] gives isovaleric aldehyde when acted on by sulphur trioxide (Schwanert, Ann. **102**, 226).

[D.] *Formic aldehyde* [91] and *isobutyric aldehyde* [94] combine under the influence of alcoholic potash to form 'pentaglycol,' $(CH_3)_2 : C(CH_2 . OH)_2$ (Just, Monats. **17**, 76). The latter by the action of 5–20 per cent. sulphuric acid gives, among other products, isovaleric aldehyde (Fischer and Winter, Monats. **21**, 301: see also Lieben, *Ibid.* **23**, 60).

III. Methylethylacetaldehyde; 2-Methylbutanal.

$CH_3 . CH_2 . CH(CH_3) . CHO$

[A.] *Tiglic aldehyde* [103] gives this valeric aldehyde on reduction with iron and acetic acid (Herzig, Monats. **3**, 123; Lieben and Zeisel, *Ibid.* **7**, 56).

[B.] *Isoamyl alcohol* [22] gives an amylene which, on conversion into bromide and treatment with alcoholic potash, yields a monobromamylene. The latter on further heating with strong alcoholic potash gives (with valerylene) a valeryl ethyl ether, which, on heating with dilute sulphuric acid at 150°, yields a valeric aldehyde probably having the above constitution (Eltekoff, Ber. **10**, 706).

Or isoamyl alcohol can be converted into isoamyl iodide and amylene, and the latter by the action of chlorine into α-ethylallyl chloride $[CH_2 : C(C_2H_5) . CH_2 Cl]$ (Kondakoff, Journ. Russ. Soc. **20**, 149). This chloride on heating with potassium carbonate solution gives the corresponding α-ethylallyl alcohol, and

the latter on heating with very dilute sulphuric acid yields the above valeric aldehyde (*Ibid.* 154).

NOTE:—For valeral from methylethyl methylcarbinol (active amyl alcohol of fusel oil) see Bemont, Comp. Rend. **133**, 1222; also Etard and Vila, *Ibid.* **134**, 122. For trimethacetaldehyde = dimethylpropanal from trimethacetic and formic acids see Tissier, Ann. Chim. [6] **29**, 353.

96. Hexoic Aldehyde; Caproic Aldehyde.

$C_5H_{11}.CHO$

NATURAL SOURCES.

Hexoic aldehyde occurs in small quantity in oil of *Eucalyptus globulus* (Bouchardat and Oliviero, Bull. Soc. [3] **9**, 429). A caproic aldehyde occurs in rancid fat, probably a bacterial product (Nagel, Am. Ch. Journ. **23**, 173).

SYNTHETICAL PROCESSES.

I. Normal Caproic Aldehyde; Hexanal.

$CH_3.CH_2.CH_2.CH_2.CH_2.CHO$

[A.] From *normal caproic* = *hexoic* and *formic acids* [Vol. II] by distilling a mixture of the calcium salts (Lieben and Janecek, Ann. **187**, 130).

II. Isocaproic Aldehyde; Isobutylacetaldehyde; 4-Methylpentanal.

$CH_3.CH(CH_3).CH_2.CH_2.CHO$

[A.] From *isobutylacetic* and *formic acids* [Vol. II] by distilling a mixture of the calcium salts (Rossi, Ann. **133**, 178).

III. Methylpropylacetaldehyde; 2-Methylpentanal.

$CH_3.CH_2.CH_2.CH(CH_3).CHO$

[A.] From *normal propyl alcohol* [15] through the aldehyde (propanal) by oxidation (Chancel, Ann. **151**, 301; Przybytek, Journ. Russ. Soc. **8**, 335; Lieben and Zeisel, Monats. **4**, 14). Propanal on heating with sodium acetate solution gives methylethylacroleïn = 2-methyl-2-pentenal (L. and Z., *loc. cit.* 16; Hoppe, *Ibid.* **9**, 637), and this, on standing in contact with iron and acetic acid for four weeks in the cold, is converted into the above hexoic aldehyde (L. and Z., *loc. cit.* 23).

Or indirectly from propyl (or isopropyl) alcohol through propylene, the bromide and cyanide, and hydrolysis of the latter to pyrotartaric acid (Simpson, Ann. **121**, 161). Subsequent steps as under **I** and **C** below.

Or through propylene chloride or bromide and glycol, and then as below under **B**. According to Michael (Journ. pr. Ch. [2] **60**, 417: see also Beilstein and Wiegand, Ber. **15**, 1496) propanal is among the products of the action of water and silver oxide on propylene bromide.

Or propylene chlorhydrin by the action of potash gives propylene oxide, and this yields propanal on heating with zinc chloride more readily than the glycol (Krassusky, Journ. Russ. Soc. **34**, 537).

NOTE:—Generators of propylene (see under glycerol [48; **B** to **G**, &c.) thus become generators of the above hexoic aldehyde.

[B.] From *glycerol* [48] through allyl alcohol (see under ethyl alcohol [14; **G**]). The latter gives methylethylacroleïn among other products when heated with 10 per cent. hydrochloric acid at 100° (Solonina, Journ. Russ. Soc. **19**, 306). Subsequent reduction as above under **A**.

Or allyl chloride from allyl alcohol gives a chlorhydrin which is decomposed by heating with water with the formation of acetone and propanal (see under acetone [106; **F**]).

Or from glycerol through glyceric acid and pyrotartaric acid (see under benzyl alcohol [54; **F**]), or through allyl cyanide and pyrotartaric acid (*Ibid.*). Pyrotartaric acid is converted into citradibrompyrotartaric acid and then treated as below under **C**. Or pyrotartaric acid gives propanal among the products of electrolysis of the potassium salt (Petersen, Zeit. physik. Ch. **33**, 704).

Or from glycerol through propylene glycol by distilling with sodium hy-

droxide (Belohoubek, Ber. **12**, 1872; Morley and Green, Trans. Ch. Soc. **47**, 132) and the action of acidified water on the glycol at 215° (Linnemann, Ann. **192**, 61 : see also Lieben, Monats. **23**, 60), or by heating with zinc chloride (Flawitzky, Ber. **11**, 1256; Journ. Russ. Soc. **10**, 348), by which propanal is formed.

Or from glycerol through *acroleïn* [101], which, on treatment with *potassium cyanide* [172] and acetic acid, gives the nitrile of vinylglycollic = 1 : 3-butenolic acid and the acid itself on hydrolysis. The latter combines with bromine to form 4 : 3 : 2-dibrombutanolic acid, and this is reduced by sodium amalgam to α-hydroxybutyric acid (Van der Sleen, Rec. Tr. Ch. **18**, 302; **21**, 209). Subsequent steps as below under **N**.

[**C.**] From *citric acid* [Vol. II] through citraconic acid (see under benzyl alcohol [**54**; **M**]). The latter combines with bromine to form citradibrompyrotartaric acid (Kekulé, Ann. Suppl. **2**, 96; Fittig and Krusemark, Ann. **206**, 2), and this on heating with alkali gives propanal (Friedrich, Ann. **203**, 355; Fittig and Krusemark, *loc. cit.* 4; Ssemenoff, Journ. Russ. Soc. **31**, 296), which can be converted into methylethylacroleïn, &c., as under **A**.

Citraconic acid gives mesaconic acid under the influence of acids, alkalis, or water (Gottlieb, Ann. **77**, 268; Kekulé, Ann. Suppl. **2**, 94; Fittig, Ann. **188**, 77, 80; Delisle, Ann. **269**, 82; Swarts, Jahresber. **1873**, 579), and this combines with bromine to form mesadibrompyrotartaric acid (Kekulé, *loc. cit.* 102), which also yields propanal among the products of its decomposition by alkalis (Fittig and Krusemark, *loc. cit.* 4).

Or citric acid by distillation, or by heating with dilute sulphuric acid, gives itaconic acid (Baup, Ann. **19**, 29; Markownikoff and Purgold, Zeit. [2] **3**, 264), which combines with hydrogen chloride to form itachlorpyrotartaric acid (Swarts, Zeit. [2] **2**, 721; Michael, Journ. pr. Ch. [2] **45**, 60). The latter on treatment with water or alkalis yields itamalic (hydroxymethylsuccinic) acid, which readily passes into its anhydride, paraconic acid (Swarts, Zeit. [2] **3**, 648; Beer, Ann. **216**, 84), and this gives citraconic anhydride on distillation.

Or from citric acid through acetonedicarboxylic, β-oxyglutaric, vinylacetic, and crotonic acid (see under n-propyl alcohol [**15**; **W**]). From crotonic acid as under **N** below.

[**D.**] From *lactic acid* [Vol. II] through citraconic acid by distillation (Engelhardt, Ann. **70**, 243; 246), and then as above. Or through pyroracemic acid and pyrotartaric acid (see under benzyl alcohol [**54**; **P** and **I**]), and then as below under **I** and above under **C**.

[**E.**] From *acetoacetic acid* (*ester*) [Vol. II] and *hydrogen cyanide* [172] through hydroxypyrotartaric and citraconic acid (see under benzyl alcohol [**54**; **M**, note]), and then as above under **C**. Or from acetoacetic ester and *α-brompropionic ester* through β-methylacetosuccinic ester and pyrotartaric acid (see under benzyl alcohol [**54**; **I**]). Or from chloracetic ester and acetoacetic ester through acetosuccinic ester, α-methylacetosuccinic ester, and pyrotartaric acid (*Ibid.*). Or from acetoacetic ester through isonitrosoacetone, acetyl cyanide, pyroracemic and pyrotartaric acid (*Ibid.*).

Or from acetoacetic ester through methylacetoacetic ester by the action of *methyl iodide* on the sodium derivative of acetoacetic ester; methylacetoacetic ester on successive treatment with bromine and alcoholic potash gives mesaconic ('oxytetric') acid (Demarçay, Ann. Chim. [5] **20**, 473; Gorboff, Journ. Russ. Soc. **19**, 605; Cloëz, Bull. Soc. [3] **3**, 598; 602 : see also under benzyl alcohol [**54**; **I**]), and this can be converted into propanal, &c., as under **C**.

Or from acetoacetic ester through the γ-bromo-derivative, succinylsuccinic ester, and ethylmalonic acid (see under n-propyl alcohol [**15**; **AA**; **Y**; **O**]). From the latter as below under **G**.

Or from ethylacetoacetic ester through 1 : 1-dinitropropane and propanal as under n-propyl alcohol [**15**; **AA**].

[**F.**] From *isovaleric acid* [Vol. II] through hydroxypyrotartaric acid, citraconic acid, &c. [**54**; **M**].

[G.] From *malonic* and *propionic acids* [Vol. II] through propanetricarboxylic ester, citraconic or mesaconic acid (see under benzyl alcohol [54; M, note]), and then as before.

Or from malonic and *acetic acid* through propanetricarboxylic ester by the interaction of sodio-methylmalonic ester and chloracetic ester, and pyrotartaric acid by hydrolysis of the tricarboxylic ester (Bischoff and v. Kuhlberg, Ber. 23, 635). Subsequent steps as under I below and C above.

Or malonic acid can be converted into ethylmalonic (*a*-isopyrotartaric) ester by the action of *ethyl iodide* on sodio-malonic ester (Conrad, Ann. 204, 134: see also Daimler, Ann. 249, 174), chlorethylmalonic ester by chlorination (Conrad, Ber. 14, 618; Conrad and Guthzeit, Ann. 209, 232), or iodethylmalonic ester by the action of iodine on sodio-ethylmalonic ester. The chloro- or iodo-esters on hydrolysis with baryta water give *a*-ethyltartronic acid (Conrad and Guthzeit, *loc. cit.* 233; Bischoff and Hausdörfer, Ann. 239, 127), and the latter on heating to 180° yields *a*-hydroxybutyric acid (Guthzeit, Ann. 209, 234; Conrad, Ber. 14, 618), from which propanal can be obtained as under N, and the latter treated as under A. Chlorethylmalonic ester also gives *a*-hydroxybutyric acid on heating with hydrochloric acid.

[H.] From *acetic* and *propionic acids* [Vol. II], *alcohol* [14], and *potassium cyanide* [172] through *a*-methyl-*β*-cyanosuccinic ester and citraconic acid (see under benzyl alcohol [54; M, note]). Or from acetic acid through acetyl cyanide, pyroracemic acid, and pyrotartaric acid (see under benzyl alcohol [54; I]).

[I.] From *tartaric acid* [Vol. II] through pyrotartaric acid (see under n-propyl alcohol [15; V]), citradibrompyrotartaric acid by the action of bromine and phosphorus on the latter Auwers and Imhäuser, Ber. 24, 2237), and then as above under C.

[J.] From *propionic* and *oxalic acids* [Vol. II] and *alcohol* [14] through methyloxalacetic ester, *β*-methylmalic acid, and citraconic or mesaconic acid (see under benzyl alcohol [54; M]).

Or from propionic acid through the *aa*-dibromo-acid, the *aβ*-acid, glyceric acid, and pyrotartaric acid; or through the *aa*-dibromo-acid, pyroracemic and pyrotartaric acids; or through propionamide, propionitrile, *aa*-dichlorpropionic acid, pyroracemic and pyrotartaric acids (see under benzyl alcohol [54; O]).

Or from propionic acid through propionyl chloride and cyanide (Claisen and Moritz, Trans. Ch. Soc. 37, 692). The latter on hydrolysis gives ethylglyoxylic acid = propionylformic or 2-butanonic acid (*Ibid.* and Ber. 13, 2121), which is reduced by sodium amalgam to *a*-hydroxybutyric acid, from which propanal can be obtained as under N, and 2-methylpentanal as under A.

Propanal is obtainable directly from propionic acid by distilling the calcium salt with *calcium formate* [Vol. II] (Rossi, Comp. Rend. 70, 129).

[K.] From *allyl isothiocyanate* [166] through allyl cyanide and pyrotartaric acid (see under benzyl alcohol [54; F and J]), and then as above under I and C.

[L.] From *ethyl alcohol* [14] through iodoform, acrylic acid, *a*-chlorlactic acid, glyceric acid (see under benzyl alcohol [54; I]), and then through pyrotartaric acid as above under B.

Or from ethyl alcohol through ethyl ether, dichlorether, chloracetaldehyde, *β*-chlorlactic acid, glyceric acid, and pyrotartaric acid [54; I].

Or from ethyl alcohol through chloracetal, chloracetaldehyde, *β*-chlorlactic, glyceric, and pyrotartaric acids [54; I].

Or through chloral, the cyanhydrin, trichlorlactic acid, dichloracetaldehyde, dichlorlactic acid, chloracetaldehyde, *β*-chlorlactic acid, &c. [54; I]. Or from ethyl alcohol through ethylene, vinyl chloride, chloracetaldehyde, *β*-chlorlactic acid, &c., as before (see under benzyl alcohol [54; A]).

NOTE:—By this last method generators of ethylene thus become generators of 2-methylpentanal.

Ethyl alcohol might be converted more directly into propanal through ethyl cyanide and propionic acid, and

distillation of the calcium salt of the latter with calcium formate.

Or from alcohol and *formic acid* [Vol. II] through diethyl carbinol by the action of zinc on ethyl iodide and formic ester, and decomposition of the product with water (Saytzeff and Wagner, Ann. **175**, 351). The carbinyl iodide gives symmetrical methylethylethylene (= 3-pentene) on treatment with alcoholic potash (S. and W. *loc. cit.* 373; **179**, 302), and the corresponding 2 : 3-dibrompentane yields symmetrical methylethylethylene glycol (= 2 : 3-dihydroxypentane) on treatment with silver acetate and hydrolysis of the acetate (*Ibid.* **179**, 308). The glycol gives α-hydroxybutyric acid on oxidation by dilute nitric acid. Subsequent steps as below under **N**.

NOTES:—The amylene from *zinc ethyl* and *chloroform* may be symmetrical methylethylethylene (Beilstein and Rieth, Ann. **124**, 245; Beilstein's 'Handbuch,' I, 116).

Diethyl oxalate interacts with *zinc ethyl* to form diethoxalic ester [21; G]. The latter by the action of phosphorus trichloride gives α-ethylcrotonic ester (Frankland and Duppa, Journ. Ch. Soc. **18**, 133; Fittig and Howe, Ann. **200**, 22), and the free acid combines with hydrogen bromide to form bromhydro-ethylcrotonic = bromhexoic acid (F. and H. *loc. cit.* 23). The latter acid is decomposed by cold sodium carbonate solution with the formation of symmetrical methylethylethylene (*Ibid.* 30).

Ethyl alcohol and *acetic acid* give ethylacetoacetic ester and, by the action of nitrous acid, the latter yields an isonitroso-derivative which is decomposed on heating with dilute sulphuric acid with the formation of acetyl-propionyl = 2 : 3-pentadione (v. Pechmann, Ber. **21**, 1412; **24**, 3956). The diketone on reduction with zinc and dilute sulphuric acid gives methylethylketol (v. P. and Dahl, Ber. **23**, 2425) and, on further reduction with sodium amalgam, symmetrical methylethylethylene glycol (*Ibid.* 2426).

Methylpropyl ketone [21; A] and *diethyl ketone* [21; G; H] give acetyl-propionyl on heating with nitric acid (Fileti and Ponzio, Gazz. **25**, 239; Journ. pr. Ch. [2] **55**, 194).

[M.] From *aconitic acid* [Vol. II] through itaconic acid by heating with water at 180° (Pébal, Ann. **98**, 94), and then as above under **C**.

[N.] From *normal butyric acid* [Vol. II] through propanal by electrolysis of the sodium salt (v. Miller and Hofer, Ber. **27**, 468; Hofer and Moest, Ann. **323**, 284). Or through the α-chloro- or α-bromo-acid and α-hydroxy-acid (Naumann, Ann. **119**, 115; Friedel and Machuca, Ann. **120**, 279; Markownikoff, Ann. **153**, 242). The latter gives propanal on oxidation (Ley, Journ. Russ. Soc. **9**, 131). Propanal can be converted as under **A** above.

NOTE:—Since crotonic acid gives α- with some β-brombutyric acid on combination with hydrogen bromide (Hemilian, Ann. **174**, 325), the generators of crotonic aldehyde and acid referred to under normal butyl alcohol [17; G, &c.] and benzyl alcohol [54; G; H, &c.] thus become generators of α-hydroxybutyric acid and propanal. These generators are:—*malonic acid* and *acetaldehyde*; *acetoacetic ester*; *glycerol*; *allyl isothiocyanate*; *β-hydroxybutyric acid*; *erythritol* and *formic acid*; *n-butyric acid*; *acetylene* and *ethylene*.

Crotonic acid on combination with hypobromous acid gives also (with the α-) some β-brom-α-hydroxybutyric acid, which yields propanal on heating the sodium salt with water (Melikoff, Journ. pr. Ch. [2] **61**, 556).

Or crotonic acid combines with chlorine to form αβ-dichlorbutyric acid, the sodium salt of which, on heating with water, gives propanal among other products (Wislicenus, Ann. **248**, 283; Michael and Browne, Am. Ch. Journ. **9**, 282).

Or crotonic acid combines with hypochlorous acid to form α-chlor-β-hydroxybutyric acid (Erlenmeyer and Müller, Ber. **15**, 49; Melikoff, Ann. **234**, 198), which, by the action of alcoholic potash, gives β-methylglycidic acid (Melikoff, *loc. cit.* 204). The latter combines with hydrogen bromide to form β-brom-α-hydroxybutyric acid, which is decomposed into propanal as above (Melikoff, Journ. pr. Ch. [2] **61**, 556).

Or from butyric acid through butyrone or methylpropyl or ethylpropyl ketone, dinitropropane, and propanal (see under n-propyl alcohol [15; P; AA]).

[O.] *Mannitol* [51] on distillation with lime gives, among other products, 'metacetone,' which is a mixture containing propanal (Favre, Ann. Chim. [3] **11**, 71; Fischer and Laycock, Ber. **22**, 101). From propanal to 2-methylpentanal as above under **A**.

[P.] From *acetic aldehyde* [92], the oxime of which combines with acid sodium sulphite to form a salt, which, on heating with hydrochloric acid, gives methylglyoxal (v. Pechmann, Ber. **20**, 2543). The dioxime of the latter yields propylene glycol by electrolytic reduction (Tafel and Pfeffermann, Ber. **35**, 1510). From the glycol through propanal as above under **B**, &c.

[Q.] From *acetol* [43], which gives

propylene glycol on reduction with sodium amalgam. From the glycol through propanal, &c., as above under **A.**

97. Heptoic Aldehyde; Œnanthol; Heptanal.

$CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CHO$

Natural Sources.

Œnanthic aldehyde occurs in rancid olive oil; probably a bacterial product derived from oleïc acid (Scala, Ch. Centr. 1898, **1**, 439; from Staz. sper. agrar. **30**, 613). This aldehyde occurs also in rancid fat (Nagel, Am. Ch. Journ. **23**, 172).

Synthetical Process.

[**A.**] *Sebacic acid* [Vol. II] gives œnanthol, among other products, when heated with lime (Calvi, Ann. **91**, 110; Petersen, Ann. **103**, 184: see also Dale and Schorlemmer, Ann. **199**, 149).

98. Octoic Aldehyde; Octanal.

$C_7H_{15}.CHO$

Natural Source.

This aldehyde possibly occurs in oil of lemon (v. Soden and Rojahn, Ber. **34**, 2809).

Synthetical Processes.

[**A.**] From *n-octyl alcohol* [**28**] by oxidation (Schimmel's Ber. April, 1899; Ch. Centr. 1899, **1**, 1043).

[**B.**] From *butyric aldehyde* [**94**] through α-ethyl-β-propylacroleïn = octenoic aldehyde, by the action of dilute caustic alkali (Raupenstrauch, Monats. **8**, 112). The acroleïn reduces, by iron and acetic acid, to a secondary octanal, which is ethylbutylacetaldehyde (*Ibid.* 115).

[**C.**] *Œnanthol* [**97**] and *nitromethane* (see under hydrogen cyanide [**172**; **J** and **Y**]) condense under the influence of alkali or sodium to form nitro-octanal, which, on heating with zinc chloride, gives nitro-octylene. The latter, by reduction with zinc and acetic acid, yields the oxime of octanal, from which the aldehyde can be obtained by hydrolysis (Bouveault and Wahl, Comp. Rend. **134**, 1226).

[**D.**] From *octoic* and *formic acids* [Vol. II] by distilling a mixture of the calcium salts (Schimmel & Co., Germ. Pat. 126736 of 1900; Ch. Centr. 1901, **2**, 1375).

Note:—An octoic aldehyde is said to occur among the products of distillation of castor-oil soap (Limpricht, Ann. **93**, 242; Bouis, Ann. Chim. [3] **48**, 99; Städeler, Journ. pr. Ch. **72**, 241; Dachauer, Ann. **106**, 270; Béhal, Bull. Soc. [2] **47**, 33; 163).

The constitution of the natural aldehyde has not been determined.

99. Ennoic or Nonoic Aldehyde; Nonanal.

$C_8H_{17}.CHO$

Natural Sources.

Occurs in oil of lemon (v. Soden and Rojahn, Ber. **34**, 2809), in oil of mandarin orange (Schimmel's Ber. Oct. 1901; Ch. Centr. 1901, **2**, 1007), and in Ceylon oil of cinnamon (Schimmel's Ber. April, 1902; Walbaum and Hüthig, Journ. pr. Ch. [2] **66**, 47).

Synthetical Process.

[**A.**] From *nonoic* and *formic acids* [Vol. II] by distilling a mixture of the calcium salts (Schimmel & Co., Germ. Pat. 126736 of 1900; Ch. Centr. 1901, **2**, 1375).

Note:—The constitution of the natural aldehyde has not yet been determined.

100. Decoic Aldehyde; Decanal.

$CH_3[CH_2]_8.CHO$

Natural Sources.

According to Schimmel & Co. (Schimmel's Ber. Oct. 1900) the oil of sweet orange contains n-decoic aldehyde

to the extent of 8·5 per cent. (Stephan, Journ. pr. Ch. [2] **62**, 523).

The aldehyde has been found also in oil of mandarin orange (Schimmel's Ber. Oct. 1901; Ch. Centr. 1901, **2**, 1007), and it may possibly occur in oil of lemon (*Ibid.* Oct. 1902; Ch. Centr. 1902, **2**, 1207).

Synthetical Process.

[A.] From *n-decoic* and *formic acids* [Vol. II] by distilling a mixture of the barium salts (Krafft, Ber. **16**, 1717; Schimmel & Co., Germ. Pat. 126736 of 1900; Ch. Centr. 1901, **2**, 1375).

101. Acroleïn; Acrylic Aldehyde; Propenal.

$CH_2 : CH . CHO$

Natural Source.

Occurs in rancid fat; probably a bacterial product (Nagel, Am. Ch. Journ. **23**, 172).

Synthetical Processes.

[A.] From *glycerol* [48] by heating with dehydrating agents (see under mannitol [51; B]).

[B.] From *acetone* [106] through the dibromide ([*Ibid.* C]; also glycerol [48; E]).

[C.] From *alcohol* [14] and *acetic acid* [Vol. II] through diiodacetone (glycerol [48; K]).

[D.] From *mannitol* [51] (glycerol [48; O]).

[E.] From *dextrose* [154], being among the products of oxidation by chromic acid or by sulphuric acid and manganese dioxide (Liebig, Ann. **113**, 1).

[F.] From *normal* or *isopropyl alcohol* [15; 16] through the compound of propylene with mercuric sulphate (benzyl alcohol [54; E]).

Note:—For generators of propylene see under glycerol [48; B to G]; also under isopropyl alcohol [16].

102. Crotonic Aldehyde; 2-Butenal.

$CH_3 . CH : CH . CHO$

Natural Source.

Said to have been found in the first runnings from spirit rectification (Krämer and Pinner, Ber. **3**, 76). Biochemical origin doubtful.

Synthetical Processes.

Syntheses of crotonic aldehyde are given under n-butyl alcohol [17].

[A.] From *acetic aldehyde* [92] (n-butyl alcohol [17; G]).

[B.] From *erythritol* [50] and *formic acid* [Vol. II] (*Ibid.* [17; I]).

[C.] From *malic acid* [Vol. II] through coumalic acid or by electrolysis (*Ibid.* [17; O]).

[D.] From *acetylene* [1; A, &c.] (*Ibid.* [17; I, note]).

[E.] From *formic* and *acetic esters* [Vol. II] (*Ibid.* [17; J]).

[F.] From *ethylene* through vinyl bromide (*Ibid.* [17; I, note]).

[G.] From *lactic acid* [Vol. II] (*Ibid.* [17; I, note]).

[H.] From *β-hydroxybutyric acid* [Vol. II] (*Ibid.* [17; I, note]).

[I.] From *tetramethylenediamine* [Vol. II] through β-butylene glycol [17; P]. Crotonic aldehyde is among the products of oxidation of the glycol.

103. Tiglic Aldehyde; Guaial; 2-Methyl-2-Butenal.

$CH_3 . CH : C(CH_3) . CHO$

Natural Source.

The aldehyde does not occur in the free state, but the complex exists in some constituent of guaiacum resin from the W. Indian *Guaiacum officinale*. The resin gives tiglic aldehyde on dry distillation (Völckel, Ann. **89**, 346; Herzig, Monats. **3**, 118; 822; 825). The acid of guaiacum resin, guaiaretic acid, does not appear to be the source

of the aldehyde (Herzig and Schiff, Monats. **18**, 714).

Synthetical Process.

[A.] From *acetic aldehyde* [92] and *propionic aldehyde* (see under hexoic aldehyde [2-methylpentanal; **96**, *III*; **A**, **C**, &c.]) by heating a mixture with sodium acetate solution at 100° (Lieben and Zeisel, Monats. **7**, 54: see also Schmalzhofer, Monats. **21**, 671).

104. Citral; Geranial; Rhodinal; Licareal; 2:6-Dimethyl-2:6-Octadiënal-8.

$$CH_3 \cdot \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} : CH \cdot CH_2 \cdot CH_2 \cdot \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} : CH \cdot CHO$$

Natural Sources.

In oil of lemon-grass from *Andropogon citratus* from India, Ceylon, Singapore, and Jamaica (Schimmel's Ber. Oct. 1888; Dodge, Am. Ch. Journ. **12**, 553; Ber. **24**, 90; Ch. Centr. 1891, **1**, 88); in oils of lemon, *Citrus limonum* (Schimmel's Ber. Oct. 1888, p. 17); of *C. medica* (*Ibid.* Oct. 1895; Burgess, 'Analyst,' **26**, 260); of *Eucalyptus staigeriana* or 'lemon-scented iron-bark' of Queensland (Schimmel's Ber. April, 1888); of *Backhousia citriodora*, Queensland (*Ibid.* and Oct. 1888); of *Tetranthera citrata*, Java (*Ibid.* Oct. 1888); and of *Xanthoxylon piperitum*, Japan (*Ibid.* Oct. 1890).

Citral occurs also in oil of *Lippia* (*Aloysia*) *citriodora* or 'lemon-scented verbena' (Umney, Imperial Inst. Journ. 1896, p. 302; Journ. Soc. Ch. Ind. **15**, 739; Pharm. Journ. **57**, 257; Barbier, Bull. Soc. [3] **21**, 635), in oil of mandarin orange from *Citrus nobilis* or *C. madurensis* (Semmler, Ber. **24**, 202; Schimmel's Ber. April, 1897; Journ. Soc. Ch. Ind. **16**, 556; Flatau and Labbé, Bull. Soc. [3] **19**, 364), and in oil of sassafras leaf from *S. officinalis* (Power and Kleber, Pharm. Rev. **14**, 103; Ch. Centr. 1897, **2**, 42).

Citronella oil from *Andropogon nardus*, according to Flatau (Bull. Soc. [3] **21**, 158), contains 2–5 per cent. citral. This aldehyde is contained also in the oils of *Eucalyptus patentinervis* and *E. vitrea* (Smith, Proc. Roy. Soc., N. S. Wales, 1900; 'Nature,' **62**, 384; Schimmel's Ber. Oct. 1901), in oil of sweet orange (Semmler, Ber. **24**, 202; Parry, 'Chemist and Druggist,' **56**, 462; 722; Fabris, Journ. Soc. Ch. Ind. **19**, 771), in oil of W. Indian bay from *Pimenta acris* (Power and Kleber, Pharm. Rund. **13**, 60), in oil of Pimenta leaf from a Trinidad sp. (Schimmel's Ber. Oct. 1896), and in German oil of rose (Walbaum and Stephan, Ber. **33**, 2305).

Note:—Citral, according to Doebner (Ber. **31**, 1888; also Tiemann, *Ibid.* 2313), is the chief unsaturated open-chain aldehyde present in lemon-grass oil. According to Stiehl (Journ. pr. Ch. **58**, 51; **59**, 497; Ch. Zeit. **22**, 1086) two other aldehydes are present, but these have not been found by Semmler (Ber. **31**, 3001), by Doebner (*Ibid.* 3195), nor by Tiemann (*Ibid.* 3336; **32**, 827). The citral from lemon-grass oil and from 'verbena' (*Lippia citriodora*) consists of a mixture of two stereo-isomerides (Tiemann, Ber. **33**, 877; Kerschbaum, *Ibid.* 885).

For bibliographical history of citral see Tiemann, Ber. **31**, 3278; **32**, 831, foot-note.

Synthetical Processes.

[A.] From *acetic acid* [Vol. II], *alcohol* [**14**], and *methylheptenone* [**111**]. Bromacetic ester (Perkin and Duppa, Ann. **108**, 106; Hell and Mühlhäuser, Ber. **11**, 241; **12**, 735; Michael, Am. Ch. Journ. **5**, 202) and methylheptenone are heated with zinc, and the product (hydroxydihydrogeranic ester) hydrolysed by dilute alcoholic potash so as to give the acid (hydroxydihydrogeranic = 2:6-dimethyl-2-octene-6-olic-8-acid). The latter, on heating with acetic anhydride and sodium acetate, gives geranic = 2:6-dimethyl-2:6-octadiëne-8-acid, and this, on distilling the calcium salt with *calcium formate* [Vol. II], yields citral (Tiemann, Ber. **31**, 827).

[B.] *Geraniol* [**36**] gives citral on oxidation with chromic acid mixture (Barbier, Bull. Soc. [3] **9**, 803; Semmler, Ber. **23**, 2966; **24**, 201; Tiemann, Ber. **31**, 3311).

[C.] *Linaloöl* [**37**] gives citral on oxidation as above (Tiemann and Semm-

ler, Ber. **25**, 1180; **26**, 2711; Bertram and Walbaum, Journ. pr. Ch. [2] **45** 590).

105. Citronellal.

$$CH_2:C(CH_3).[CH_2]_3.CH(CH_3).CH_2.CHO$$

Natural Sources.

In citronella oil from the Indian *Andropogon nardus* (Dodge, Am. Ch. Journ. **11**, 460; **12**, 553; Flatau, Bull. Soc. [3] **21**, 158: see also Gladstone, Journ. Ch. Soc. **25**, 7; Wright, *Ibid.* **27**, 1; Pharm. Journ. **5**, 233); in oils of *Eucalyptus maculata*, *E. citriodora*, *E. dealbata*, and *E. planchoniana* (Schimmel's Ber. April, 1888; Oct. 1890; April, 1891; April, 1893; Oct. 1893; Kremers, Am. Ch. Journ. **14**, 203: see also Gildemeister and Hoffmann, p. 702); probably in oil of balm from the S. European *Melissa officinalis* (Semmler, Ber. **24**, 208: see also Schimmel's Ber. Oct. 1895) and in 'oleum citri' (Doebner, Ber. **27**, 2026).

The aldehyde occurs to a small extent in lemon-grass oil (Tiemann and Schmidt, Ber. **29**, 918; Labbé, Bull. Soc. [3] **21**, 77), in oil of mandarin orange (Schimmel's Ber. April, 1897; Ch. Centr. 1897, **1**, 992), and of sweet orange (Flatau and Labbé, Bull. Soc. [3] **19**, 361). Citronellal is present in oil of lemon (Schimmel's Ber. Oct. 1902; Ch. Centr. 1902, **2**, 1207: compare Burgess and Child, 'Chemist and Druggist,' **60**, 812).

The natural product is d-citronellal. For quantities present in citronella oils from Java and Ceylon see Schimmel's Ber. April, 1900; Journ. Soc. Ch. Ind. **19**, 556. A l-citronellal has recently been found in a citronella oil from Java (Schimmel's Ber. April, 1903; Ch. Centr. 1903, **1**, 1086).

Note:—The l-citronellol of oil of rose [38] corresponds with an aldehyde (rhodinal: Bouveault, Bull. Soc. [3] 23, 458; 463), which is *isomeric* with the above citronellal and which probably has the constitution:—$(CH_3)_2:C:CH.CH_2.CH_2.CH(CH_3).CH_2.CHO$. An aldehyde of this constitution has been synthesised from menthone (Wallach, Ann. 278, 302; 296, 131; Harries and Schauwecker, Ber. 34, 2981).

Synthetical Process.

[A.] From *acetic acid* [Vol. II], *alcohol* [14], and *methylheptenone* [111] through geranic acid (see under citral [104; A]). The latter on reduction with sodium in boiling amyl alcohol gives citronellic acid (Tiemann, Ber. **31**, 2901), the calcium salt of which on distillation with *calcium formate* [Vol. II] yields citronellal (*Ibid.* 2902).

106. Acetone; Dimethyl Ketone; 2-Propanone.

$$CH_3.CO.CH_3$$

Natural Sources.

Acetone has been found in the distillate from the leaves of *Erythroxylon coca*; also in oil of tea (Schimmel's Ber. April, 1898; Ch. Centr. 1898, **1**, 991), and (traces) in the ethereal oil (aqueous distillate) from the wood of the Atlas cedar, *Cedrus atlantica*, and of *C. libani* (Grimal, Comp. Rend. **135**, 582).

Phasecolunatin, a cyanogenetic glucoside found in *Phaseolus lunatus*, is the dextrose ether of acetone-cyanhydrin (Dunstan and Henry, Proc. Roy. Soc. **72**, 291).

Acetone occurs in small quantity in the urine of cattle, dogs, and cats; in human blood and urine, and in larger quantity in cases of diabetes and acetonuria. Traces occur in expired air and in emanations from the skin of man (Johannes Müller, Arch. exp. Path. **40**, 351; Ch. Centr. 1898, **1**, 626: for production and origin of acetone in the animal organism see Cotton in Journ. Pharm. [6] **10**, 193; Ch. Centr. 1899, **2**, 722; Neuberg and Blumenthal, Beit. ch. Physiol. u. Path. **2**, 238).

Acetone has been found in the liquid from a hydatid cyst of the liver (Malméjac, Journ. Pharm. [6] **13**, 406). The acetone in these cases probably results from the decomposition of fat (Schumann-Leclerq, Ch. Centr. 1901, **1**, 1113).

Occurs among the products of fermentation (putrefaction) of fish (Mörner, Zeit. physiol. Ch. **22**, 514), and among the products of fermentation of milk sugar by *Bacterium lactis aërogenes* of Escherich = *Bact. aceticum* of Baginsky (Zeit. physiol. Ch. **12**, 461), and of dextrose by Dunbar's and other *Vibrios* (Gosio: quoted by Emmerling in 'Die Zersetzung, &c.,' pp. 47 and 56).

Synthetical Processes.

[A.] From *acetic acid* [Vol. II] by dry distillation of the calcium or barium salt (Liebig, Ann. **1**, 223; Dumas, Ann. Chim. [2] **49**, 208), or by passing the vapour over heated pumice and barium carbonate (Squibb, Journ. Soc. Ch. Ind. **14**, 506; **15**, 612; Conroy, *Ibid.* **21**, 309).

Or from acetic acid and *methyl alcohol* [13] by the interaction of zinc methyl and acetyl chloride (Chiozza, Ann. **85**, 232; Freund, Ann. **118**, 1); or by the action of nascent zinc methyl on acetic anhydride, or of zinc-sodium alloy on methyl iodide and acetic anhydride (Saytzeff, Zeit. [2] **7**, 104).

Or zinc methyl and dichloracetyl chloride give dimethylisopropyl carbinol (see under tertiary butyl alcohol [19; A]), which yields acetone on oxidation as under K below.

[B.] From *normal* or *isopropyl alcohol* [15; 16] through propylene (see under glycerol [48; A]), the chloride or bromide, chlor- or brompropylene by the action of alcoholic potash, and the action of hypochlorous acid and mercuric oxide on the halo-propylene. The chloracetone thus formed gives acetone on reduction.

Or from brompropylene by heating with mercuric oxide and acetic acid at 100° or with water at 190°. Also from propylene bromide by heating with water at 180° (Linnemann, Ann. **138**, 125; **161**, 58; Bull. Soc. [2] **6**, 216), or with water and silver oxide (Michael, Journ. pr. Ch. [2] **60**, 418).

Also by dissolving 2-chlorpropylene in strong sulphuric acid and distilling the product with water (Oppenheim, Ann. Suppl. **6**, 365). 2-(β)-Chlorpropylene is formed (with 3-(α)-chlorpropylene) by the action of alcoholic potash on propylene chloride (see under isopropyl alcohol [16; B]),

Or from propylene bromide or chloride through propylene glycol (Wurtz, Ann. Chim. [3] **55**, 438; Eltekoff, Journ. Russ. Soc. **10**, 210; Niederist, Ann. **196**, 359), and the action of water at 180–190° on the latter, acetone and propanal being simultaneously formed (Eltekoff, *loc. cit.* **11**, 409: see also Lieben, Monats. **23**, 60),

Propylene gives acetone also by direct oxidation with chromic acid (Berthelot, Ann. **150**, 373).

Or from propylene through *acroleïn* [101] and pyroracemic or pyrotartaric acid (see under benzyl alcohol [54; E]), and then as under P below.

Note:—Generators of propylene (see under glycerol [48; B to I] and under isopropyl alcohol [16]) thus become generators of acetone.

Isopropyl alcohol gives acetone directly by oxidation with chromic acid (Linnemann, Ann. **140**, 178; Berthelot, Comp. Rend. **68**, 334). Also by electrolysis in sulphuric acid solution (Elbs and Brunner, Zeit. Elektroch. **6**, 604), by passing over a heated platinum spiral (Trillat, Comp. Rend. **132**, 1495), or by pyrogenic contact decomposition by heated brass (Ipatieff, Ber. **35**, 1057).

Propylene bromide may also be converted into allylene (see under benzyl alcohol [54; E]), the latter giving acetone on treatment with a solution of mercuric bromide or chloride (Kutscheroff, Ber. **14**, 1541; **17**, 15). Or allylene, when dissolved in strong sulphuric acid and the product distilled with water, gives (with mesitylene) acetone (Schrohe, Ber. **8**, 367). At 0° sulphuric acid with allylene yields only acetone (Michael and Leighton, Journ. pr. Ch. [2] **60**, 442).

Allylene is formed when the vapour of propyl alcohol is passed over hot magnesium and the product decomposed by water (Keiser and Breed, Ch. News, **71**, 118; Am. Ch. Journ. **18**, 328).

Note:—The generators of allylene referred to under benzyl alcohol [54; F; G; H; I, &c.] thus become generators of acetone:—

glycerol [48]; *malonic acid* [Vol. II] and *aldehyde* [92]; *acetoacetic ester* [Vol. II]; *allyl isothiocyanate* [166]; *β-hydroxybutyric acid*; *normal butyric acid*; *citric acid*; *lactic acid*; *isovaleric acid*; *malonic* and *propionic acids*; *tartaric* and *racemic acids*; *isobutyl* and *amyl alcohols* [18; 22].

[C.] *Isobutyl alcohol* [18] gives acetone among other products on oxidation with chromic acid (Krämer, Ber. **7**, 252; Schmidt, *Ibid.* 1361). Or from isobutyl alcohol through isobutylene (see under tertiary butyl alcohol [19; B]). The latter gives acetone among other products on oxidation with chromic acid or potassium permanganate (F. and O. Zeidler, Ann. **197**, 251; Wagner, Ber. **21**, 1232).

Or indirectly from isobutyl iodide and *potassium cyanide* [172] through the nitrile of isobutylformic acid and the acid by hydrolysis (Erlenmeyer and Hell, Ann. **166**, 266; Schmidt and Sachtleben, Ann. **193**, 92). The acid on oxidation with dilute alkaline permanganate gives β-hydroxyisovaleric (2-methyl-2-butanolic-3) acid (v. Miller, Ann. **200**, 273), and this yields acetone on oxidation with chromic acid mixture.

Isobutyl alcohol gives allylene when the vapour is passed over hot magnesium and the product decomposed by water (Keiser and Breed, Ch. News. **71**, 118; Am. Ch. Journ. **18**, 328). From allylene to acetone as under **B**.

[D.] From *tertiary butyl alcohol* [19] through isobutylene (see under isobutyl alcohol [18; A]). Acetone is among the products formed by passing the vapour of this alcohol over a heated platinum spiral (Trillat, Comp. Rend. **132**, 1495).

Or from tertiary butyl alcohol and *hydrogen cyanide* [172] through tertiary amyl alcohol (see under formic aldehyde [91; X]), and then as under **E** below.

Acetone is among the products of oxidation of tertiary butyl alcohol by chromic acid mixture (Butleroff, Zeit. [2] **7**, 485).

[E.] From *amyl alcohol* from fusel oil [22]. Isobutylene is among the products of decomposition by passing through a hot tube (Wurtz, Ann. **104**, 249; Butleroff, Ann. **145**, 277; Ipatieff, Ber. **35**, 1053).

Or the amyl alcohol can be converted into amylene by the usual methods (Balard, Ann. Chim. [3] **12**, 320; Frankland, Ann. **74**, 41; Wurtz, Ann. **128**, 225; 316; Bauer, Journ. pr. Ch. **84**, 257; Etard, Comp. Rend. **86**, 488; Eltekoff, Ber. **10**, 1904; Wischnegradsky, Ann. **190**, 332: fusel oil amylene prepared by the action of zinc chloride contains, in addition to trimethylethylene, some isopropylethylene and a trace of the symmetrical methylethylethylene, Kondakoff, Journ. Russ. Soc. **24**, 113). By the action of strong sulphuric acid and subsequent hydrolysis this amylene is converted into tertiary amyl alcohol = dimethylethyl carbinol (Osipoff, Ber. **8**, 1240; Wischnegradsky, *loc. cit.* 336; Kondakoff, *loc. cit.* **25**, 354), and the latter, when chlorinated in the presence of water, yields acetone among other products (Brochet, Ann. Chim. [7] **10**, 381).

Amyl alcohol also gives acetone among the products of its oxidation, or by passing the vapour over a heated platinum spiral (Trillat, Comp. Rend. **132**, 1495).

Or fusel oil amylene (trimethylethylene) may be converted into the bromide and trimethylethylene glycol (Wurtz, Ann. Chim. [3] **55**, 458; Wagner, Ber. **21**, 1235). The latter gives acetone among the products of its oxidation by chromic acid mixture (Flawitzky, Ber. **10**, 2240).

Trimethylethylene yields acetone by oxidation with potassium permanganate, the glycol being formed as an intermediate product (Wagner, *loc. cit.*). Trimethylethylene chlorhydrin from the hydrocarbon and hypochlorous acid gives methylisopropyl ketone on heating with water, or by passing over heated zinc oxide (Krassusky, Journ. Russ. Soc. **34**, 287). Or the chlorhydrin, on treatment with potash, yields trimethylethylene oxide (Eltekoff, *Ibid.* **14**, 361). This oxide on heating with lead chloride to 200° gives methylisopropyl ketone (Krassusky, *loc. cit.* 537). The ketone yields acetone as below.

Or trimethylethylene bromide on heating with alcoholic potash gives

dimethylallylene (3-methyl-1 : 2-butadiëne), which also yields acetone among the products of its oxidation (Faworsky, Journ. pr. Ch. [2] **37**, 392).

Trimethylethylene bromide on heating with water and lead oxide at 150°, or with water alone, gives methylisopropyl ketone (Eltekoff, Journ. Russ. Soc. **10**, 215; Niederist, Ann. **196**, 369; Nägeli, Ber. **16**, 2983), and this yields acetone among the products of its oxidation by chromic acid.

Trimethylethylene glycol also gives α-hydroxyisobutyric = 2-methyl-2-propanolic acid on oxidation with nitric acid (Wurtz, Ann. **107**, 197), and this yields acetone as under **O**.

Or fusel oil amyl alcohol by conversion into the iodide, isopropylethylene (Wischnegradsky, Ann. **190**, 358), isopropylethylene bromide, and the action of alcoholic potash on the latter gives isopropylacetylene, which also yields acetone among the products of its oxidation (Eltekoff, *loc. cit.* **9**, 222; 224; Flawitzky and Kryloff, *Ibid.* **10**, 342). Isopropylethylene gives acetone, among other products, on oxidation by potassium permanganate (Wagner, Ber. **21**, 1233).

Amyl alcohol gives allylene on passing the vapour over hot magnesium and decomposing the product with water (see above under **C**). Subsequent steps as under **B**.

[F.] From *glycerol* [**48**], acetone being among the products formed by distilling glycerol with lime (Tawilderoff, Ber. **12**, 1487), or by oxidation with hydrogen peroxide (Cotton, Journ. Pharm. **10**, 194).

Or from glycerol through allyl iodide (see under isobutyl alcohol [**18**; **D**]), propylene by the action of zinc and sulphuric acid or mercury and hydrochloric acid (Berthelot and De Luca, Ann. **92**, 306), or of acetic acid and zinc (Linnemann, Ann. **161**, 54; Gladstone and Tribe, Ber. **6**, 1550; Niederist, Ann. **196**, 358), and then as above under **B**. Allyl iodide also gives propylene by treatment with hydriodic acid (Butleroff, Ann. **145**, 271; Malbot, Comp. Rend. **107**, 114; Bull. Soc. [2] **50**, 449).

Or glycerol can be converted into allyl alcohol (see under ethyl alcohol [**14**; **G**]), and this gives propylene (with ethylene) by heating with phosphorus pentoxide (Béhal, Ann. Chim. [6] **16**, 360). Or allyl chloride from allyl alcohol gives a chlorhydrin by the action of sulphuric acid (Oppenheim, Ann. Suppl. **6**, 367), and this yields acetone (with propaldehyde) on heating with water (Krassusky, Journ. Russ. Soc. **34**, 287).

Glycerol gives propylene (with allyl iodide) by the action of iodine and phosphorus (Berthelot and De Luca, *loc. cit.*; Oppenheim, Ann. Suppl. **6**, 354).

Or from glycerol through allylene as under benzyl alcohol [**54**; **F**], and then as above under **B**.

Or glycerol can be converted into allyl bromide (Tollens, Ann. **156**, 152; Henry, Zeit. [2] **6**, 575; Grosheintz, Bull. Soc. [2] **30**, 98), the latter into tribromhydrin = 1 : 2 : 3-tribrompropane (Tollens, Ann. **156**, 168: see also under glycerol [**48**; **A**]), the latter into 1 : 2-dibrompropylene by the action of solid potash or sodium in ethereal solution (Henry, Ann. **154**, 371; Tollens, *loc. cit.*), and the dibrompropylene into 'allene' ($CH_2 : C : CH_2$) by reduction in alcoholic solution with zinc (Gustavson and Demjanoff, Journ. pr. Ch. **38**, 201 : compare Béhal, Bull. Soc. [2] **48**, 788). Allene dissolves in sulphuric acid, and the product gives acetone on distillation with water (G. and D., *loc. cit.*).

Allyl bromide also gives propylene by the action of zinc dust in alcoholic solution (Wolkoff and Menschutkin, Ber. **31**, 3072), and this yields acetone as above.

Glycerol gives propylene glycol directly when the monosodium compound is distilled (Belohoubek, Ber. **12**, 1873; Morley and Green, Trans. Ch. Soc. **47**, 132), and this yields acetone as under **B**.

Propylene glycol may also be obtained from glycerol by the action of sodium amalgam on the monochlorhydrin (Lourenço, Ann. **120**, 91), or by the action of acetyl bromide on glycerol, and reduction of the product (glycerol-acetobromhydrin) with coppered zinc and

hydrochloric acid (Hanriot, Ann. Chim. [5] 17, 84).

Or from glycerol through crotonic acid and tertiary heptyl alcohol (see below under **L**).

Or from glycerol through glyceric and pyroracemic acids (see under benzyl alcohol [54; **F**]), and then as under **P** below.

[**G.**] *Acetic aldehyde* [92] gives acetone when the vapour is passed over red-hot lime (Schloemilch, Zeit. [2] 5, 336). Or indirectly from aldehyde through crotonic acid and tertiary heptyl alcohol (see below under **L**). Or from aldehyde through butyrochloral and allylene (see under benzyl alcohol [54; **H**]), and then as above under **B**.

[**H.**] *Isovaleric aldehyde* [95] on treatment with phosphorus pentachloride and decomposition of the product with alcoholic potash gives isopropylacetylene = 3-methyl-1-butine, and this yields acetone among the products of its oxidation by chromic acid mixture (Bruylants, Ber. 8, 407; 413).

[**I.**] From *propionic acid* [Vol. II] through tertiary amyl alcohol by the interaction of propionyl chloride and zinc methyl and decomposition of the product with water (Popoff, Ann. 145, 292; Jermolajeff, Zeit. [2] 7, 275; Wischnegradsky, Ann. 190, 336), and then as above under **E**.

Or propionic acid may be brominated (see under aldehyde [92; **E**]), and the α-brompropionic acid converted into α-brompropionyl bromide, which, by interaction with zinc methyl and decomposition of the product with water, gives dimethylisopropyl carbinol (Kaschirsky, Journ. Russ. Soc. 13, 82). The latter yields acetone among other products on oxidation by potassium permanganate (see below under **K**).

Or from propionic acid through pyroracemic acid (see under benzyl alcohol [54; **O**]), and then as under **P** below.

Or from propionic and *acetic acids*, *alcohol* [14] and *potassium cyanide* [172] through α-methyl-β-cyanosuccinic ester and citraconic acid (see under benzyl alcohol [54; **M**]), and then as under **Q** below.

Or from propionic acid through propionamide and propionitrile (Dumas, Malaguti, and Leblanc, Ann. 64, 334), and then as below under **S**.

[**J.**] *Acetoacetic acid* [Vol. II] splits up readily into acetone and carbon dioxide on heating (Ceresole, Ber. 15, 1328).

Or indirectly from acetoacetic ester through acetonedicarboxylic acid (see under orcinol [75; **D**]), and then as under **Q** below.

Or from acetoacetic ester and *hydrogen cyanide* [172] through hydroxypyrotartaric acid and citraconic acid (see under benzyl alcohol [54; **M**, note]), and then as under **Q** below.

Or from acetoacetic ester through methylacetoacetic ester and mesaconic acid (see under benzyl alcohol [54; **I**]), and then as under **Q** below.

Or from acetoacetic ester through isonitrosoacetone and pyroracemic acid [54; **I**], and then as under **P** below.

Or from acetoacetic ester and α-brompropionic ester through β-methylacetosuccinic ester and pyrotartaric acid as under benzyl alcohol [54; **I**], and from the latter through allylene [*Ibid.* **F**; **M**; and **N**], and as above under **B**.

Or from acetoacetic ester, chloracetic ester, and methyl alcohol through acetosuccinic ester, the α-methyl-derivative, pyrotartaric acid, and allylene [54; **I**].

Or from acetoacetic ester through the β-chlorcrotonic acids, tetrolic acid and allylene (*Ibid.*).

[**K.**] *Isobutyric acid* [Vol. II] gives acetone when heated with chromic acid solution at 140° (Popoff, Zeit. [2] 7, 4).

Or on oxidation with alkaline permanganate isobutyric acid gives α-hydroxyisobutyric (2-methyl-2-propanolic) acid, which yields acetone as below under **O**.

Note:—Ketones which yield isobutyric acid on oxidation are thus likely to give acetone, e.g. diisopropyl ketone from calcium isobutyrate or the corresponding diisopropyl carbinol (Popoff, Ber. 6, 1255; Münch, Ann. 180, 327; 333).

Methylisopropyl ketone from isobutyryl chloride and zinc methyl (Béhal, Ann. Chim. [6] 15, 284) gives β-dichlorisopentane on treatment with phosphorus pentoxide, and this by alco-

holic potash yields isopropylacetylene (*Ibid.* 286), which gives acetone on oxidation (see under **E**).

Note :—Methylisopropyl ketone is obtained also from acetoacetic ester and isobutyryl chloride through isobutyrylacetoacetic ester, and the action of hydrochloric acid on the latter at 140–150° (Bouveault, Comp. Rend. 131, 45).

Ethylisopropyl ketone from isobutyryl chloride and zinc ethyl (Butleroff, Ann. 189, 44 ; Pawloff, Journ. Russ. Soc. 8, 242 ; Wagner, *Ibid.* 16, 697) gives acetone among the products of its oxidation by chromic acid.

Dimethylisopropyl carbinol from isobutyryl chloride and zinc methyl (Prianischnikoff, Zeit. [2] 7, 275) gives acetone among the products of its oxidation by potassium permanganate (Wagner, Journ. pr. Ch. [2] 44, 310). Or dimethylisopropyl carbinol yields tetramethylethylene and pinacone (see under tertiary butyl alcohol [19 ; **E**]). The latter gives acetone on oxidation with chromic acid mixture.

A mixture of calcium isobutyrate and *heptoate* [Vol. II] gives isopropylhexyl ketone on dry distillation, and this yields acetone among the products of its oxidation by chromic acid (Fuchs, Journ. Russ. Soc. 7, 334).

Isobutyric acid also gives the *α*-bromo-acid on bromination (Markownikoff, Ann. 153, 229 ; Hell and Waldauer, Ber. 10, 448 ; Michael and Graves, Ber. 34, 4043), and the latter, on heating with water or barium hydroxide or sodium carbonate solution, yields the *α*-hydroxy-acid (Markownikoff, *loc. cit.* ; Fittig, Ann. 200, 70), from which acetone can be produced as below under **O**.

Or *α*-bromisobutyric ester and *aldehyde* [92] condense under the influence of zinc to form trimethylethylenelactic = 2 : 2-dimethyl-3-butanolic-1-acid (ester) (Ephrussi and Reformatsky, Journ. Russ. Soc. 28, 600). The acid gives tertiary amyl alcohol (with trimethylacrylic acid) on distillation with dilute sulphuric acid (Giljaroff, *Ibid.* 508). The amyl alcohol yields acetone as above under **E**.

[**L.**] From *normal butyric acid* [Vol. II] and *methyl alcohol* [13] through the tertiary heptyl alcohol produced by the interaction of *α*-brom-n-butyryl bromide and zinc methyl and decomposition of the product with water (Kaschirsky, Journ. Russ. Soc. 13, 89). This heptyl alcohol gives acetone among the products of its oxidation. Or n-butyric acid may be converted into crotonic acid (see under benzyl alcohol [54 ; **K**]) and allylene [*Ibid.* **G**], and then into acetone as above under **B**.

Note :—Crotonic acid gives *α*- (with some *β*-) brombutyric acid on combination with hydrogen bromide (Hemilian, Ann. 174, 325). The generators of crotonic acid referred to under benzyl alcohol [54 ; **G** ; **H**, &c.] thus become, with methyl alcohol, generators of acetone.

[**M.**] From *isovaleric acid* [Vol. II] and *ethyl alcohol* [14] through ethylisobutyl ketone (2-methyl-4-hexanone), which is obtained by passing carbon monoxide over a mixture of sodium isovalerate and ethylate at 160° (Loos, Ann. 202, 327). The ketone gives acetone among the products of its oxidation by chromic acid mixture.

Ethylisobutyl ketone is also obtained from the same materials by the interaction of isovaleryl chloride and zinc ethyl (Wagner, Journ. pr. Ch. [2] 44, 274).

Or isovaleric acid, by the action of nitric acid, gives 2 : 2-(= *β*) dinitropropane, which on reduction by tin and hydrochloric acid yields acetone (Bredt, Ber. 15, 2322 ; Meyer and Locher, Ann. 180, 147).

Also from isovaleric acid and *normal propyl alcohol* [15] through propylisobutyl ketone (2-methyl-4-heptanone) by the interaction of isovaleryl chloride and zinc propyl (Wagner, Journ. Russ. Soc. 16, 668). This ketone also gives acetone among the products of its oxidation by chromic acid mixture.

Or from isovaleric acid through hydroxypyrotartaric acid and citraconic acid (see under benzyl alcohol [54 ; **M**, note]), and then as under **Q** below.

Or from isovaleric acid and ethyl alcohol through *α*-bromisovaleric ester, *β*-dimethylacrylic acid by heating the latter with quinoline or diethylaniline (see under isobutyl alcohol [18 ; **C**]), and oxidation of the acid with potassium

permanganate followed by potassium dichromate and sulphuric acid (Crossley and Le Sueur, Trans. Ch. Soc. **75**, 164).

[**N.**] From *lactic acid* [Vol. II] and *methyl alcohol* [**13**] through α-brompropionic acid by heating lactic acid with saturated bromhydric acid (Kekulé, Ann. **130**, 16), and then dimethylisopropyl carbinol by the interaction of α-brompropionyl bromide and zinc methyl, &c., as above under **I** and **K**.

Or from lactic acid through pyroracemic acid (see under benzyl alcohol [**54**; **P**]), and then as below under **P**.

Or from lactic acid through citraconic acid (see under benzyl alcohol [**54**; **M**, note]) and β-chlorcitramalic acid as under **Q** below.

[**O.**] From *oxalic acid* [Vol. II] and *methyl alcohol* [**13**] through α-hydroxyisobutyric (2-methyl-2-propanolic) acid by the interaction of zinc methyl and dimethyl oxalate (Frankland and Duppa, Ann. **133**, 80; **135**, 25). The acid gives acetone on oxidation with chromic acid mixture, or on fusion with caustic alkali; also on electrolysis of the potassium salt (v. Miller and Hofer, Ber. **27**, 468), on decomposition of the silver salt by iodine (Herzog and Leiser, Monats. **22**, 357), or on heating with phosphorus pentoxide (Bischoff and Walden, Ann. **279**, 111).

Or from oxalic and propionic acids and alcohol through methyloxalacetic ester, β-methylmalic acid, and citraconic acid (see under benzyl alcohol [**54**; **M**, note]), and then as under **Q** below.

[**P.**] *Tartaric acid* [Vol. II] gives acetone among the products of dry distillation (Völckel, Ann. **89**, 57), or of oxidation by hydrogen peroxide (Cotton, Journ. Pharm. **10**, 195).

Or from tartaric (or racemic) acid through pyroracemic acid (see under benzyl alcohol [**54**; **N**]), the calcium salt of which gives acetone on distillation (Hanriot, Bull. Soc. [2] **43**, 417; **45**, 81). A mixture of potassium pyroracemate and acetate yields acetone on electrolysis (Hofer, Ber. **33**, 654).

Or from tartaric acid through pyrotartaric acid and allylene, as under benzyl alcohol [**54**; **N**], and then as under **B** above.

[**Q.**] *Citric acid* [Vol. II] gives acetone among other products when heated with strong sulphuric acid (Wilde, Ann. **127**, 170), on dry distillation with glycerol (Clermont and Chautard, Comp. Rend. **105**, 520), or on heating the sodium salt with lime (Freydl, Monats. **4**, 151). Citric acid yields acetone among the products of dry distillation or of oxidation by potassium permanganate, by sulphuric acid and manganese dioxide (Robiquet, Berz. Jahresber. **18**, 502; Péan de St. Gilles, Ann. Chim. [3] **55**, 374), or by hydrogen peroxide (Cotton, Journ. Pharm. **10**, 195).

Acetone is formed by adding potassium permanganate solution drop by drop to a boiling solution of citric acid, or by exposure of citric acid to air in presence of iron or ferric chloride; also from Kämmerer's iron citrate under similar conditions (Sabbatani, Atti Accad. Sci. Torino, **35**, 678; Journ. Ch. Soc. **78**, Abst. I, 536).

Or citric acid may be converted into acetonedicarboxylic acid (see under orcinol [**75**; **G**]), and this gives acetone on heating at 135° *per se* or by boiling with water, acid, or alkaline solutions.

Or from citric acid through citraconic acid (see under benzyl alcohol [**54**; **M**]) and β-chlorcitramalic acid by the action of hypochlorous acid or chlorine on the latter (Gottlieb, Ann. **160**, 101; Carius, Ann. **126**, 204; Melikoff and Feldmann, Ann. **253**, 87). The chloro-acid gives acetone on heating with water at 110–120°.

Mesaconic acid, the isomeride of citraconic acid, also gives β-chlorcitramalic acid when a solution of the sodium salt is chlorinated (Morawski, Journ. pr. Ch. [2] **12**, 392).

Or from citraconic acid through allylene as under benzyl alcohol [**54**; **M**], and then as above under **B**.

[**R.**] From *malonic* and *propionic acids* [Vol. II] through propanetricarboxylic ester, citraconic, and mesaconic acid (see under benzyl alcohol [**54**; **M**, note]), and then as above under **Q**.

Or from malonic acid and *acetic aldehyde* [**92**] through crotonic acid and allylene (see under benzyl alcohol [**54**; **G**]), and then as above under **B**.

Or malonic ester, by the action of sodium at 70–90°, gives acetonetricarboxylic ester, and this yields acetone on heating with strong acids (Willstätter, Ber. **32**, 1274).

[**S.**] From *methyl* and *ethyl alcohols* [**13**; **14**] and *hydrogen cyanide* [**172**] through propionitrile (Pelouze, Ann. **10**, 249; Williamson, Phil. Mag. [4] **6**, 205; Buckton and Hofmann, Journ. Ch. Soc. **9**, 250; Rossi, Ann. **159**, 79). The latter, on treatment with sodium in ethereal solution, gives a product which by interaction with methyl iodide followed by aqueous hydrogen chloride yields 'trimethylpyrolone' ($C_7H_{11}NO$). The latter, on heating with strong aqueous hydrogen chloride at 140–150°, gives ethylisopropyl ketone, from which acetone is obtained by oxidation as under **K** (E. v. Meyer, Journ. pr. Ch. [2] **38**, 336; Hanriot and Bouveault, Comp. Rend. **108**, 1171; Bull. Soc. [3] **1**, 549).

Or from ethyl and methyl alcohols through chloral and dimethylisopropyl carbinol (see under tertiary butyl alcohol [**19**; **G**]), and then as above under **K**.

Or from methyl alcohol and hydrogen cyanide through methyl cyanide (acetonitrile). The latter interacts with magnesium methobromide to form an intermediate compound, which is decomposed by acids with the formation of acetone (general method of Blaise: Comp. Rend. **132**, 38).

Or from ethyl alcohol through iodoform, acrylic acid, α-chlorlactic acid, and glyceric acid (see under benzyl alcohol [**54**; **I**]). From the latter through pyrotartaric acid and allylene as under benzyl alcohol [**54**; **F** and **E**], and above under **B**; or through pyroracemic acid as under benzyl alcohol [**54**; **E**], and above under **F** and **P**. Allylene is formed when the vapour of ethyl alcohol is passed over heated magnesium and the product decomposed by water (Keiser and Breed, Ch. News, **71**, 118; Keiser, Am. Ch. Journ. **18**, 328).

Or from ethyl alcohol through propionitrile as above, and from the latter through αα-dichlorpropionic acid and pyroracemic acid as under benzyl alcohol [**54**; **I**], and then as above under **P**.

Or from ethyl alcohol and hydrogen cyanide through ethylene, vinyl chloride, chloracetaldehyde, β-chlorlactic acid, and glyceric acid (see under benzyl alcohol [**54**; **A**]). From the latter, as above, through pyrotartaric acid and allylene, or through pyroracemic acid.

Note:—Other methods of passing from ethyl alcohol through chloracetaldehyde to glyceric acid are given under benzyl alcohol [**54**; **I**].

Generators of ethylene thus become (with hydrogen cyanide) generators of acetone through glyceric acid.

[**T.**] From *β-hydroxybutyric acid* [Vol. II] through crotonic acid and allylene (benzyl alcohol [**54**; **L**]), and then as above under **B**.

[**U.**] From *erythritol* [**50**] and *formic acid* [Vol. II] through *crotonic aldehyde* [**102**], crotonic acid and allylene (see under n-butyl alcohol [**17**; **I**], and benzyl alcohol [**54**; **G**]), and then as above under **B**.

[**V.**] *Methylheptenone* [**111**] gives acetone among the products of its oxidation with chromic and sulphuric acids (Tiemann and Semmler, Ber. **28**, 2128).

[**W.**] *Dimethylheptenol* [**35**] gives acetone among the products of its oxidation by chromic acid mixture (Barbier, Comp. Rend. **126**, 1424).

[**X.**] *Ethane* [**14**; **D**] and carbon monoxide give an acetone (C_3H_6O) when submitted to the action of the silent electric discharge in a cooled apparatus (De Hemptinne, Bull. Acad. Roy. Belg. [3] **34**, 275). The product has not been identified specifically as 2-propanone.

[**Y.**] *Citronellal* [**105**] and *citronellol* [**38**] give acetone (with β-methyladipic acid) on oxidation with potassium permanganate, followed by potassium dichromate and sulphuric acid (Tiemann and Schmidt, Ber. **29**, 908; Barbier and Bouveault, Comp. Rend. **122**, 673: see also Harries and Schauweeker, Ber. **34**, 2981).

[**Z.**] *Pulegone* [**128**] gives acetone among the products of its decomposition by heating with formic acid (Wallach, Ann. **289**, 338), or by oxidation with potassium permanganate.

[**AA.**] *Dextrose* [**154**] gives acetone among the products of dry distillation (Tollens, 'Handbuch d. Kohlenhydrate,'

I, 46), and among the products of oxidation by hydrogen peroxide (Cotton, Journ. Pharm. **10**, 195), or of dry distillation with lime (Pereire and Guignard, Fr. Pat. 316060 of 1901; Journ. Soc. Ch. Ind. **21**, 1096).

[**BB.**] From *aconitic acid* [Vol. II] through itaconic acid (Pébal, Ann. **98**, 94), allylene (see under benzyl alcohol [**54**; **M**]), and then as above under **B**.

[**CC.**] From *mannitol* [**51**] through *acroleïn* [**101**] and acrylic acid (see under benzyl alcohol [**54**; **E** and **AA**]), and then as above under **S**.

Acetone is among the products of fusion of mannitol with alkali (Gottlieb, Ann. **52**, 122), and of oxidation by hydrogen peroxide (Cotton, Journ. Pharm. **10**, 195).

[**DD.**] *Isobutyric aldehyde* [**94**], on treatment with caustic potash, forms a trimeric polymeride (Pfeiffer, Ber. **5**, 700; Urech, Ber. **12**, 191; W. H. Perkin, junr., Trans. Ch. Soc. **43**, 91), which, on bromination (in CS_2) and by the action of heat on the polymeride, gives α-bromisobutyric aldehyde = 2-methyl-2-brompropanal. The oxime of the latter, on heating with acetic anhydride, yields a nitrile which is decomposed by sodium carbonate solution with the formation of acetone (Franke, Monats. **21**, 205; 210).

Or isobutyric and acetic aldehydes condense to form an aldol ($C_6H_{12}O_2$), which, on oxidation with potassium permanganate, gives trimethylethylene lactic acid (Lilienfeld and Tauss, Monats. **19**, 81). From the latter, through tertiary amyl alcohol, &c., as above under **K** and **E**.

Or isobutyric and formic aldehydes condense to form a glycol, which gives methylisopropyl ketone among the products of decomposition by heating with water (Lieben, Monats. **23**, 60). From the ketone as under **K** above.

Or isobutyric aldehyde condenses in contact with alkali with the formation of diisopropylglycol = 2:2:4-trimethylpentanediol, and this gives diisopropyl ketone on oxidation with potassium permanganate (Fossek, Monats. **4**, 664; Brauchbar, *Ibid.* **17**, 641; Franke, *Ibid.* 673). The ketone yields acetone on further oxidation as under **K** above.

[**EE.**] *Phloroglucinol* [**86**] gives acetone among other products on heating with 25 per cent. caustic potash solution at 160° (Combes, Bull. Soc. [3] **11**, 716).

[**FF.**] *Chelidonic acid* [Vol. II] gives acetone (and oxalic acid) on heating with aqueous alkali (Lieben and Haitinger, Ber. **16**, 1259).

[**GG.**] *Menthone* [**129**] gives an oxime and the latter a nitrile, which can be converted into an aldehyde isomeric with citronellal. The aldehyde, on oxidation, yields first menthonic acid and finally (β-methyladipic acid and) acetone (Wallach, Ann. **278**, 302; **296**, 131).

[**HH.**] *Acetyl carbinol* [**43**] gives acetone when reduced in acid solution in the cold (Kling, Comp. Rend. **135**, 970).

107. Methyl-n-amyl Ketone; 2-Heptanone.

$$CH_3 . CO . [CH_2]_4 . CH_3$$

Natural Sources.

Occurs in small quantity in oil of cloves (Schimmel's Ber. April, 1897, and April, 1902; Ch. Centr. 1902, **1**, 1058: see also Erdmann, Journ. pr. Ch. [2] **56**, 155; Gerber, Mon. Sci. [4] **11**, 880), and in Ceylon oil of cinnamon (Schimmel's Ber. April, 1902; Walbaum and Hüthig, Journ. pr. Ch. [2] **66**, 47).

Synthetical Processes.

[**A.**] *Normal heptane* [**2**], on chlorination, gives (with n-heptyl chloride) 2-chlorheptane (Pelouze and Cahours, Jahresber. **1863**, 528; Schorlemmer, Ann. **136**, 266; Morgan, Ann. **177**, 307), from which the secondary alcohol (2-heptanol) can be obtained by the usual methods (Schorlemmer, Ann. **127**, 315; **161**, 278; Journ. Ch. Soc. **26**, 319); Morgan, *loc. cit.*). The alcohol gives the ketone on oxidation (Schorlemmer, Ann. **161**, 279).

Or n-heptane may be nitrated and the 2-nitroheptane reduced to methylamyl

ketone (Konowaloff, Journ. Russ. Soc. **25**, 487; Ber. **26**, Ref. 881).

[B.] *Heptoic aldehyde* or *œnanthol* [97] by the action of phosphorus pentachloride gives 1 : 1-dichlorheptane = œnanthylidene chloride (Limpricht, Ann. **103**, 81), which by the extreme action of alcoholic potash is converted into 6-(*a*)-heptine = œnanthine or œnanthylidene (*Ibid.* 84; Rubien, Ann. **142**, 294; Welt, Ber. **30**, 1496). The latter, on dissolving in sulphuric acid and distillation with water, yields 2-heptanone (Béhal, Ann. Chim. [6] **15**, 270).

The ketone is formed also by heating the heptine with acetic acid to 280° and decomposing the product with water (Béhal and Desgrez, Comp. Rend. **114**, 1074: see also Desgrez, Ann. Chim. [7] **3**, 228, and Moureu and Delange, Comp. Rend. **131**, 710; 800).

Or the sodium derivative of heptine interacts with chlorocarbonic ester (from carbon oxychloride and the alcohol) to form amylpropiolic ester, the free acid of which, on heating with alcoholic potash, gives hexoylacetic acid. The latter decomposes readily at 60° into carbon dioxide and methyl-n-amyl ketone (Moureu and Delange, *loc. cit.* **132**, 1121).

Or the free acid on esterification with hydrogen chloride and an alcohol gives amyl-β-chloracrylic ester, and this also yields methyl-n-amyl ketone on treatment with alcoholic potash (*Ibid.*).

Or the sodium derivative of heptine interacts with *ethyl formate* to form amylpropiolic aldehyde, $CH_3[CH_2]_4 . C \vdots C . CHO$, and this gives methyl-n-amyl ketone among the products of its decomposition by boiling aqueous alkali (*Ibid.* **133**, 96).

[C.] From *n-heptyl alcohol* [26] and *palmitic acid* [Vol. II]. Heptyl palmitate gives n-heptylene on heating to 350° in an atmosphere of carbon dioxide, and the heptylene combines with bromine to form a dibromide (1 : 2-dibromheptane), which, by the action of alcoholic potash, yields heptine = n-amylacetylene (Welt, *loc. cit.* 1493). From heptine as above under **B.**

108. Methyl-n-heptyl Ketone; 2-Nonanone.

$CH_3 . CO . [CH_2]_6 . CH_3$

Natural Sources.

Occurs to the extent of about 5 per cent. in oil of rue from *Ruta graveolens* (Thoms, Ch. Centr. 1901, **1**, 524; Ber. deut. pharm. Gesell. **11**, 3; Houben, Ber. **35**, 3587). This ketone is the chief constituent of Algerian oil of rue (v. Soden and Henle, Pharm. Zeit. **46**, 277; 1026; Pharm. Journ. **67**, 1619; Ch. Drug. **60**, 304; Power and Lees, Trans. Ch. Soc. **81**, 1588). Has been found also in oil of cloves (Schimmel's Ber. April, 1903; Ch. Centr. 1903, **1**, 1086).

Synthetical Processes.

[A.] From *acetic* and *n-octoic acids* [Vol. II] by distilling a mixture of the barium salts (Thoms, *loc. cit.*).

[B.] From *n-heptyl* [26] and *n-propyl alcohol* [15], a mixture of which on heating with sodium to 230° gives a decanol = 8-methyl-9-nonanol. The latter, on fusion with alkali, yields a decoic acid, $CH_3 . [CH_2]_6 . CH(CH_3) . COOH$, which on oxidation with chromic acid gives the above ketone among other products (Guerbet, Comp. Rend. **135**, 172; Ann. Chim. [7] **27**, 67).

109. Methyl-n-nonyl Ketone; 2-Undecanone.

$CH_3 . CO . [CH_2]_8 . CH_3$

Natural Sources.

Occurs as the principal constituent of oil of rue from *Ruta graveolens* (Greville Williams, Phil. Trans. 1858, **1**, 99; Hallwachs, Ann. **113**, 109; Harbordt, Ann. **123**, 293; Giesecke, Zeit. [2] **6**, 429; Carette, Journ. Pharm. [6] **10**, 255; Thoms, Ch. Centr. 1901, **1**, 524; Houben, Ber. **35**, 3590); in Algerian oil of rue (v. Soden and Henle, Ch. Centr. 1901, **1**, 1006; Pharm. Zeit. **46**,

277; 1026; Ch. Drug. **60**, 304; Power and Lees, Trans. Ch. Soc. **81**, 1588).

The ketone occurs also in the essential oil of lime leaves from *Citrus limetta* (Watts, Trans. Ch. Soc. **49**, 316).

Synthetical Processes.

[A.] From *octyl alcohol* [28] and *acetoacetic acid* (*ester*) [Vol. II]. The alcohol is converted into n-octyl iodide (Zincke, Ann. **152**, 2; Möslinger, Ann. **185**, 55), and the latter by interaction with sodio-acetoacetic ester gives octyl-acetoacetic ester (Guthzeit, Ann. **204**, 2), which, on decomposition with alcoholic potash, yields the ketone (*Ibid.* 4).

[B.] From *acetic* and *decoic acids* [Vol. II] by the dry distillation of a mixture of the calcium salts (Gorup-Besanez and Grimm, Ann. **157**, 275; Ber. **3**, 518).

110. Methyl-n-decyl Ketone; 2-Dodecanone.

$CH_3 . CO . [CH_2]_9 . CH_3$

Natural Source.

Possibly in oil of rue with the preceding ketone (references as under undecanone [109] above).

Synthetical Processes.

[A.] From *acetic* and *lauric acids* [Vol. II] through methylundecyl ketone (2-tridecanone) by distilling a mixture of the barium salts (Krafft, Ber. **12**, 1667). This ketone on oxidation gives (with acetic acid) undecanoic acid (*Ibid.*), the barium salt of which, on distillation with barium acetate, yields 2-dodecanone (*Ibid.* **15**, 1708).

Note:—The identity of the natural with the artificial product requires confirmation.

111. Methylheptenone; 2-Methyl-2-heptene-6-one.

$(CH_3)_2 : C : CH . CH_2 . CH_2 . CO . CH_3$

Note:—For constitution see Tiemann and Semmler, Ber. **26**, 2721; **28**, 2128; Harries, Ber. **35**, 1179.

Natural Sources.

In lemon-grass oil (Barbier and Bouveault, Comp. Rend. **118**, 983; Bertram and Tiemann, Ber. **32**, 834), in oil of Mexican 'lignaloe' (Schimmel's Ber. April, 1892; Oct. 1894; Barbier and Bouveault, *loc. cit.* **121**, 168), and in citronella oil (Schimmel's Ber. April, 1895). In oil of lemon (*Ibid.* Oct. 1902; Ch. Centr. 1902, **2**, 1207).

The ketone is probably present in other essential oils containing geraniol, linaloöl, and citral (see Tiemann, Ber. **31**, 3286).

Synthetical Processes.

[A.] From *methyl* and *ethyl alcohols* [13; 14], *acetic* and *propionic acids* [Vol. II], and *acetone* [106]. Dimethylethyl carbinol is prepared by the interaction of zinc methyl and propionyl chloride (Popoff, Ann. **145**, 292; Jermolajeff, Zeit. [2] **7**, 275; Wischnegradsky, Ann. **190**, 336). On bromination this alcohol gives as chief product the amylene bromide, $(CH_3)_2 : CBr . CHBr . CH_3 = 2 : 3$-dibrom-3-methylbutane, which by the extreme action of alcoholic potash is converted into dimethylallylene = 3-methyl-1 : 2-butadiëne (see under acetone [106; E], and Ipatieff, Ber. **29**, Ref. 91). The latter, on combination with hydrogen bromide, gives the amylene bromide, $(CH_3)_2 : CBr . CH_2 . CH_2Br = \beta$-dimethyltrimethylene bromide = 1 : 3-dibrom-3-methylbutane (Ipatieff, *loc. cit.* 92). The latter reacts with sodio-acetylacetone to form a diketone, $(CH_3)_2 : C : CH . CH_2 . CH(CO . CH_3)_2$, which, on decomposition with strong caustic soda solution, yields (with acetic acid) a small quantity of methyl-heptenone (Barbier and Bouveault, Comp. Rend. **122**, 1423).

Note:—Acetylacetone is obtained by the action of sodium on a mixture of acetone and ethyl acetate (Claisen and Ehrhardt, Ber. **22**, 1011; also Germ. Pat. 49542 of 1899: see also under n-primary amyl alcohol [20; B and C]).

The dimethylethyl carbinol may also be prepared from the *amyl alcohol* of fusel oil [22] through the correspond-

ing amylene (see under acetone [106; E]). Or the fusel oil amylene (trimethylethylene) may be combined directly with bromine to form 2 ; 3-dibrom-3-methylbutane (Wurtz, Ann. Chim. [3] **55**, 458; Bauer, Bull. Soc. **2**, 149), and the latter treated as above. Or fusel oil amyl alcohol may be converted into isopropylacetylene (as under acetone [106; E]), and the latter into dimethylallylene by heating with alcoholic potash to 150° (Faworsky, Journ. pr. Ch. [2] **37**, 392). Subsequent steps as above.

Or from ethyl alcohol and acetic acid through *acetoacetic ester* [Vol. II] and the above dimethyltrimethylene bromide. The latter interacts with sodioacetoacetic ester and sodium ethoxide to form dimethylallylacetoacetic ester, which, on heating with barium hydroxide solution or dilute alcoholic potash, gives methylheptenone (Ipatieff, Ber. **34**, 594).

Or from ethyl alcohol, acetic acid, and acetone through acetopropyl alcohol by the action of sodium ethylate on acetoacetic ester and ethylene bromide, and decomposition of the product (bromethylacetoacetic ester) by boiling with dilute hydrochloric acid (W. H. Perkin, junr., and Freer, Trans. Ch. Soc. **51**, 833; Lipp, Ber. **22**, 1197). Acetopropyl alcohol is converted by the action of fuming hydriodic acid into the corresponding iodide, $CH_3.CO.[CH_2]_2.CH_2I$; the latter, by the action of zinc and acetone and the decomposition of the intermediate product with water, into the tertiary alcohol, $CH_3.CO.[CH_2]_3.C(CH_3)_2.OH$; the tertiary alcohol into the oxide by dry distillation, and then into the iodide, $CH_3.CO.[CH_2]_3.C(CH_3)_2.I$, by the addition of hydrogen iodide. The tertiary iodide gives methylheptenone by the action of caustic alkali in dilute solution (Verley, Bull. Soc. [3] **17**, 122).

[B.] *Isovaleric aldehyde* [95] and *acetone* [106] condense in the presence of alkali to form methylheptenone (Leser, Bull. Soc. [3] **17**, 108 : according to Tiemann, Ber. **31**, 817, note 5, this product is not a pure ketone: see also Tiemann and Krüger, Ber. **28**, 2115).

[C.] *Cineole* [40] on oxidation with potassium permanganate gives cineolic acid, $C_{10}H_{16}O_5$ (Wallach and Gildemeister, Ann. **246**, 268), the anhydride of which on dry distillation yields methylheptenone (Wallach, Ann. **258**, 325). The latter is identical with the natural product (Tiemann and Semmler, Ber. **28**, 2126, note 1 ; also Schimmel's Ber. Oct. 1894).

[D.] *Dimethylheptenol* [35] gives methylheptenone among the products of its oxidation by chromic acid mixture (Barbier, Comp. Rend. **126**, 1424 : see also Schimmel's Ber. Oct. 1898, and Tiemann, Ber. **31**, 2991).

[E.] *Citral* [104] gives methylheptenone (with acetic aldehyde) on boiling with sodium carbonate solution (Verley, Bull. Soc. [3] **17**, 175).

[F.] *Geraniol* [36], on heating with strong alcoholic potash at 150°, gives methylheptenol, and this yields methylheptenone on oxidation (Tiemann, Ber. **31**, 2989 ; **32**, 111).

112. Phorone ; 2 : 6-Dimethyl-2 : 5-heptadiënone-4.

$(CH_3)_2:C:CH.CO.CH:C(CH_3)_2$

A phorone ($C_9H_{14}O$) is said to have been obtained from glycerol by bacterial fermentation (hay *bacilli* : Schulze, Ber. **15**, 64). This has been regarded as possibly identical with the phorone obtained from *acetone* [106] by heating with lime or with hydrochloric acid followed by alcoholic potash (Fittig, Ann. **110**, 32; Baeyer, Ann. **140**, 301 : also **61**; **B**, p. 126). The phorone obtained by Fittig's method is isophorone (Bredt and Rübel, Ann. **289**, 10; **299**, 160).

The identity of the biochemical with the synthetical product has not been fully established.

113. Diacetyl ; Dimethyldiketone ; Diketobutane ; Butadione.

$CH_3.CO.CO.CH_3$

Natural Sources.

This diketone has been found in aqueous distillates from oil of caraway (Schimmel's Ber. Oct. 1899; Ch. Centr.

1899, **2**, 880), from vetiver oil from *Andropogon muricatus*, E. and W. Indies, Brazil, &c. (*Ibid.* April, 1900; Ch. Centr. 1900, **1**, 907), and from oil of bay (*Ibid.* April, 1901). Occurs also in the lower boiling-point fraction of oil of savin from *Juniperus sabina* (*Ibid.* Oct. 1900; Ch. Centr. 1900, **2**, 970), in the cohobation water of the same oil, and in the distillation water of W. Indian sandal-wood oil (*Ibid.* April, 1903; Ch. Centr. 1903, **1**, 1086).

NOTE:—It has not yet been proved that diacetyl pre-exists ready formed in these oils.

SYNTHETICAL PROCESSES.

[A.] From *methyl alcohol* [13] and *acetoacetic ester* [Vol. II] through isonitrosomethylethyl ketone, &c., or through acetosuccinic ester, &c., as under quinol [71; O]. Or through γ-brom-methylacetoacetic ester and tetrinic acid, or through lævulic acid (*Ibid.*). Or through pyroracemic acid, &c. (*Ibid.* DD).

Or from methyl alcohol and acetoacetic ester through methylethyl ketone (methylacetyl carbinol [44; B]). The ketone is converted into the isonitroso-derivative by the action of amyl nitrite in presence of sodium ethylate or hydrogen chloride according to the method of Claisen and Manasse (Ber. **20**, 656; 2194; **22**, 526; Kalischer, Ber. **28**, 1518; Diels and Jost, Ber. **35**, 3290). From the isonitroso-ketone = diacetylmonoxime as under quinol [71; O].

NOTE:—All generators of methylethyl ketone given under methylacetyl carbinol [44] thus become generators of diacetyl.

[B.] From *oxalic* and *acetic acids* [Vol. II] and *alcohol* [14] through ketipic acid, &c. [71; S].

[C.] From *dextrose* [154], *lævulose* [155], or *mannose* [156] through lævulic acid (see under erythritol [50; H; I; J] and quinol [71; O]).

[D.] From *glycerol* [48] and *acetic* or *malonic acid* [Vol. II] through lævulic acid (erythritol [50; F; G]). Or from glycerol through glyceric and pyroracemic acids (quinol [71; X]); or from glycerol and *acetoacetic ester* through allylacetone and lævulic acid (erythritol [50; G]).

[E.] From *hydrogen cyanide* [172] and *acetic acid* [Vol. II] through pyroracemic acid (quinol [71; DD]). Or from hydrogen cyanide and *ethyl alcohol* [14] through pyroracemic acid (*Ibid.* CC).

[F.] From *isohexoic acid* [Vol. II] through lævulic acid (erythritol [50; E]).

[G.] From *acetic aldehyde* [92] through lævulic acid (erythritol [50; N]). Or from aldehyde and *zinc ethyl* through secondary butyl alcohol = 2-butanol (secondary butyl mustard oil [165; D]). The secondary alcohol gives diacetyl when oxidised by nitric acid (Ponzio, Gazz. **31**, 401).

NOTE:—The generators of secondary butyl alcohol given under secondary butyl mustard oil thus become generators of diacetyl. These are:—*methyl* [13]; *ethyl* [14]; *normal* and *isobutyl alcohols* [17; 18]; *erythritol* [50]; *formic acid*; *isovaleric acid*; *acetoacetic ester*; and all generators of methylethyl ketone.

[H.] From *n-propyl* [15] or *isopropyl alcohol* [16] through propylene and pyroracemic acid (quinol [71; HH]).

NOTE:—All generators of propylene thus become, through pyroracemic acid, generators of diacetyl.

[I.] From *acetone* [106] and *ethyl acetate* through acetylacetone and lævulic acid (erythritol [50; G]).

[J.] From *methylheptenone* [111] through lævulic acid (erythritol [50; Q]).

[K.] From *dimethylheptenol* [35] through lævulic acid (*Ibid.* N).

[L.] From *propionic acid* [Vol. II] through pyroracemic acid (quinol [71; FF]).

[M.] From *lactic acid* [Vol. II] through pyroracemic acid (*Ibid.* GG).

[N.] From *tartaric* or *racemic acid* [Vol. II] through pyroracemic acid (*Ibid.* BB).

[O.] From *citric acid* [Vol. II] through pyroracemic acid (*Ibid.* EE).

AROMATIC ALDEHYDES AND KETONES.

114. Benzoic Aldehyde; Benzaldehyde; Phenal.

Natural Sources.

The complex exists in the glucoside amygdalin, first discovered in the bitter almond, *Amygdalus communis*, var. *amara* (Robiquet and Boudron, Ann. Chim. [2] **44**, 352; Henry and Boudron, Journ. Pharm. **22**, 118).

Amygdalin, either alone or in association with its amorphous form, laurocerasin, exists also in seeds of *Prunus domestica*, *P. spinosa*, *P. armenica*, *P. avium*, *P. cerasus*, *P. cerasus-austera*, *P. chamæcerasus*, *P. laurocerasus*, *P. padus*, *P. mahaleb*, *Persica vulgaris*, *Amygdalus nana*, *Pyrus malus*, *Cydonia vulgaris*, *Sorbus aucuparia*, *Cotoneaster vulgaris*, *Cratægus oxyacantha*, *Mespilus japonica* (Van Rijn, 'Die Glykoside,' p. 232).

Amygdalin occurs also in leaves of *Gymnema latifolium*, and in the bark of species of *Pygium* (Greshoff, Ber. **23**, 3548).

Note:—For full references see Van Rijn as above; for occurrence of amygdalin in Drupaceous and Pomaceous plants see Lehmann, Jahresber. **1885**, 1799; for recent confirmation of occurrence in seeds of Pomaceae, viz. *Malus communis*, *Cydonia vulgaris*, *C. japonica*, *Sorbus aria*, and *S. aucuparia*, see Lutz, Rép. d. Pharm. 1897, 312.

Benzaldehyde occurs in niauli oil from the fresh leaves of *Melaleuca viridiflora*, New Caledonia (Bertrand, Bull. Soc. [3] **9**, 433); in cajeput oil from the leaves and stems of *Melaleuca leucadendron* (Voiry, Comp. Rend. **106**, 1538; Bull. Soc. [2] **50**, 108); in oil of cinnamon from *Cinnamomum zeylanicum* (Weber, Arch. Pharm. **230**, 728: for occurrence in oil of Ceylon cinnamon see Schimmel's Ber. April, 1902; Walbaum and Hüthig, Journ. pr. Ch. [2] **66**, 47).

The aldehyde occurs in oil from the leaves of *Indigofera galegoïdes* (Schimmel's Ber. Oct. 1894, and April, 1896).

Oroxylin from the bark of *Oroxylon indicum* may contain the benzoic aldehyde complex (Naylor and Dyer, Trans. Ch. Soc. **79**, 954). The aldehyde is contained in rassamala resin from the Javan *Attingia excelsa* (Tschirch and Van Itallie, Arch. Pharm. **239**, 541).

A condensation product of benzaldehyde and methyl-n-nonyl ketone occurs in oil of rue (Thoms; Schimmel's Ber. Oct. 1901).

Synthetical Processes.

[A.] All generators of *benzene* and *toluene* (see under cymene [6] and under benzyl alcohol [54]) become generators of benzoic aldehyde through the following processes:—

Benzyl chloride by oxidation with dilute nitric acid or lead nitrate (Bertagnini, Ann. **85**, 183; Lauth and Grimaux, Bull. Soc. [2] **7**, 106).

Or toluene can be chlorinated up to the stage of benzylidene = benzal chloride (Beilstein, Ann. **116**, 336; **146**, 322; Schramm, Ber. **18**, 608). The latter gives benzoic aldehyde on heating with water, alkalis, or alkaline carbonates in aqueous solution (Cahours, Comp. Rend. **56**, 222; Meunier, Bull. Soc. [2] **38**, 159; Limpricht, Ann. **139**, 319), or with milk of lime (technical process: Espenschied, Germ. Pat. 47187 of 1880), or with water at 95° in presence of iron or iron salts (Schultze, Germ. Pats. 82927 of 1894 and 85493 of 1895; Ber. **28**, Ref. 879; **29**, Ref. 314). Benzal bromide yields the aldehyde on contact with water at ordinary temperatures (Curtius and Quedenfeldt, Journ. pr. Ch. [2] **58**, 390).

A mixture of benzyl and benzal chlorides gives benzaldehyde on oxida-

tion with manganese dioxide suspended in water (Schmidt, Germ. Pat. 20909 of 1882; Ber. 16, 448).

Benzal chloride gives benzoic aldehyde on heating with acetic acid in presence of zinc chloride, &c. (Jacobsen, Ber. 13, 2013; 14, 1425; Germ. Pat. 11494 of 1879, and suppl. Pat. 13127 of 1880; Ch. Ind. 3, 384; 4, 202); or with strong sulphuric acid and subsequent treatment with water (Oppenheim, Ber. 2, 213); or with anhydrous oxalic acid (Anschütz, Ann. 226, 18).

Or benzylamine (from benzyl chloride and ammonia; see under benzyl mustard oil [169; H]) gives the oxime of benzoic aldehyde among the products of oxidation by monopersulphuric acid (Bamberger and Scheutz, Ber. 34, 2262). Benzylamine gives the aldehyde by oxidation with sulphuric acid and a dichromate (De Coninck and Combe, Comp. Rend. 127, 1222).

Or benzylaniline (from benzyl chloride and aniline) gives benzaldehyde on oxidation with dichromate and sulphuric acid, &c. (Meister, Lucius, and Brüning, Eng. Pat. 10689 of 1896); the sulphonic acid of benzylaniline also gives benzaldehyde when oxidised in alkaline or neutral solution (*Ibid.* Ch Centr. 1897, 2, 1063). Benzylidene derivatives are formed as the first products, and the aldehyde results from their hydrolysis in these processes. Dibenzylaniline can be similarly converted into benzaldehyde by oxidation (*Ibid.* Ch. Centr. 1900, 2, 460: for further list of patents by this firm relating to the production of aldehydes from benzylidene compounds see under p-hydroxybenzaldehyde [119; E]). Benzylideneaniline gives benzoic aldehyde by the action of acid chlorides (Garzarolli-Thurnlackh, Ber. 32, 2277).

Toluene on treatment with chromium oxychloride and decomposition of the product with water gives benzoic aldehyde (Etard, Ann. Chim. [5] 22, 225). The aldehyde is also among the products of the electrolysis of a mixture of toluene, alcohol, and dilute sulphuric acid (Renard, Jahresber. 1881, 352; also Merzbacher and Smith, Journ. Am. Ch. Soc. 22, 723; Puls, Ch. Zeit. 25, 263), and among the products of oxidation of toluene by potassium persulphate (Moritz and Wolffenstein, Ber. 32, 433), by manganese peroxide in presence of sulphuric acid (Soc. Chim. d. Usines du Rhône, Germ. Pat. 191221 of 1897; Ch. Centr. 1899, 1, 959; 107722 of 1898; Ch. Centr. 1900, 1, 1113; Weiler, Ber. 33, 464), or by nickel or cobalt oxides (Bad. An. Sod. Fab. Germ. Pat. 127388 of 1900; Ch. Centr. 1902, 1, 150).

Benzene gives benzoic aldehyde when carbon monoxide and hydrogen chloride are passed through the hydrocarbon in the presence of aluminium chloride and cuprous chloride (Farb. vorm. F. Bayer & Co., Germ. Pat. 98706 of 1897; Ch. Centr. 1898, 2, 951: see also Reformatsky, Journ. Russ. Soc. 33, 154). According to Küchler and Buff (Germ. Pat. 126421 of 1899; Ch. Centr. 1901, 2, 1372) this process does not work with aluminium chloride, but gives good results with the bromide or iodide.

Benzene and chloroform give a small quantity of benzaldehyde among other products by the action of ferric chloride (Meissel, Ber. 32, 2422).

Or from benzene and *hydrogen cyanide* [172] by passing the latter gas with hydrogen chloride through the hydrocarbon in presence of aluminium chloride, and decomposing the product with acid (Farb. vorm. F. Bayer & Co., Eng. Pat. 19204, Aug. 1897; Journ. Soc. Ch. Ind. 17, 838).

From benzene, *acetic acid*, and *hydrogen cyanide* [172] through iminobenzoylmethyl cyanide (benzacetodinitrile) by the action of sodium on a mixture of benzonitrile and acetonitrile in dry ether (Holzwart, Journ. pr. Ch. [2] 39, 242), 1^2-cyanacetophenone by the action of hydrochloric acid on the imino-cyanide (Meyer, *Ibid.* 243), benzoylacetiminoethyl ether by the action of alcoholic hydrochloric acid on the cyanoketone (Haller, Bull. Soc. [2] 48, 24), benzoylacetic ester by the action of dilute alcohol on benzoylacetiminoethyl ether (*Ibid.* 25), and then as below under C.

NOTES:—Acetonitrile is obtained from *ammonium acetate* [Vol. II] through acetamide and

the dehydration of the latter by heat or phosphorus pentoxide, &c. (Dumas, Comp. Rend. 35, 383; Buckton and Hofmann, Journ. Ch. Soc. 9, 242; Henry, Ann. 152, 149; Wallach, Ann. 184, 21; Demarçay, Bull. Soc. [2] 33, 456). Also from *methyl alcohol* [13] by distilling methyl sulphates with *potassium cyanide* or *ferrocyanide* [172] (Dumas, Malaguti, and Leblanc, Comp. Rend. 25, 474; Frankland and Kolbe, Mem. Ch. Soc. 3, 386; Ann. 65, 288). *Hydrogen cyanide* [172] and diazomethane combine to form acetonitrile (v. Pechmann, Ber. 28, 857). *Ethylamine* [Vol. II] gives acetonitrile among the products of oxidation by monopersulphuric acid (Bamberger, Ber. 35, 4293).

Benzonitrile can be obtained from benzene by the action of *cyanogen chloride* [172] in presence of aluminium chloride (Friedel and Crafts, Ann. Chim. [6] 1, 528); by the action of aluminium chloride on a mixture of benzene vapour and *cyanogen* [172] (Desgrez, Bull. Soc. [3] 13, 735); by distilling benzenesulphonates with potassium cyanide (Merz, Zeit. [2] 4, 33) or (practically) by the diazo-method through nitrobenzene, aniline, &c. (Sandmeyer, Ber. 17, 2653).

Also from benzene and *formic* or *oxalic acid* [Vol. II], aniline and oxalic acid giving benzonitrile on distillation (Hofmann, Ann. 142, 125) and formanilide giving the nitrile on distillation over zinc dust (Gasiorowski and Merz, Ber. 17, 73; 18, 1001).

Also from aniline and *acetic acid* [Vol. II] by the action of sodium hydroxide on aniline dichloracetate (Cech and Schwebel, Ch. Centr. 1877, 134); from chlor- or brombenzene and *potassium ferrocyanide* [172] at 400° (Merz and Weith, Ber. 8, 918; 10, 749); from iodobenzene and *silver cyanide* (Merz and Schelnberger, Ber. 8, 1630); from benzene and *cyanogen* [172] by pyrogenic synthesis (*Ibid.*; Merz and Weith, Ber. 10, 753); from aniline and *methyl alcohol* [13] through dimethylaniline and the action of heat on the latter (Nietzki, Ber. 10, 474); or from aniline through phenyl isocyanide and isomeric transformation at 220° (Weith, Ber. 6, 213) and from aniline and *carbon disulphide* [160] through phenyl thiocarbimide and the action of copper on the latter (*Ibid.* and 7, 725); from magnesium nitride and *benzoic anhydride* (Emmerling, Ber. 29, 1635); from benzoic acid and *ethylene cyanide* (Mathews, Journ. Am. Ch. Soc. 20, 650); from *benzoyl chloride* and *methylamine* through benzenylmethylimido-chloride (v. Pechmann, Ber. 33, 611).

From benzene and *acetic acid* through acetophenone, by the action of acetyl chloride on benzene in presence of aluminium or ferric chloride (Friedel and Crafts, Ann. Chim. [6] 1, 507; 14, 455; Nencki and Stoeber, Ber. 30, 1768; Boeseken, Rec. Tr. Ch. 20, 102), and then as under **G** and **C** below.

From benzene and *ethyl alcohol* [14]. The latter, on treatment with nitric acid in presence of mercury, gives mercury fulminate (Howard, Phil. Trans. 1800; Liebig, Ann. 95, 284; Steiner, Ber. 9, 787; Lobry de Bruyn, Ber. 19, 1370). The fulminate interacts with benzene in presence of a mixture of aluminium chloride and hydroxide, giving benzaldehyde (with its oxime, benzonitrile and benzamide) (Scholl, Ber. 32, 3492; 36, 10).

Or from benzene and *methyl alcohol* [13] through nitromethane by the interaction of methyl iodide and silver nitrite (see under glycerol [48; **L**]). Sodium-nitromethane on treatment with mercuric chloride solution gives a compound which yields mercury fulminate on treatment with hydrochloric acid (Jones, Am. Ch. Journ. 20, 33; also Nef, Ann. 280, 276). Subsequent steps as above.

Or from benzene and *ethyl alcohol* [14] through ethylbenzene and styrene bromide (see under styrene [7; **A**] and under phlorol [64; **A**]). The latter can be converted into styrene glycol or into phenyl-β-lactic acid, and either of these into benzaldehyde as below under **B**. Or ethylbenzene can be converted into acetophenone by oxidation with chromic and acetic acids, or by decomposing its chromoxychloride with water (Friedel and Balsohn, Bull. Soc. [2] 32, 616; v. Miller and Rohde, Ber. 23, 1078), and the ketone treated as under **G**. (See also Fournier, Comp. Rend. 133, 634).

Or from benzene and *normal* or *isopropyl alcohol* [15; 16] through isopropylbenzene by the interaction of the alkyl bromide and benzene in presence of aluminium bromide, or of the alkyl chloride and benzene in presence of aluminium chloride (see under cymene [6; **A**]), or of brombenzene and the iso-alkyl iodide by sodium (Jacobsen, Ber. 8, 1260). Isopropylbenzene gives acetophenone (with hydratropic aldehyde) on oxidation with chromium oxychloride (v. Miller and Rohde, Ber. 24, 1358).

Trimethylene bromide [15; **E**] from *glycerol* [48] and benzene condense under the influence of aluminium chloride with the formation of diphenylpropane and propyl and isopropylbenzene. Propylene bromide produces the same hydrocarbons (Bodroux, Comp. Rend. 132, 155).

Note:—Generators of isopropylbenzene are also given under cymene [6; A, note].

Or from benzene and *oxalic acid* [Vol. II] by the action of ethyloxalyl chloride = chlorethanalic ester, $ClCO.CO_2.C_2H_5$, on the hydrocarbon in the presence of aluminium chloride. Phenylglyoxylic ester is synthesised by this method, and the acid gives benzaldehyde as below under **C** (Bouveault, Bull. Soc. [3] **15**, 1017; **17**, 363: see also Roser, Ber. **14**, 940).

Or from benzene and *acetic aldehyde* [**92**] through aniline and phenylhydrazine and acetaldehydephenylhydrazone. The latter gives acetophenone when oxidised by air in alcoholic potash solution (Biltz and Wienands, Ann. **308**, 16: see also v. Pechmann, Ber. **31**, 2125).

[**B.**] *Styrene* [**7**] on heating with nitric acid, or by the action of 'nitrous' gas, gives phenylnitroethylene, $C_6H_5.CH:CH.NO_2$ (Simon, Ann. **31**, 269; Blyth and Hofmann, Ann. **53**, 297; Priebs, Ann. **225**, 328). The latter yields benzoic aldehyde on heating with water, aqueous alkali, or dilute sulphuric acid (Priebs, *loc. cit.*). Or phenylnitroethylene, on heating with strong hydrochloric acid, gives phenylchloracetic acid (Priebs, *loc. cit.* 337), and this yields mandelic acid on boiling with aqueous alkali (Spiegel, Ber. **14**, 239). The latter acid gives benzoic aldehyde on dry distillation, on oxidation (Liebig, Ann. **18**, 321), or on electrolysis of a solution of the potassium salt (v. Miller and Hofer, Ber. **27**, 469).

Or styrene can be converted into the bromide by bromination (Blyth and Hofmann, Ann. **53**, 306; Glaser, Ann. **154**, 154; Zincke, Ann. **216**, 288), the corresponding phenylglycol by boiling with aqueous potassium carbonate (Zincke, *loc. cit.* 293), and into benzoic aldehyde by oxidising the glycol with chromic acid mixture. Or on oxidation with nitric acid the glycol gives phenylglyoxylic acid (Zincke and Hunäus, Ber. **10**, 1488), from which benzoic aldehyde can be obtained as below under **C**.

Or styrene bromide on heating with strong alcoholic potash gives phenylacetylene (Glaser, Ann. **154**, 155; Friedel and Balsohn, Bull. Soc. [2] **35**, 55; Holleman, Ber. **20**, 3081), which can be converted into acetophenone as under **E**, and the latter treated as under **G**.

Or styrene bromide on heating with water, alcoholic potash, or potassium acetate gives 1^1-bromstyrene (Radziszewski, Ber. **6**, 493; Glaser, Ann. **154**, 168; Zincke, Ann. **216**, 290: according to Nef, Ann. **303**, 273, 1^2-(ω)-bromstyrene is also formed by these methods), and this, by the action of sodium and carbon dioxide, yields phenylpropiolic acid (Erlenmeyer, Ber. **16**, 152), the ester of which, when dissolved in strong sulphuric acid and the solution poured on to ice, gives benzoylacetic ester (Baeyer, Ber. **15**, 2705). The latter can be reduced to phenyl-β-lactic acid, and the acid converted into benzaldehyde as below under **C**. Or phenylpropiolic ester can be converted into benzoylacetic ester by the action of dilute caustic alkali (Baeyer and W. H. Perkin, junr., Ber. **16**, 2128; W. H. P., junr., Trans. Ch. Soc. **45**, 174).

Or 1^1-bromstyrene on heating with water at 180° gives acetophenone (Friedel and Balsohn, Bull. Soc. [2] **32**, 614), which can be treated as below under **G**.

Or phenylpropiolic acid can be converted into phenylacetylene and acetophenone as below under **E**.

[**C.**] From *benzoic* and *formic acids* [Vol. II] by distilling a mixture of the calcium salts (Piria, Ann. **100**, 104); by reduction of benzoic acid with sodium amalgam in dilute acid solution (Kolbe, Ann. **118**, 122), or with stannous compounds (Dusart, Comp. Rend. **55**, 448); or by electrolytic reduction (Nithack, Germ. Pat. 123554 of 1899; Ch. Centr. 1901, **2**, 715); or by heating with zinc dust (Baeyer, Ann. **140**, 296). Also through benzoyl chloride and benzoyl cyanide and the action of zinc and hydrochloric acid on the latter (Kolbe, Ann. **98**, 344). Or from benzoyl chloride and copper hydride (Chiozza, Ann. **85**, 232).

Benzoyl cyanide by the action of hydrochloric acid in the cold gives phenylglyoxylic = benzoylformic acid (Claisen, Ber. **10**, 430; 845; Hübner and Buchka, *Ibid.* 479). The latter yields benzoic aldehyde among other products on distillation (Claisen, *loc. cit.* 1666). Or phenylglyoxylic acid

may be heated with aniline, and the anilide hydrolysed by heating with acid (Fab. Prod. Chim. Thann & Mulhouse, Germ. Pat. 94018 of 1896; Ch. Centr. 1897, **2**, 1166: see also Bouveault, Bull. Soc. [3] **17**, 363).

Or from benzoic acid and ethyl alcohol and acetic acid through *benzoylacetic ester* [Vol. II] by the action of sodium ethylate on a mixture of ethyl benzoate and acetic ester (Claisen and Lowman, Ber. **20**, 653), and reduction of the benzoylacetic ester to phenyl-β-lactic acid by sodium amalgam (W. H. Perkin, junr., Trans. Ch. Soc. **47**, 254). The latter acid gives benzoic aldehyde on electrolysis of a dilute solution of the potassium salt (v. Miller, Hofer, and Moog, Ber. **27**, 469).

From benzoic acid and *acetoacetic ester* [Vol. II] through benzoylacetoacetic ester (Bonné, Ann. **187**, 1; Fischer and Bülow, Ber. **18**, 2131; Nef, Ann. **266**, 99), the sodium derivative of which is decomposed by aqueous ammonia with the formation of benzoylacetic ester (Claisen, Ann. **291**, 71). From the ester through phenyl-β-lactic acid as above.

Benzoic acid is converted into benzonitrile by dehydrating the ammonium salt by heat or dehydrating agents (Fehling, Ann. **49**, 91; Laurent and Gerhardt, Jahresber. **1849**, 327; Hofmann and Buckton, Ann. **100**, 155; Henke, Ann. **106**, 276; Wöhler, Ann. **192**, 362; Anschütz and Schultz, Ann. **196**, 48; Henry, Ber. **2**, 307). Benzonitrile and acetonitrile give benzaldehyde through iminobenzoylmethyl cyanide, 1^2-cyanacetophenone, benzoylacetiminoethyl ether, benzoylacetic ester (see under **A**), and then through phenyl-β-lactic acid as above.

Note:—For further references to the production of benzonitrile from benzoic acid see under benzyl mustard oil [169; A]. For syntheses of benzonitrile from benzene see the note under **A** above.

Or benzonitrile and *ethyl alcohol* combine in presence of hydrogen chloride to form benzimidoethyl ether (Pinner, Ber. **16**, 353: general synthesis). The ether on reduction with sodium amalgam in acid solution gives benzoic aldehyde (Henle, Ber. **35**, 3041).

Or from benzoic acid and *methyl alcohol* by the interaction of benzoyl chloride and zinc methyl (Popoff, Ber. **4**, 720), and treatment of the acetophenone so produced as under **G**.

Benzoic acid and hydrazine interact with the formation of benzhydrazide, and this in presence of alkali condenses to benzalbenzoylhydrazine. The latter is decomposed by dilute acids into benzoic acid and aldehyde and hydrazine (Curtius, Ber. **33**, 2559).

[**D.**] *Phenylacetic acid* [Vol. II] gives a trace of benzoic aldehyde on electrolysis of an acidified solution of the potassium salt (Petersen, Bull. Acad. Roy. Dane. 1897; Ch. Centr. 1897, **2**, 520). Benzoic aldehyde is also among the products of oxidation of phenylacetic acid by dilute sulphuric acid and manganese dioxide.

Phenylacetic acid gives dibenzyl ketone on distillation of its calcium salt (Popoff, Ber. **6**, 560; Young, Trans. Ch. Soc. **59**, 623). Benzoic aldehyde is among the products of the photochemical oxidation of the ketone (Emily Fortey, Trans. Ch. Soc. **75**, 871).

[**E.**] From *cinnamic acid* [Vol. II] through phenyl-α-chlor-β-lactic acid by combination with hypochlorous acid (Glaser, Ann. **147**, 79), phenyl-β-lactic acid by reducing the chloro-acid with sodium amalgam (*Ibid.* 86), and then as above under **C**.

Or the chloro-acid, on treatment with alcoholic potash, gives β-phenyloxyacrylic = phenylglycidic acid (Glaser, Ann. **147**, 98), and this yields phenyl-β-lactic acid on reduction with sodium amalgam (Plöchl, Ber. **16**, 2823).

Or cinnamic acid can be combined with hydrogen bromide to form 1^1-bromhydrocinnamic = phenyl-β-brompropionic acid (Fittig and Binder, Ann. **195**, 132; Anschütz and Kinnicutt, Ber. **11**, 1221). The latter gives phenyl-β-lactic acid on boiling with water (F. and B. *loc. cit.* 138).

Or cinnamic ester can be brominated so as to give phenyl-$\alpha\beta$-dibrompropionic = $\alpha\beta$-dibromhydrocinnamic ester, and this, by the action of alcoholic potash, gives phenylpropiolic acid (W. H. Perkin, junr., Trans. Ch. Soc. **45**, 172; Lieber-

mann and Sachse, Ber. **24**, 4113, note). The latter yields benzoylacetic acid, phenyl-β-lactic acid, and benzaldehyde as above under **B** and **C**. Or the phenyl dibrompropionic ester by the limited action of alcoholic potash gives a mixture of two bromcinnamic esters, of which the α-ester (1^2-bromcinnamic ester) yields benzoylacetic ester when treated successively with strong sulphuric acid and water (Michael and Browne, Ber. **19**, 1393).

Cinnamic acid can also be brominated (Michael, Journ. pr. Ch. [2] **52**, 292), and the dibromo-acid debrominated in two stages by successive treatment with alkali (*Ibid.* Ber. **34**, 3648). The final product is phenylpropiolic acid, which can be treated as above.

Or the dibromo-acid on heating with 10 per cent. sodium carbonate solution at 100° gives 1^2-(ω)-bromstyrene, and this on heating with strong alcoholic potash at 130–135° yields phenylacetylene (Nef, Ann. **308**, 267). The latter gives acetophenone as below (Friedel and Balsohn, Bull. Soc. [2] **35**, 55), and benzaldehyde as under **G**. Or the dibromo-ester by the action of sodium ethylate gives β-ethoxycinnamic acid (Leighton, Am. Ch. Journ. **20**, 136), and this on heating with alcoholic hydrochloric acid yields benzoylacetic acid (*Ibid.* 137).

The β-iodo-cinnamic acid obtained by iodising the acid in presence of pyridine gives benzoylacetic acid and acetophenone on treatment with sodium hydroxide solution (Ortoleva, Gazz. **29**, 503).

Or phenylpropiolic acid can be converted into phenylacetylene by heating with water or phenol (Glaser, Ann. **154**, 155; Holleman, Ber. **20**, 3081). Phenylacetylene on treatment with sulphuric acid and water gives acetophenone (Friedel and Balsohn, as above), which can be treated as below under **G**.

Or from cinnamic acid through phenylnitroethylene by distilling the acid with sodium nitrite in steam (Erdmann, Ber. **24**, 2773), and then as above under **B**. Or by the direct oxidation of cinnamic acid with potassium permanganate phenylglyceric acid is obtained (Fittig and Rür, Ann. **268**, 27); benzaldehyde is among the products of the electrolysis of the potassium salt of this acid in strong aqueous solution (v. Miller and Hofer, Ber. **27**, 470).

NOTE:—Phenylglyceric acid is also obtained from cinnamic acid through phenyl-α-chlor-β-lactic acid (see above), and the action of aqueous alkali on the latter (Lipp, Ber. **16**, 1286).

[**F.**] *Vulpic acid* [Vol. II] can be converted into pulvic anhydride by heating, and the latter into pulvic acid by the action of caustic potash solution; or vulpic acid is directly convertible into pulvic acid by boiling with milk of lime (Spiegel, Ann. **219**, 6). Pulvic acid on oxidation with alkaline permanganate gives phenylglyoxylic acid (*Ibid.* Ber. **14**, 1689), and this yields benzaldehyde as above under **C**.

[**G.**] From *acetic* and *benzoic acids* [Vol. II] through acetophenone (Friedel, Ann. **108**, 122), phenylglyoxylic acid by oxidation with alkaline permanganate (Glücksmann, Monats. **11**, 248), and then as above under **C**.

Or acetophenone can be converted into $1^2 : 1^2$-dibromacetophenone by bromination (Hunnius, Ber. **10**, 2010), and this on heating with dilute caustic potash solution gives mandelic acid (Engler and Wöhrle, Ber. **20**, 2202), from which benzaldehyde can be obtained as above under **B**.

Or acetophenone can be converted into the 1^2-nitroso-derivative by the action of amyl nitrite and sodium (Claisen, Ber. **20**, 656). The sodium bisulphite compound of the nitroso-ketone gives benzoylformaldehyde (phenethylal = phenylglyoxal) on heating with dilute sulphuric acid (v. Pechmann, Ber. **20**, 2904; Müller and v. Pechmann, Ber. **22**, 2557), and the aldehyde yields mandelic acid on heating with aqueous alkali (v. Pechmann, Ber. **20**, 2905).

Or the nitroso-ketone gives benzoyl cyanide on heating with acetyl chloride or acetic anhydride (Claisen and Manasse, Ber. **20**, 2196). The cyanide yields benzaldehyde as above under **C**.

From acetophenone through benzoylacetic acid by the action of diethyl

carbonate and sodium ethylate on the ketone (Claisen, Ber. **20**, 656), or by the action of carbon dioxide on the sodium compound of acetophenone suspended in dry ether (Beckmann and Paul, Ann. **266**, 17). Benzoylacetic ester can be converted into phenyl-β-lactic acid, and the latter into benzoic aldehyde as above under **C**.

Acetophenone, *formic acid* [Vol. II], and *ethyl alcohol* [14] give benzoylacetaldehyde by the action of sodium ethylate on a mixture of the ketone and formic ester (Claisen and Fischer, Ber. **20**, 2192; **21**, 1135). The oxime of this aldehyde gives 1^2-cyanacetophenone by dehydration (Claisen and Stock, Ber. **24**, 133), and this yields benzoylacetiminoethyl ether (see above under **A**), benzoylacetic ester, phenyl-β-lactic acid, and benzoic aldehyde as under **C**. Or benzoylacetaldoxime by the action of acetyl chloride gives phenylisoxazole, and this yields 1^2-cyanacetophenone by the action of sodium ethylate (*Ibid.* 134).

Or acetophenone, *oxalic acid* [Vol. II], and *ethyl alcohol* [14] give benzoylpyroracemic acid by the action of sodium ethylate (Beyer and Claisen, Ber. **20**, 2184; Claisen and Brömme, Ber. **21**, 1132), the oxime of which, treated with acetyl chloride, gives phenylisoxazolecarboxylic acid (Salvatori, Gazz. **21**, II, 286). The latter yields 1^2-cyanacetophenone on heating (*Ibid.* 287).

[**H.**] From *phenol* [**60**] through triphenyl phosphate by the action of phosphorus pentachloride or oxychloride (Williamson and Scrugham, Journ. Ch. Soc. **7**, 240; Heim, Ber. **16**, 1765), benzonitrile by distilling the phosphate with *potassium cyanide* [**172**] (Scrugham, Ann. **92**, 318; Heim, *loc. cit.* 1771), and then (with acetonitrile) through iminobenzoylmethyl cyanide, &c., as above under **A** and **C**.

[**I.**] *Hippuric acid* [Vol. II] gives benzonitrile on heating *per se* or with zinc chloride (Limpricht and Uslar, Ann. **88**, 133; Gössmann, Ann. **100**, 74). Subsequent steps as above.

[**J.**] From *naphthalene* [**12**] (see under hydrojuglone [**90**]), through phthalic acid (benzyl alcohol [**54**; **R**]), and phthalimide by the action of ammonia on phthalic anhydride (Laurent, Ann. **41**, 110; Lansberg, Ann. **215**, 181). The imide gives benzonitrile on distillation with lime (Laurent, Jahresber. **1868**, 549; Reese, Ann. **242**, 5). Subsequent steps as above.

[**K.**] From *cymene* [**6**] through *cumic aldehyde* [**116**] and cumic acid by oxidation (Gerhardt and Cahours, Ann. **38**, 74; Beilstein and Kupfer, Ann. **170**, 302; R. Meyer, Ann. **219**, 244), isopropylbenzene (cumene) by distilling the acid with lime or baryta (G. and C. *loc. cit.* 88; Ann. Chim. [3] 1, 87; 372; **14**, 107), acetophenone, &c., as above under **A**, **G**, and **C**.

[**L.**] *Benzyl alcohol* [**54**] gives benzoic aldehyde on oxidation with dilute nitric acid, &c. Or by pyrogenic contact decomposition by heated copper (Ipatieff, Ber. **35**, 1055).

[**M.**] From *racemic* or *tartaric acid* [Vol. II] and *n-propyl alcohol* [**15**] through pyroracemic acid, ethylisophthalic acid, and ethylbenzene (see under phlorol [**64**; **J**]), and then as above under **A**.

Or from pyroracemic acid and *isobutyric aldehyde* [**94**] through isopropylbenzene (see under cymene [**6**; **A**, note]), and then as above under **A**.

115. Hydrocinnamic Aldehyde; Phenylpropionic Aldehyde; Phenepropylal.

$C_6H_5 . CH_2 . CH_2 . CHO$

Natural Source.

May possibly occur in Ceylon oil of cinnamon (Schimmel's Ber. April, 1902; Walbaum and Hüthig, Journ. pr. Ch. [2] **66**, 52).

Synthetical Processes.

[**A.**] From *n-propyl alcohol* [**15**] and *benzene* [**6**; **I**, &c.] through propylbenzene by the condensation of propyl bromide and brombenzene by the action of sodium (Fittig, Schäffer, and König, Ann. **149**, 324), or of aluminium chloride (Heise, Ber. **24**, 768). Propylbenzene

forms a compound with chromium oxychloride which gives the above aldehyde on decomposition by water (Etard, Ann. Chim. [5] **22**, 254: according to later experiments by v. Miller and Rohde, Ber. **23**, 1070, this process gives benzoic and not hydrocinnamic aldehyde).

NOTE:—Propyl chloride and benzene give also isopropylbenzene = cumene by the action of aluminium chloride unless the temperature is kept below 0° (Konowaloff, Journ. Russ. Soc. 27, 457).

[B.] From *benzoic aldehyde* [114] and *ethyl alcohol* [14] through ethylphenyl carbinol by the interaction of the aldehyde and magnesium ethiodide, the chloride by the action of phosphorus pentachloride on the alcohol, and propenylbenzene by heating the chloride with pyridine. Propenylbenzene gives propylbenzene on reduction with sodium in alcoholic solution (Klages, Ber. **36**, 621: see also Wagner, Journ. Russ. Soc. **16**, 324).

NOTE:—Generators of propenylbenzene are: bromhydroxyphenylcrotonic acid (Perkin, Journ. Ch. Soc. **32**, 660); α-methyl-β-phenylhydroxypropionic acid (W. H. Perkin, junr., and Stenhouse, Trans. Ch. Soc. **59**, 1010); methylbenzyl ketone or ethylphenyl ketone or the chlorides from the corresponding secondary alcohols (Errera, Gazz. 14, 504; 16, 318); phenopropyltrimethylammonium hydroxide (Senfter and Tafel, Ber. **27**, 2312); brompropiophenone from brompropionic acid and benzene through α-chlor-β-brompropenylbenzene (Kunkell and Dettmar, Ber. **36**, 771: compare with respect to this process Klages, Ber. **36**, 2572).

[C.] From *glycerol* [48] through allyl bromide (see under n-propyl alcohol [15; E]) and *benzene*, a mixture of the bromide and hydrocarbon giving propylbenzene among other products when heated with zinc dust (Shukowski, Journ. Russ. Soc. **27**, 297).

[D.] From *quinoline* [Vol. II], propylbenzene being among the products of reduction by hydriodic acid and phosphorus at 300–310° (Bamberger and Williamson, Ber. **27**, 1477).

[E.] From *cinnamic aldehyde* [123]. The hydrochloride of a formimino-ether (prepared by the interaction of *hydrogen cyanide* [172] and an alcohol in presence of hydrogen chloride; Pinner, 'Die Imidoaether,' 1892) condenses with the aldehyde to form an acetal (Claisen, Ber. **31**, 1016). The latter, after reduction by sodium in alcohol, is decomposed into hydrocinnamic aldehyde on heating with dilute sulphuric acid (Fischer and Hoffa, Ber. **31**, 1991). The dimethyl acetal is also formed from cinnamic aldehyde and methyl alcohol by the condensing action of hydrogen chloride (F. and H. *loc. cit.* 1990).

[F.] From *hydrocinnamic* and *formic acids* [Vol. II] by distilling a mixture of the calcium salts (v. Miller, Rohde, and Gerdeissen, Ber. **23**, 1080: see also Dollfuss, Ber. **26**, 1971).

116. Cumic Aldehyde; Cuminol; Para-isopropylphenal; Cuminal; 4-Methoethylphenemethylal.

NATURAL SOURCES.

Occurs (with cymene) in Roman oil of cumin from *Cuminum cyminum* (Gerhardt and Cahours, Ann. **38**, 70; Ann. Chim. [3] **1**, 60; Bertagnini, Ann. **85**, 275; Kraut, Ann. **92**, 66), and in oil of water-hemlock from *Cicuta virosa* (Trapp, Journ. pr. Ch. **74**, 428; Arch. Pharm. **231**, 212; Ann. **108**, 386).

Said to occur also in oil of thyme from *Thymus vulgaris* and *T. serpyllum*, in oil of true bishop's weed from *Ptychotis ajowan*, in oil of pepperwort from *Satureia hortensis*, and in oils of *Eucalyptus globulus*, ginger, nutmeg, sage, and citron (Sawer's 'Odorographia,' Vol. II, p. 140: authorities not given).

Cuminal is contained in the oils of *Eucalyptus hæmastoma* (Schimmel's Ber. April, 1888), *E. odorata* (*Ibid.* April, 1889), *E. oleosa* (Gildemeister and Hoffmann, p. 695), *E. populifera* (Schimmel's Ber. April, 1893), (?) *E.*

viridis (*Ibid.* Oct. 1901), and *E. hemiphloia* (*Ibid.* April, 1892).

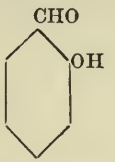
Note :—According to H. G. Smith (Proc. Roy. Soc. N. S. Wales, 34) the aldehyde of *Eucalyptus* oils is not cumic aldehyde, but a new aldehyde, 'aromadendral.'

Cuminal is contained in Ceylon oil of cinnamon (Schimmel's Ber. April, 1902; Walbaum and Hüthig, Journ. pr. Ch. [2] **66**, 55).

Synthetical Process.

[A.] *Cymene* [6] on chlorination at its boiling point gives 1¹-chlorcymene = cymyl chloride (Errera, Gazz. **14**, 277). The latter yields cuminal on boiling with lead nitrate and water (*Ibid.* 278). A small quantity of the aldehyde is obtained by the oxidation of cymene with sulphuric acid and manganese dioxide (Fournier, Comp. Rend. **133**, 634).

117. Salicylic Aldehyde; Orthohydroxybenzaldehyde; Orthohydroxyphenal; 2-Phenolmethylal.



Natural Sources.

The complex is contained in some compound present in the flowers and herb (but not in the root) of *Spiræa ulmaria* (Pagenstecher, Berz. Jahresber. **18**, 336; Löwig, *Ibid.* **20**, 355; Pogg. Ann. **36**, 383; Dumas, Ann. **29**, 306; Ettling, *Ibid.* 309; **35**, 247); in the herbs of *Spiræa digitata*, *S. lobata*, and *S. filipendula*; in the flowers of *S. aruncus* (Wicke, Ann. **83**, 175), and in the root and stem of hawk's-beard, *Crepis fœtida* (Wicke, Ann. **91**, 374). The glucoside, spiræin, contained in the old roots of *Spiræa kamschatica* is a glucoside of salicylic aldehyde (Beyerinck, Centr. Bakter. II, **5**, 425; Ch. Centr. 1899, **2**, 259).

Mould fungi (*Aspergillus oryzæ*) split off saligenin from salicin [157], and then oxidise the alcohol to the aldehyde (Brunstein; Abst. in Journ. Fed. Inst. **7**, 367; **8**, 507).

The aldehyde is said to have been obtained from the larva and imago of the beetle, *Chrysomela populi* (Jahresber. **1850**, 583; Enz, *Ibid.* **1859**, 312).

Synthetical Processes.

[A.] From *phenol* [60] (with p-hydroxybenzaldehyde) by heating with *chloroform* [1; D] in presence of sodium hydroxide solution (Tiemann and Reimer, Ber. **9**, 423; 824).

Or from phenol and *ethyl alcohol* [14] through coumarone (see under phlorol [64; C]). The latter on nitration gives a nitrocoumarone, which yields salicylic aldehyde among the products of its decomposition by sodium ethylate (Stoermer and Richter, Ber. **30**, 2094; Stoermer and Kahlert, Ber. **35**, 1640).

[B.] *Saligenin* [55] gives salicylic aldehyde on oxidation (Piria, Ann. **30**, 153).

[C.] *Salicin* [157] gives salicylic aldehyde on oxidation with sulphuric acid and potassium dichromate, &c. (Piria, *loc. cit.*; Schiff, Ann. **150**, 193; **210**, 115).

[D.] *Acetophenone* (see under benzoic aldehyde [114; A; G, &c.]) on nitration at a low temperature gives (with m-nitro-) o-nitroacetophenone (Engler, Ber. **18**, 2238; Camps, Arch. Pharm. **240**, 6), and this on reduction yields o-aminoacetophenone (Gevekoht, Ann. **221**, 326; Camps, *loc. cit.* 15). By the diazo-method the latter is converted into *o-hydroxyacetophenone* [130] (Friedländer and Neudörfer, Ber. **30**, 1080; Dunstan and Henry, Trans. Ch. Soc. **75**, 71). The hydroxy-ketone by acetylation and bromination gives acetyl-o-hydroxy-ω-acetophenone bromide, which, on boiling with water and chalk, yields *ketocoumaran = coumaranone* [132] (F. and N. *loc. cit.* 1081). The latter on heating in alkaline solution gives salicylic aldehyde (*Ibid.*).

[E.] From *cinnamic acid* [Vol. II] through o-nitrocinnamic acid and ester

by nitration (Beilstein and Kuhlberg, Ann. **163**, 125; Morgan, Ch. News, **36**, 269; Baeyer, Ber. **13**, 2258; Müller, Ann. **212**, 142; Drewsen, *Ibid.* 151; Fischer and Küzel, Ann. **221**, 265), o-nitrophenylpropiolic acid by bromination of o-nitrocinnamic acid and the action of excess of caustic soda on the product (Baeyer, *loc. cit.*), and o-nitrophenylacetylene by heating o-nitrophenylpropiolic acid with water (*Ibid.* 2259). o-Nitrophenylacetylene on reduction with zinc dust and ammonia gives o-aminophenylacetylene (Baeyer and Landsberg, Ber. **15**, 60; Baeyer and Bloem, Ber. **17**, 964). The latter, on treatment with sulphuric acid and water, yields o-aminoacetophenone (B. and B. Ber. **15**, 2154), which can be converted into o-hydroxyacetophenone, ketocoumaran, and salicylic aldehyde as above under **D**.

Or from cinnamic acid through phenylpropiolic acid, phenylacetylene, and acetophenone (see under benzoic aldehyde [**114**; **E**]), and then as above under **D**.

Or from cinnamic acid through coumarone (see under phlorol [**64**; **F**]), and then as under **A** above.

[**F.**] From *benzoic acid* and *acetoacetic ester* [Vol. II]. Benzoic acid on nitration gives (with m- and p-nitro-) some o-nitro-acid (Griess, Ann. **166**, 129; Ber. **10**, 1871; Ernst, Jahresber. **1860**, 299; Holleman, Zeit. physik. Ch. **31**, 79). o-Nitrobenzoyl chloride and sodio-acetoacetic ester give o-nitrobenzoylacetoacetic ester (Gevekoht, Ann. **221**, 323), which on hydrolysis with dilute sulphuric acid yields o-nitroacetophenone (*Ibid.* 325). Subsequent steps as above under **D**.

Or from benzoic and acetic acids through acetophenone (see under benzoic aldehyde [**114**; **G**]), and then as above under **D**.

Or from benzoic acid (benzoyl chloride) and *zinc methyl* through acetophenone [**114**; **C**], and then as under **D**.

[**G.**] From *salicylic acid* [Vol. II] through the ethyl ester of the methyl ether (Cahours, Ann. **92**, 315; Graebe, Ann. **139**, 137), and condensation of the latter with *acetic ester* [Vol. II] to form 2-methoxybenzoylacetic ester (Tahara, Ber. **25**, 1306). The latter on hydrolysis with dilute sulphuric acid gives o-methoxyacetophenone, which can be demethylated by heating with hydrochloric acid at 130° (*Ibid.* 1309). The o-hydroxyacetophenone can be treated as above under **D** (see also Besthorn, Banzhaf, and Jaeglé, Ber. **27**, 3035).

[**H.**] *Coumarin* [Vol. II] on combination with bromine forms a dibromide, which on treatment with alcoholic potash gives o-coumarilic acid (Perkin, Journ. Ch. Soc. **24**, 45; Fittig and Ebert, Ann. **216**, 163). The ethyl ether of the coumarilic acid on heating with dilute hydrochloric acid yields, among other products, o-ethoxyacetophenone (Fittig and Claus, Ann. **269**, 10), which might be de-alkylated and treated as above under **G**. Or from coumarin through coumarone (see under phlorol [**64**; **D**]), and then as above under **A**.

[**I.**] *Orthocoumaric acid* [Vol. II] on ethylation gives the β-ethyl ether of the acid (Fittig and Ebert, Ann. **216**, 146), and this on combination with bromine yields the ethyl ether of dibrom-melilotic acid (*Ibid.* 158). The latter, by the action of alcoholic potash, gives the ethyl ether of o-coumarilic acid (Fittig and Claus, Ann. **269**, 6), which can be treated as above under **H**.

[**J.**] From *toluene* [**54**; **A** and **D** to end] through o-nitrotoluene (see under o-cresol [**61**; **A**]) and o-nitrobenzoic acid by oxidation of the latter (Widmann, Ann. **193**, 225; Noyes, Ber. **16**, 53; Monnet, Reverdin, and Noelting, Ber. **12**, 443). Subsequent steps through o-nitrobenzoylacetoacetic ester as above under **F**.

Or from o-nitrotoluene through o-nitrobenzaldehyde (see under saligenin [**55**; **C**]), which condenses with *malonic acid* [Vol. II] in presence of aniline to form o-nitrocinnamic acid (Knoevenagel and Baebenroth, Ber. **31**, 2609). From the latter through o-nitrophenylpropiolic acid, &c., as above under **E**.

Or from *benzene* [**6**; I, &c.] through nitrobenzene, aniline, o-nitraniline (Nietzki and Benckiser, Ber. **18**, 295; Lellmann, Ann. **221**, 6; Turner, Ber.

25, 986), and o-nitrobenzonitrile (Sandmeyer, Ber. 18, 1492). The latter can be hydrolysed to o-nitrobenzoic acid, and then treated as before.

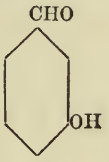
Or from benzene through acetophenone by direct synthesis, or *via* ethylbenzene or isopropylbenzene or acetaldehydephenylhydrazone (see under benzoic aldehyde [114; A]) and acetophenone, and then as above under D.

Acetanilide (from aniline and acetic acid) on heating with acetic and phosphoric acids and subsequent hydrolysis of the acetyl-derivatives gives a mixture of o- and p-aminoacetophenone (Köhler, Germ. Pat. 56971 of 1889; Ber. 24, Ref. 685). From the o-aminoketone as under D above.

[K.] From *styrene* [7] through acetophenone (see under benzoic aldehyde [114; B]), and then as above under D.

[L.] From *cymene* [6] through *cumic aldehyde* [116] and acid and acetophenone (see under benzoic aldehyde [114; K]), and then as above under D.

118. Metahydroxybenzoic Aldehyde; Metahydroxyphenal; 3-Phenolmethylal.



Natural Source.

The glucoside, salinigrin, occurs in the bark of *Salix discolor* (Jowett, Trans. Ch. Soc. 77, 707; Jowett and Potter, Pharm. Journ. [4] 15, 157).

Synthetical Processes.

[A.] From *benzoic aldehyde* [114] through the m-nitro-aldehyde by nitration, the m-amino-aldehyde by reduction, and decomposition of the diazostannichloride by boiling with water (Tiemann and Ludwig, Ber. 15, 2045: see also under vanillin [121; C]).

[B.] From *benzoic acid* [Vol. II] through the m-hydroxy-acid (see under phenol [60; E]). The latter gives the m-hydroxy-aldehyde on reduction with sodium amalgam in presence of dilute acid (Sandmann, Ber. 14, 969).

Note :—Other generators of m-hydroxybenzoic acid are *m-cresol* [62], *cinnamic acid* [Vol. II], and *naphthalene* [12]. For references see under phenol [60; F; I; J].

119. Parahydroxybenzoic Aldehyde; Parahydroxyphenal; 4-Phenolmethylal.

Natural Sources.

Occurs in yellow Botany Bay or acaroid resin from *Xanthorrhœa hastilis* (L. Bamberger, Monats. 14, 339); also in red *Xanthorrhœa* resin (Tschirch and Hildebrand, Arch. Pharm. 234, 698; Ch. Centr. 1897, 1, 422).

The complex (p-hydroxymandelonitrile) is contained in a cyanogenetic glucoside (dhurrin) occurring in the young plants of *Sorghum vulgare*, the great millet (Dunstan and Henry, Proc. Roy. Soc. 70, 153).

Synthetical Processes.

[A.] From *phenol* [60] (with salicylic aldehyde) by the action of *chloroform* [1; D] in presence of sodium hydroxide solution (Tiemann and Reimer, Ber. 9, 824; Tiemann and Herzfeld, Ber. 10, 63).

Or from phenol and *hydrogen cyanide* [172] by combining the two compounds in benzene solution in presence of aluminium chloride and hydrogen chloride, and decomposing the product with dilute acid (Gattermann and Berchelmann, Ber. 31, 1766; also Eng. Pat. 13453 of 1898, Bayer & Co.). Zinc chloride may be used as a condensing agent instead of aluminium chloride (Gattermann and Köbner, Ber. 32, 278).

Or from phenol, *ethyl alcohol* [14],

and *oxalic acid* [Vol. II] through the following stages:—Picric acid (from phenol) is converted into picrylphenol by the action of picryl chloride on potassium phenate. Oxalic acid is converted into ethyl oxalate, and the latter into ethyloxalyl chloride [120; B], which combines with picrylphenol in the presence of aluminium chloride to form picryl-p-hydroxyphenylglyoxylic ester:—

$(NO_2)_3C_6H_2.O.C_6H_4.CO.CO_2C_2H_5$.

The latter on hydrolysis with alcoholic potash gives p-hydroxyphenylglyoxylic acid, and this on distillation *in vacuo*, or on heating with dimethylaniline, yields (with p-hydroxybenzoic acid) p-hydroxybenzoic aldehyde (Bouveault, Bull. Soc. [3] **17**, 947).

Note:—For technical production from phenol by condensation with *formic aldehyde* [91] and p-toluylhydroxylamine-m-sulphonic acid (from p-nitrotoluene-m-sulphonic acid), and decomposition of the condensation product by heating with dilute acids or alkalis, see Geigy's Germ. Pats. 103578 of 1898; Ch. Centr. 1899, 1, 926; 105103 of 1898; Ch. Centr. 1900, 1, 239; 105798 of 1898; *Ibid.* 523.

[B.] *Cinnamic acid* [Vol. II] or its ester on nitration gives (with ortho-) paranitrocinnamic acid or ester (Mitscherlich, Journ. pr. Ch. **22**, 192; Ann. Chim. [3] **4**, 73; Kopp, Comp. Rend. **53**, 634; Beilstein and Kuhlberg, Ann. **163**, 126; Tiemann and Opermann, Ber. **13**, 2059; Müller, Ann. **212**, 124; Drewsen, *Ibid.* 150). The p-nitro-acid (or ester) on oxidation gives p-nitrobenzoic aldehyde (Baeyer, Ber. **14**, 2317: see also Basler, Ber. **16**, 2714), which combines with hydroxylamine to form an oxime (Gabriel and Herzberg, Ber. **16**, 2000), and this reduces to the oxime of p-aminobenzoic aldehyde (*Ibid.* 2001), which, by the action of acids, yields the p-amino-aldehyde (*Ibid.* 2002). The latter gives the hydroxy-aldehyde by the diazo-method (Walther and Bretschneider, Journ. pr. Ch. [2] **57**, 538).

Or cinnamic acid can be combined with bromine or with hypobromous acid, and the product converted into ω-bromstyrene by heating with water (Glaser, Ann. **154**, 168). The bromstyrene on nitration gives (with another isomeride and p-nitrobenzoic acid) α-p-nitrophenyl-β-bromnitroethylene, $NO_2.C_6H_4.CH:CBrNO_2$, and this, on boiling with water, yields p-nitrobenzoic aldehyde among other products (Flürscheim, Journ. pr. Ch. [2] **66**, 16).

[C.] *Styrene* [7] by the action of nitric or nitrous acid gives 1^2-nitrostyrene = phenylnitroethylene (Simon, Ann. **31**, 269; Blyth and Hofmann, Ann. **53**, 297; Priebs, Ann. **225**, 328), which, by further nitration, yields 4 : 1^2-dinitrostyrene (Priebs, *loc. cit.* 348). The latter, on heating with strong sulphuric acid at 110°, gives p-nitrobenzoic aldehyde (Friedländer and Mähly, Ann. **229**, 213). Subsequent steps as above.

[D.] From *benzoic aldehyde* [114] and *methyl alcohol* [13] by the action of nitromethane on the aldehyde at 160° in presence of zinc chloride (Priebs, Ann. **225**, 321), which gives 1^2-nitrostyrene. Subsequent steps through dinitrostyrene, p-nitrobenzoic aldehyde, &c., as above.

Note:—Nitromethane is prepared from methyl iodide and silver nitrite (Bewad, Journ. Russ. Soc. **24**, 126; Meyer, Ann. **171**, 32). Formed also from potassium chloracetate and potassium nitrite (Kolbe, Journ. pr. Ch. [2] **5**, 427; Preibisch, *Ibid.* **8**, 310: see also under glycerol [48; K; L], and hydrogen cyanide [172; J; Y]).

Or from benzoic aldehyde and *succinic acid* [Vol. II] through phenylisocrotonic acid by heating the aldehyde with succinic anhydride and sodium succinate (Perkin, Journ. Ch. Soc. **31**, 394), or with sodium succinate and acetic anhydride (Jayne, Ann. **216**, 100; Leoni, Ann. **256**, 64). Phenylisocrotonic acid by the action of fuming nitric acid gives 1^2-nitrostyrene (Erdmann, Ber. **17**, 412), which can be treated as above.

[E.] From *benzene* [6; I, &c.] or *toluene* [54] by various processes:—

From benzene and *formic aldehyde* [91] through phenylhydroxylamine (Bamberger, Ber. **27**, 1347; 1548; Wohl, *Ibid.* 1432), which condenses with the aldehyde to form a polymeric anhydro-derivative of p-hydroxylamine-benzyl alcohol. The diazo-derivative of the latter, on heating with water, gives p-hydroxybenzoic aldehyde (Kalle

& Co., Germ. Pat. 87972 of 1895; Ber. **29**, Ref. 747: see also Germ. Pat. 89601 of 1896; Ber. **29**, Ref. 1195). The same polymeric anhydro-derivative is obtained by the electrolysis of nitrobenzene in the presence of hydrochloric acid and formic aldehyde (Löb, Zeit. Elektroch. 1898, **4**, 428).

From benzene through p-phenylenediamine (see under quinol [**71**; **T**]). The latter combines with *alloxan* [Vol. II] to form a product which, on heating with sulphuric acid, gives p-aminobenzoic aldehyde, which can be treated as above under **B** (Pellizari, Gazz. **17**, 412; Böhringer & Söhne, Germ. Pat. 108026 of 1898; Ch. Centr. 1900, **1**, 1114).

From toluene through p-nitrotoluene and p-nitrobenzyl chloride (Wachendorff, Ann. **185**, 271), or through benzyl chloride and nitration of the latter (Beilstein and Geitner, Ann. **139**, 337; Strakosch, Ber. **6**, 1056). The nitrobenzyl chloride on oxidation with lead nitrate and dilute nitric acid gives p-nitrobenzoic aldehyde (Fischer and Greiff, Ber. **13**, 670), which can be treated as above under **B**.

Or p-nitrotoluene can be oxidised by a mixture of sulphuric and chromic acids in presence of acetic acid and anhydride, when p-nitrobenzaldehyde diacetate is formed, and this gives the aldehyde on hydrolysis (Farbenfab. vorm. F. Bayer & Co., Germ. Pat. 121788 of 1899; Ch. Centr. 1901, **2**, 70).

Or p-nitrobenzyl chloride can be combined with aniline or its sulphonic acid (Strakosch, Ber. **6**, 1056; Paal and Sprenger, Ber. **30**, 69), and the p-nitrobenzyl compounds oxidised to benzylidene-compounds by acid and dichromate, or with alkaline or neutral oxidising mixtures (Meister, Lucius, and Brüning, Germ. Pats. 91503 of 1896; Ch. Centr. 1897, **1**, 1007; 92084 of 1896; Ch. Centr. 1897, **2**, 456; 93539 of 1897; Ch. Centr. 1897, **2**, 1063; 97847 of 1896; Ch. Centr. 1898, **2**, 696; 97948 of 1897; Ch. Centr. 1898, **2**, 742; 103859 of 1898; Ch. Centr. 1899, **2**, 949; 109608 of 1897; Ch. Centr. 1900, **2**, 408; and 110173 of 1898; Ch. Centr. 1900, **2**, 460). The p-nitrobenzylideneaniline or sulphonic acid obtained by this process gives p-nitrobenzoic aldehyde (with the base or its sulphonic acid) on hydrolysis with dilute mineral acid (see also under benzoic aldehyde [**114**; **A**]).

Or p-nitrobenzylideneaniline or its sulphonic acid can be reduced to the p-aminobenzylidene compound by alkaline sulphides: the latter on hydrolysis gives p-aminobenzoic aldehyde, which can be converted into the hydroxy-aldehyde by the diazo-method as above under **B** (Meister, Lucius, and Brüning, Germ. Pat. 99542 of 1897; Ch. Centr. 1899, **1**, 238; Germ. Pat. 100968 of 1897; *Ibid.* 958: also Journ. Soc. Ch. Ind. **17**, 658; **18**, 363 and 488 for Eng. Patents).

Or p-nitrobenzyl chloride can be converted into p-nitrobenzyl alcohol (or its phenolsulphonic ether), which gives p-aminobenzoic aldehyde on heating with alkaline sulphides (Meister, Lucius, and Brüning, Germ. Pat. 106509 of 1898; Ch. Centr. 1900, **1**, 1084).

p-Nitrobenzyl chloride on combination with hydroxylamine gives β-ϕ-nitrobenzylhydroxylamine, which forms a nitroso-derivative by the action of nitrous acid. The nitroso-compound decomposes on solution in acetic (with nitric) acid with the formation of bisnitrosyl-p-nitrobenzyl, $(NO_2 . C_7H_6)_2 (NO)_2$ (Behrend and König, Ann. **263**, 216). Or the bisnitrosyl-compound can be obtained by the action of bromine water on p-nitrobenzylhydroxylamine hydrochloride (Kjellin and Kuylenstjerna, Ber. **30**, 1897). The bisnitrosyl-compound is decomposed by caustic potash solution with the formation of p-nitrobenzaldoxime (α and β) (Behrend and König, *loc. cit.* 347). Nitrobenzaldoxime is also formed from nitrobenzylhydroxylamine as one product of the action of bromine (Kjellin and Kuylenstjerna, *loc. cit.*). The nitrobenzaldoxime can be converted into the amino-oxime, the amino-aldehyde, and the hydroxy-aldehyde as above under **B**. (For convertibility of α- and β-oximes see Behrend, Ber. **24**, 3088.)

According to Geigy & Co. (Germ. Pat. 86874 of 1895; Ber. **29**, Ref. 530) p-nitrotoluene gives p-aminobenzoic

aldehyde on reduction with alkaline sulphide in dilute alcohol, or with sulphur in hot fuming sulphuric acid.

p-Nitrotoluene and *oxalic ester* combine in the presence of sodium ethoxide to form p-nitrophenylpyroracemic acid, which gives p-nitrobenzoic aldehyde on oxidation with chromic acid mixture (Reissert, Ber. **30**, 1049). p-Nitrotoluene by the action of amyl nitrite in presence of sodium ethoxide gives p-nitrobenzaldoxime (Angeli and Angelico, Atti Real. Accad. [5] **8**, II, 28; Ch. Centr. 1899, **2**, 371; Meister, Lucius, and Brüning, Germ. Pat. 107095 of 1898; Ch. Centr. 1900, **1**, 886; Lapworth, Trans. Ch. Soc. **79**, 1274).

[F.] *Paracresol* [63], on oxidation with sulphuric and chromic acids in presence of acetic anhydride, gives p-hydroxybenzaldehyde triacetate (Thiele and Winter, Ann. **311**, 357). The triacetate is decomposed with the formation of the aldehyde on heating with dilute acid (*Ibid.*).

120. Anisic Aldehyde; Paramethoxybenzoic Aldehyde.

Natural Sources.

Russian oil of aniseed (from *Pimpinella anisum*) contains a small quantity of this aldehyde (Bouchardat and Tardy, Bull. Soc. [3] **15**, 612). French oil of bitter fennel contains anisic aldehyde (Tardy, *Ibid.* [3] **17**, 580). In Chinese star-anise oil (*Ibid.* [3] **27**, 990). The existence of the aldehyde in these oils may be due to the oxidation of anethole.

Synthetical Processes.

[A.] From *p-hydroxybenzaldehyde* [119] by methylation with potassium hydroxide and *methyl iodide* [13] in methyl alcoholic solution (Tiemann and Herzfeld, Ber. **10**, 63).

[B.] From *phenol* [60] through anisole by methylation (Cahours, Ann. **78**, 226; Vincent, Bull. Soc. [2] **40**, 106; Kolbe, Journ. pr. Ch. [2] **27**, 425; Auer, Ber. **17**, 672; Krafft and Roos, Germ. Pat. 76574 of 1893; Ber. **17**, Ref. 955; Ullmann and Wenner, Ber. **33**, 2476). The latter combines with *hydrogen cyanide* [172] in presence of hydrogen chloride and aluminium chloride to form a compound which gives anisic aldehyde on decomposition with dilute acids (Gattermann, Ber. **31**, 1151).

Or from anisole and carbon monoxide, the latter being converted into carbonyl chloride, and then into chlorcarbamide by the action of ammonium chloride (Gattermann and Schmidt, Ber. **20**, 118; 858; Ann. **244**, 30). Chlorcarbamide and anisole combine in the presence of aluminium chloride to form anisamide (Gattermann, Ann. **244**, 62), and this on reduction with sodium amalgam in acid solution gives anisyl alcohol (Hutchinson, Ber. **24**, 175), from which the aldehyde can be obtained as under **E**. Or anisamide can be hydrolysed to anisic acid and treated as under **F**.

Or from anisole and *ethyl alcohol* [14] through mercury fulminate (see under benzoic aldehyde [114; A]). The latter condenses with anisole in presence of aluminium chloride and hydrate to form o- and p-anisic aldehyde and oxime and p-anisic nitrile (Scholl and Hilgers, Ber. **36**, 648).

Anisole also combines with ethyloxalyl chloride = chlorethanalic ester (from *oxalic acid* [Vol. II] and *ethyl alcohol* [14]; Henry, Ber. **4**, 599; Anschütz, Ber. **19**, 2159; Peratoner and Strazzeri, Gazz. **21**, 301) in presence of aluminium chloride to form anisoleglyoxylic ester. The acid (p-methoxyphenylglyoxylic) obtained from the latter by hydrolysis gives anisic aldehyde on heating *per se*, or (better) with aniline (Bouveault, Bull. Soc. [3] **17**, 943).

[C.] From *anethole* [68] by oxidation (Cahours, Ann. Chim. [3] **14**, 484; **23**,

354; Rossel, Ann. **151**, 25; Labbé, Bull. Soc. [3] **21**, 1076; Otto and Verley, Germ. Pat. 97620 of 1895; Ch. Centr. 1898, **2**, 693), or by the action of boron fluoride (Landolph, Ber. **12**, 286).

[D.] From *salicylic acid* [Vol. II] through anisole by distilling the methyl ether with baryta (Cahours, Ann. **48**, 65), and then as above under **B**.

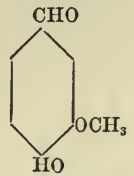
[E.] From *p-hydroxybenzyl alcohol* [56] through p-methoxybenzyl=anisyl alcohol by methylation (Biedermann, Ber. **19**, 2376) and the aldehyde by oxidation (Cannizzaro and Bertagnini, Ann. **98**, 189).

[F.] *Anisic acid* [Vol. II] gives the aldehyde on distilling the calcium salt with *calcium formate* [Vol. II] (Piria, Ann. **100**, 105).

[G.] From *benzene* [6; I, &c.] through nitrobenzene and aniline. The latter, on conversion into a diazonium salt and treatment with methyl alcohol, gives anisole (Beeson, Am. Ch. Journ. **16**, 234; Cameron, *Ibid.* **20**, 250: see also Hantzsch and Spear, Ber. **33**, 2538; Hantzsch and Jochem, Ber. **34**, 3337). Subsequent steps as above under **B**.

Or benzenesulphonic acid gives anisole directly on distilling its sodium salt with sodium methylate (Moureu, Bull. Soc. [3] **19**, 403).

121. Vanillin; Methylprotocatechuic Aldehyde; 3-Methoxy-4-hydroxybenzoic Aldehyde.



NATURAL SOURCES.

In pods of the vanilla bean, from *Vanilla planifolia* and its varieties, *V. sativa*, *V. sylvestris*, and *V. pompona*, all from Mexico. In *V. guyanensis* from Guiana and Surinam; in *V. palmarum* from Bahia; in *V. aromatica* from Brazil and Peru; in *V. planifolia var.* from Réunion, and in *V. ensifolia* from New Granada. The isolation of vanillin from the pods of *V. aromatica* is due to Gobley (Jahresber. **1858**, 534: see also Stokkebye, *Ibid.* **1864**, 612).

Vanillin occurs in Siam benzoïn (Jannasch and Rump, Ber. **11**, 1635; Lüdy, Arch. Pharm. **231**, 461), in assafœtida (Schmidt, Arch. Pharm. [3] **24**, 534; Tschirch and Poláček, *Ibid.* **235**, 126), in small quantities in certain beet sugars (Weger, Ding. poly. Journ. **237**, 146; Scheibler, Ber. **13**, 335; v. Lippmann, *Ibid.* 662), in asparagus (v. Lippmann, Ber. **18**, 3335), in the seeds of *Lupinus albus* (Campani and Grimaldi, Gazz. **17**, 545), in flowers of the orchid, *Nigritella suaveolens* (v. Lippmann, Ber. **27**, 3409), and in resins from pine and larch (Max Bamberger and Landsiedl, Monats. **18**, 481; 502). Vanillin is possibly present in yellow acaroid or Botany Bay resin from *Xanthorrhœa hastilis* (Tschirch and Hildebrand, Arch. Pharm. **234**; Ch. Centr. 1897, **1**, 422).

Vanillin occurs in cinnameïn from Peru balsam, San Salvador (Thoms, Ber. deutsch. pharm. Gesell. **8**, 264; Ch. Centr. 1898, **2**, 1030; Tschirch and Knitl, Arch. Pharm. **237**, 271; Ch. Centr. 1899, **2**, 315), and in opoponax from *Opoponax chironium* (Tschirch and Knitl, *loc. cit.* 256; Ch. Centr. 1899, **2**, 315).

Vanillin has been found in oriental storax from *Liquidambar orientalis* and American storax from *L. styraciflua* (Tschirch and Van Itallie, Arch. Pharm. **239**, 506; 532).

A vanillin glucoside occurs in the husk of oats (Rawton, Comp. Rend. **125**, 797). According to Singer (Monats. **3**, 409), vanillin is widely distributed in traces in all woody portions of plants (see also Czapek, Zeit. physiol. Ch. **27**, 148). Vanillin occurs in cork (Kügler, Journ. Pharm. [5] **10**, 123; Bräutigam, Ch. Centr. 1898, **2**, 858; 889; Thoms, *Ibid.* 1102), and in the volatile oil of *Spiræa* (Schneegans and Gerock, as quoted by Gildemeister and Hoffmann, p. 551). According to Bräutigam, potato peel contains a compound which gives vanillin under the influence of heat and atmospheric oxygen (Pharm.

Zeit. **45**, 164; Ch. Centr. 1900, **1**, 728). Vanillin has been extracted in small quantity from the new bark of the lime tree, *Tilia* sp.? (Bräutigam, Arch. Pharm. **238**, 556).

According to Busse (see Ch. Centr. 1900, **1**, 557), vanillin is produced in *Vanilla* species in the first place as a glucoside. The same view is expressed by Behrens (*Ibid.* **2**, 769: see also Molisch, Ber. deutsch. bot. Gesell. **19**, 350). Lecomte attributes the formation to the hydrolysis of coniferin and oxidation of coniferyl alcohol by an oxidase (Comp. Rend. **133**, 745).

Synthetical Processes.

[A.] From *catechol* [**69**] through guaiacol by methylation with potassium methyl sulphate (Gorup-Besanez, Ann. **147**, 248), and the action of *chloroform* [**1**; **D**] and caustic alkali on guaiacol (Reimer and Tiemann, Ber. **9**, 424; Tiemann and Koppe, Ber. **14**, 2023; Traub, Germ. Pat. 80195 of 1894; Ber. **28**, Ref. 524; Soc. Chim. d. Usines du Rhône, Eng. Pat. 21106 of 1896; Journ. Soc. Ch. Ind. **16**, 758).

Or guaiacol can be converted into its carboxylic acid by heating its salts in an atmosphere of carbon dioxide (F. v. Heyden, Nachf. Germ. Pat. 51381 of 1889; Ber. **23**, Ref. 418). Guaiacolcarboxylic acid on heating with chloroform and alkali gives aldehydoguaiacolcarboxylic acid, and the latter is decomposed into vanillin on heating (*Ibid.* Germ. Pat. 71162 of 1892; Ber. **26**, Ref. 995; Germ. Pat. 72600 of 1893; Ber. **27**, Ref. 218).

The aldehyde group can also be introduced into guaiacol by means of nitrobenzenesulphonic acid and *formic aldehyde* [**91**], and hydrolysis of the product (Geigy & Co., Eng. Pat. 27236 of 1898; Journ. Soc. Ch. Ind. **19**, 41). Or by the action of *hydrogen cyanide* [**172**] and hydrogen chloride, in presence or absence of aluminium chloride, and hydrolysis of the product (Bayer & Co., Germ. Pat. 106508 of 1898 and previous Patents; Ch. Centr. 1900, **1**, 742).

Or aniline and formic aldehyde may be condensed with guaiacol to form hydroxymethoxybenzylaniline, which can be oxidised to a benzylidene derivative, and finally to vanillin (Meister, Lucius, and Brüning, Germ. Pat. 109498 of 1898; Ch. Centr. 1900, **2**, 457: see also the Pats. of this Firm under p-hydroxybenzaldehyde [**119**; **E**]).

Note:—Catechol can be converted into protocatechuic aldehyde by chloroform and alkali (Tiemann and Reimer, Ber. **9**, 1269; T. and Koppe, Ber. **14**, 2015), or by the action of formic aldehyde and aromatic hydroxylamine sulpho-acids, &c., as in the process applied to guaiacol above (Geigy & Co., *loc. cit.* and Germ. Pat. 105798 of 1898; Ch. Centr. 1900, 1, 523). From protocatechuic aldehyde as below under **E**.

[B.] From *phenol* [**60**] through o-nitrophenol and its methyl ether (o-nitroanisole), o-anisidine, and guaiacol (for references see under catechol [**69**; **A**]), and then as above.

Or from anisidine through its compound with *alloxan* [Vol. II], which is decomposed on heating with sulphuric acid with the formation of p-amino-m-methoxybenzoic aldehyde (Pellizari, Gazz. **17**, 412; Böhringer & Söhne, Germ. Pat. 108026 of 1898; Ch. Centr. 1900, **1**, 1115). The latter can be converted into vanillin as below under **C**.

Or phenol on bromination at 150–180° gives o-bromphenol (see under catechol [**69**; **A**]). The latter can be converted into 3-brom-4-hydroxybenzoic aldehyde (Geigy & Co., Germ. Pat. 105798 of 1898; Ch. Centr. 1900, **1**, 523), and this yields protocatechuic aldehyde on heating with caustic soda-lye to 150–200° (Baum, Germ. Pat. 82078 of 1894; Ber. **28**, Ref. 803). From the aldehyde as below under **E**.

Note:—o-Bromphenol is obtained also from o-nitrophenol through o-aminophenol by the diazo-method (Meldola and F. H. Streatfeild, Trans. Ch. Soc. **73**, 685).

[C.] From *benzoic aldehyde* [**114**] through the m-nitro-aldehyde by nitration (Widmann, Ber. **13**, 678; Friedländer and Henriques, Ber. **14**, 2802; Ehrlich, Ber. **15**, 2010; Camps, Arch. Pharm. **240**, 1), the m-amino-aldehyde by reduction, and the *m-hydroxy-aldehyde* [**118**] by the diazo-method (Meister, Lucius, and Brüning, Germ. Pat. 18016

of 1881; Ber. 15, 1098; Tiemann and Ludwig, *Ibid.* 2044). The hydroxy-aldehyde by methylation gives the methoxy-aldehyde, and this, on heating with acetic anhydride and sodium acetate, yields m-methoxycinnamic acid. The latter (methyl ester) on nitration gives m-methoxy-p-nitrocinnamic ester, and this, on hydrolysis and oxidation with potassium permanganate, yields m-methoxy-p-nitrobenzoic aldehyde. The latter, on reduction and application of the diazo-method, gives vanillin (M. L. & B. *loc. cit.*; Ulrich, Ber. 18, 2571; Germ. Pat. 32914 of 1884; Ber. 18, Ref. 682).

[D.] From *p-hydroxybenzoic aldehyde* [119] through the m-nitro-aldehyde by nitration (Mazzara, Jahresber. 1877, 617; Paal, Ber. 28, 2413), the m-amino-aldehyde by reduction, and replacement of the amino- by the methoxy-group by the diazo-method followed by methylation (Bergmann, Am. Pat. 571917 of 1896; Ber. 29, Ref. 1192). Or p-hydroxybenzoic aldehyde on bromination gives the 3-bromo-derivative (Paal, Ber. 28, 2409). From the latter through protocatechuic aldehyde (Baum: see above under **B**), and then as below under **E**.

NOTE:—*m-Hydroxybenzoic aldehyde* [118] on bromination gives 4-brom-3-hydroxybenzoic aldehyde, and this also yields protocatechuic aldehyde on heating with soda-lye (Baum, *loc. cit.*).

[E.] *Piperonal* [122] on heating with dilute hydrochloric acid at 200°, or on boiling the dichloro-derivative with water, gives protocatechuic aldehyde (Fittig and Remsen, Ann. 159, 148; 168, 97: see also Wegscheider, Monats. 14, 382). The disodium salt of the aldehyde, or the sodium salt of the monoacetyl derivative, on methylation by methyl chloride or by methyl alkali sulphate, yields vanillin or its acetyl-derivative; the latter can be hydrolysed (Bertram, Germ. Pat. 63007 of 1890; Ber. 25, Ref. 823: the yield is better with dimethyl sulphate and alkali, Sommer, Germ. Pat. 122851 of 1900; Ch. Centr. 1901, 2, 517).

Or the potassium salt of the aldehyde on treatment with chloroformic-methyl ester gives two carboxylic esters of protocatechuic aldehyde, of which the p-modification yields vanillin on heating with dimethyl sulphate in alcoholic alkaline solution and subsequent acidification (Soc. Chim. d. Usines du Rhône, Germ. Pat. 93187 of 1896; Ch. Centr. 1897, 2, 1016; Eng. Pat. 16239 of 1896; Journ. Soc. Ch. Ind. 16, 633).

NOTES:—The chloroformic ester (= methyl-chlorocarbonate) is obtained by the action of phosgene on *methyl alcohol* (Dumas, Ann. 10, 277; Ann. Chim. 58, 52; Meyer and Wurster, Ber. 6, 965; Klepl, Journ. pr. Ch. [2] 26, 447; Hentschel, Ber. 18, 1177).

Processes depending on the combination of protocatechuic aldehyde with benzene- or toluenesulphonic acid, methylation of the ester, and subsequent decomposition into vanillin will be found in the following Germ. Pats. of the Ch. Fab. vorm. E. Schering:—80498 of 1893; Ber. 28, Ref. 581; 82747 of 1894; Ber. 28, Ref. 878. The aldehyde may also be converted first into a benzyl ether, and the latter methylated and then decomposed by heating with acid (*Ibid.* 82816 of 1893; Ber. 28, Ref. 878).

[F.] From *m-cresol* [62], which gives on nitration a mixture of 6-nitro- and 4-nitro-m-cresol (Städel, Ann. 217, 51; 259, 208; Ber. 22, 215; Reissert and Scherk, Ber. 31, 393). The methyl ether of the latter condenses with *oxalic ester* in the presence of sodium ethylate or methylate, with the formation of the nitromethoxyphenylpyroracemic acid (see under p-hydroxybenzoic aldehyde [119; **E**, p. 218]; Reissert, Ber. 31, 397). The latter can be converted into vanillin by replacement of the nitro-group by hydroxyl, and the pyroracemic acid residue by the aldehyde-group, CHO (Reissert, Germ. Pat. 94630 of 1897; Ch. Centr. 1898, 1, 296).

[G.] From *vanillic acid* [Vol. II] by distilling the calcium salt with *calcium formate* (Tiemann, Ber. 8, 1124), or by heating with *chloroform* [1; D] and caustic alkali in aqueous solution (Tiemann and Mendelsohn, Ber. 9, 1280).

[H.] *Ferulaïc acid* [Vol. II] gives vanillin on oxidation (Ulrich, Germ. Pat. 32914 of 1884; Ber. 18, Ref. 682).

[I.] From *veratric acid* [Vol. II] through veratrole (see under catechol [69; F]). The latter combines with ethyloxalyl chloride or amyloxalyl chloride in presence of aluminium chloride to form veratroylglyoxylic esters (Bouveault: see under anisic aldehyde

[120; B]), which hydrolyse to veratroylcarbonic acid. The latter, on heating with aqueous potash at 160–170°, gives, among the products of its demethylation, vanilloylcarbonic acid, and this yields vanillin as below under K.

[J.] *Isoeugenol* [79] gives vanillin on oxidation by ozone or on electrolysis of a solution of one of its salts (F. v. Heyden, Nachf. Germ. Pat. 92007 of 1895; Ch. Centr. 1897, **2**, 454; Otto and Verley, Germ. Pat. 97620 of 1895; Ch. Centr. 1898, **2**, 693; Verley, Am. Pats. 553593 and 563039 of 1896). Also by oxidation with metallic peroxides in alkaline solution (Haarmann and Reimer, Germ. Pat. 93938 of 1896; Ch. Centr. 1897, **2**, 1166). Isoeugenol gives vanillin by 'contact' oxidation on passing the vapour mixed with air over heated platinum (Trillat, Comp. Rend. **133**, 822).

Isoeugenylsulphuric acid (potassium salt) on oxidation with ozone gives potassium vanillyl sulphate, and this yields vanillin on decomposition by dilute acids (Verley, Bull. Soc. [3] **25**, 48). Or isoeugenol can be benzylated by means of benzyl chloride (see under benzyl alcohol [54; A]), and the benzyl ether oxidised to the methyl benzyl ether of protocatechuic aldehyde, which splits off benzyl and gives vanillin on heating with hydrochloric acid (Böhringer & Söhne, Germ. Pat. 65937 of 1891; Ber. **26**, Ref. 211).

Or isoeugenyl acetate, on oxidation with potassium permanganate, gives vanilloylcarbonic = p-hydroxy-m-methoxybenzoylcarbonic acid, and this yields vanillin on heating above its melting point (Tiemann, Ber. **24**, 2878), on heating with aniline and decomposing the anilide by heating with dilute sulphuric acid (Gassmann, Comp. Rend. **124**, 38), or by heating with dimethylaniline (Bouveault, Bull. Soc. [3] **19**, 76).

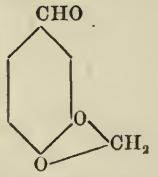
Note:—For production of vanillin by the oxidation of isoeugenyl acetate or benzoate see also Haarmann and Reimer, Germ. Pat. 57568 of 1890; Ber. 25, Ref. 93; also Germ. Pat. 63027 of 1891; Ber. 25, Ref. 824.

Isoeugenol can be combined with phenylhalogenacetic acids or their amides, nitriles, or ethers, or with ω-halogen-toluic acids so as to form the corresponding isoeugenol-ether acids. These are oxidised by acid and a dichromate with the formation of the corresponding vanillin-ether acids, and the latter give vanillin (and the ether-acid) on decomposition by mineral acid (Majert, Germ. Pat. 82924 of 1894; Ber. **28**, Ref. 878).

[K.] From *toluene* [54] through m-chlor-p-nitrotoluene, the corresponding chlornitrobenzyl chloride or bromide, and the corresponding aldehyde by oxidation with lead or copper nitrate. The chlornitrobenzoic aldehyde on heating with sodium methoxide exchanges chlorine for the methoxy-group, and the p-nitro-m-methoxybenzoic aldehyde can be converted into vanillin as above under C (Landsberg, Germ. Pat. 37075 of 1886; Ber. **19**, Ref. 861).

Or from toluene through ortho- or paratoluidine, m-(3)-nitro-p-toluidine, and m-nitrotoluene (Beilstein and Kuhlberg, Ann. **158**, 346). The latter gives m-nitrobenzoic aldehyde by electrolytic oxidation (Pierron, Bull. Soc. [3] **25**, 852). Subsequent steps as above under C.

122. Piperonal; Protocatechuic Aldehyde Methylene Ether; Heliotropin.



Natural Sources.

Said to occur in oil of *Spiræa* (Schneegans and Gerock, as quoted by Gildemeister and Hoffmann, p. 551). Accompanies vanillin from certain species of *Vanilla* (Busse, Ch. Centr. 1900, **1**, 558).

Synthetical Processes.

[A.] From *catechol* [69] through protocatechuic aldehyde by the action of

chloroform [1; D] in presence of aqueous caustic soda (Tiemann and Reimer, Ber. **9**, 1269; Tiemann and Koppe, Ber. **14**, 2015). The aldehyde gives piperonal on treatment with *methylene iodide* (see under ethyl alcohol [**14**; **I**; **M**]) and potassium hydroxide in methyl alcohol (Wegscheider, Monats. **14**, 388).

[B.] *Piperic acid* [Vol. II] gives piperonal on oxidation with potassium permanganate in neutral or alkaline solution (Fittig and Mielck, Ann. **152**, 35; Doebner, Ber. **23**, 2375).

123. Cinnamic Aldehyde; Phenepropenylal; β-Phenylacroleïn.

Natural Sources.

In oil of cinnamon from *Cinnamomum zeylanicum*, Ceylon (Dumas and Peligot, Ann. Chim. **57**, 305; Ann. **14**, 50), and in oil of cassia from *C. cassia* (*Ibid.*; Ann. **12**, 24; **13**, 76; **14**, 50). The oil is obtained from the bark, waste twigs, and root of *C. zeylanicum*. Oil of cinnamon leaf contains eugenol and but little cinnamic aldehyde (Weber, Arch. Pharm. **230**, 728).

Oil of cassia (Chinese) is prepared from leaves, flower and leaf stalks, buds and twigs of *C. cassia*, the oils from these parts of the shrub all containing the aldehyde as well as the oil from the bark (Schimmel's Ber. Oct. 1892).

Occurs also in oil of *Cinnamomum loureirii* from Japan (Shimoyama; Gildemeister and Hoffmann, p. 509), and in rassamala resin from the Javan *Altingia excelsa* (Tschirch and Van Itallie, Arch. Pharm. **239**, 541).

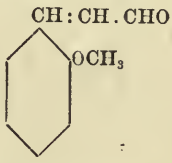
Cinnamic aldehyde is said to be among the products of the pancreatic fermentation of fibrin (Ossikowszky, Ber. **13**, 326).

Synthetical Processes.

[A.] From *benzoic aldehyde* [**114**] and *acetic aldehyde* [**92**] by saturating a mixture of the two aldehydes with hydrogen chloride, and then heating (Chiozza, Ann. **97**, 350). Or by allowing the mixed aldehydes to remain in contact with dilute caustic soda solution (Peine, Ber. **17**, 2117). The condensation of the aldehydes is best effected by alcoholic sodium hydroxide at −10° (Böhringer & Söhne, Eng. Pat. 10003 of 1896; Journ. Soc. Ch. Ind. **16**, 463).

[B.] From *cinnamic acid* [Vol. II] by distilling the calcium salt with *calcium formate* [Vol. II] (Piria, Ann. **100**, 105).

124. Orthocoumaric Aldehyde Methyl Ether; Orthomethoxycinnamic Aldehyde.



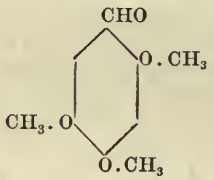
Natural Source.

In oil of cassia from *Cinnamomum cassia* (Bertram and Kürsten, Journ. pr. Ch. [2] **51**, 316).

Synthetical Process.

[A.] From *salicylic* [**117**] and *acetic aldehydes* [**92**] and *methyl alcohol* [**13**]. Salicylic aldehyde is converted into its methyl ether by methylating the sodium salt with methyl iodide (Perkin, Trans. Ch. Soc. **55**, 550; Voswinckel, Ber. **15**, 2024). o-Methoxybenzoic aldehyde and acetic aldehyde condense when allowed to stand in contact with dilute caustic soda solution to form o-coumaric aldehyde methyl ether (Bertram and Kürsten, Journ. pr. Ch. [2] **51**, 316).

125. Asaryl Aldehyde; 2:4:5-Trimethoxybenzoic Aldehyde; 2:4:5-Phenetriolmethylal Trimethyl Ether.



Natural Source.

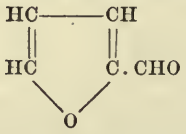
The complex, if not the free aldehyde, occurs with asarone [89] in oil of *Acorus calamus* (Thoms and Beckstroem, Ber. **34**, 1021; **35**, 3188).

Synthetical Processes.

[A.] From *asarone* [89] by oxidation with chromic acid or potassium permanganate and sulphuric acid (Butleroff and Rizza, Journ. Russ. Soc. **19**, 3).

[B.] From *hydroxyquinol* [85], *methyl alcohol* [13], and *hydrogen cyanide* [172]. The trimethyl ether of hydroxyquinol is treated in benzene solution with hydrogen cyanide and hydrogen chloride in the presence of dry aluminium chloride, and the product decomposed by cold water (Gattermann and Eggers, Ber. **32**, 289).

126. Furfural; Furfurol; Pyromucic Aldehyde; Furancarboxylic Aldehyde.



Natural Sources.

Furfural has been found in oil of cloves (Schimmel's Ber. Oct. 1896; Ch. Centr. 1896, **2**, 977; E. Erdmann, Journ. pr. Ch. [2] **56**, 154; Schimmel's Ber. April, 1897; Gerber, Mon. Sci. [4] **11**, 880), in the distillation water from oil of caraway and oil of ambrette seeds from *Hibiscus abelmoschus* (Schimmel's Ber. Oct. 1899; Ch. Centr. 1899, **2**, 880). Also in the distillation water from vetiver oil from *Andropogon muricatus*, E. and W. Indies, Brazil, &c. (*Ibid.* April, 1900; Ch. Centr. 1900, **1**, 907), and from oil of bay (*Ibid.* April, 1901).

Ceylon oil of cinnamon contains furfural (Schimmel's Ber. April, 1902; Walbaum and Hüthig, Journ. pr. Ch. [2] **66**, 47).

The aldehyde is contained also in petit-grain oil from Paraguay (Schimmel's Ber. Oct. 1902; Ch. Centr. 1902, **2**, 1208), in the cohobation water of savin oil from *Juniperus sabina*, and in the distillation water of W. Indian sandal-wood oil (*Ibid.* April, 1903; Ch. Centr. 1903, **1**, 1086).

Furfural has been found in brandy, in certain fusel oils, in malt wort, and beer (Morin, Comp. Rend. **105**, 1019; Udránszky, Zeit. physiol. Ch. **13**, 248; Förster, Ber. **15**, 230; 322; Brand, Journ. Fed. Inst. **4**, 562; Windisch, *Ibid.* 561; Heim, *Ibid.* 563).

According to Van Laer the furfural found in the secondary products of alcoholic fermentation is not of biochemical origin, but due to subsequent decomposition of furfural-yielding compounds (Journ. Fed. Inst. **4**, 2). This may be true also of the furfural found in the above plant oils.

Synthetical Processes.

[A.] From *dextrose* [154] by heating with dilute acids (Berthelot and André, Comp. Rend. **123**, 567). It has long been known that sugars and other carbohydrates yield furfural on dry distillation or on heating with dilute acids (Döbereiner, Ann. **3**, 141; Völckel, Ann. **85**, 65; Förster, Ber. **15**, 230; 322; Stenhouse, Phil. Mag. [3] **18**, 122; **37**, 226; Fownes, Phil. Trans. 1845, 253; Cahours, Ann. Chim. [3] **24**, 277; Emmet, Am. Journ. Sci. **32**, 140; Gudkoff, Zeit. [2] **6**, 362; Guyard, Bull. Soc. [2] **41**, 289; Schiff, Ber. **20**, 540; Ann. **239**, 382; Stone and Tollens, Ann. **249**, 237).

[B.] *Mannose* [156] gives furfural on heating with water at 140° (Fischer and Hirschberger, Ber. **22**, 369).

[C.] From *formic aldehyde* [91] through α-acrose and α-acrosone (see under mannitol [51; A]). The latter gives furfural on heating with acids or *per se* (Loew, Ber. **20**, 141; 3039; Fischer and Tafel, Ber. **22**, 99).

[D.] From *glycerol* [48] through α-acrose (see under mannitol [51; B]), and then as above.

[E.] *Tartaric acid* [Vol. II] on oxidation with hydrogen peroxide in presence of ferrous salts gives dihydroxymaleïc acid, the aqueous solution of which decomposes on heating with the formation of glycollic aldehyde. The latter on heating at 100° in a vacuum polymerises to a 'sugar,' which yields furfural on heating with water at 140° (Fenton, Trans. Ch. Soc. **65**, 899; **67**, 48; 774; **69**, 546; **71**, 375).

Note:—The 'sugar' is a mixture of α- and β-acrose (Jackson, Trans. Ch. Soc. **77**, 129). The polymerisation of glycollic aldehyde takes place in presence of dilute caustic soda at 0° (*Ibid.*).

[F.] From *acetal* [93] through bromacetal (Pinner, Ber. **5**, 149; Fischer and Landsteiner, Ber. **25**, 2551), bromacetaldehyde by distilling bromacetal with dry oxalic acid (F. and L. *loc. cit.*), glycollic aldehyde by the action of barium hydroxide solution (*Ibid.* 2552), and then as above under **E**.

Or brom- or chloracetal on heating with alcoholic potash gives the acetal of glycollic aldehyde (Pinner, *loc. cit.* 150; Marckwald and Ellinger, Ber. **25**, 2984), from which the aldehyde can be obtained by heating with very dilute hydrochloric acid (M. & E. *loc. cit.*).

[G.] From *ethyl alcohol* [14] through ethylene, ethylene iodide, and 2-iodoethyl ether by heating the latter with water (Baumstark, Ber. **7**, 1172). The iodo-ether, by the action of sodium ethylate, gives vinyl ethyl ether (Henry, Bull. Soc. [2] **44**, 458), which combines with bromine to form 1 : 2-dibromethyl ether (Wislicenus, Ann. **192**, 111), from which bromacetal is obtained by the action of sodium ethylate (*Ibid.* 112). Subsequent steps as above under **F** and **E**.

Or from ethyl alcohol through chloracetal by the action of chlorine (Lieben, Ann. **104**, 114), glycollic aldehyde acetal, and the aldehyde, &c., as above under **F**.

Or from ethyl alcohol through ethyl ether, 1 : 2-dichlorethyl ether by chlorination (Malaguti, Ann. **32**, 15), chloracetal by the action of sodium ethylate or alcohol on the dichlorether (Lieben, Ann. **146**, 193; Paternò and Mazzara, Ber. **6**, 1202; Natterer, Monats. **3**, 444), and then as above.

Note:—Generators of ethylene thus become generators of furfural through glycollic aldehyde and the 'sugar' obtainable from it.

[H.] From *choline* [Vol. II] through *ethylene glycol* [45] (see under isopropyl alcohol [16; NN]), and then as below under **K** and above under **G**.

[I.] *Glycuronic acid* [Vol. II] gives furfural on distillation with acids (Mann, Inaug. Diss. Göttingen, 1894; Udránszky, Zeit. physiol. Ch. **12**, 389; Günther and Tollens, Ber. **23**, 1751; De Chalmot, Inaug. Diss. Göttingen, 1891).

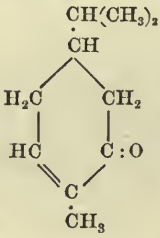
[J.] *d-Arabinose* [153] gives furfural on distillation with dilute sulphuric acid (Wohl, Ber. **26**, 735).

[K.] From *ethylene glycol* [45], the glycol ethyl ether by the interaction of ethyl iodide and sodium glycol (Wurtz, Ann. Ch. [3] **55**, 429), 2-iodoethyl ether by the action of phosphorus triiodide on the glycol ether (Demole, Ber. **9**, 746), and then vinyl ethyl ether, 1 : 2-dibromethyl ether, and bromacetal, &c., as above.

Or ethylene glycol gives glycollic aldehyde directly by oxidation with hydrogen peroxide and ferrous sulphate (Fenton and Jackson, Trans. Ch. Soc. **75**, 2).

Note:—The alcohol, $C_4H_3O.CH_2.OH$, corresponding to the aldehyde, has been found in the oil (steam distilled) from roasted coffee berries (E. Erdmann, Ber. **35**, 1846). It is not strictly a biochemical product. The alcohol can be obtained from furfural by the action of alcoholic or aqueous potash (Ulrich, Jahresber. 1860, 269; Schiff, Ann. **239**, 374; Wissell and Tollens, Ann. **272**, 293; E. Erdmann, Ber. **35**, 1855), or by reduction with sodium amalgam (Beilstein and Schmelz, Ann. Suppl. **3**, 275; Baeyer, Ber. **10**, 357).

127. Carvone.



Natural Sources.

d-Carvone occurs in oil of caraway from *Carum carui* (Völckel, Ann. **35**, 308; **85**, 246; Wallach, Ann. **277**, 107), and in oil of dill from *Peucedanum graveolens* (Gladstone, Journ. Ch. Soc. **25**, 1; Beyer, Arch. Pharm. **221**, 283).

l-Carvone occurs in oil of spearmint from *Mentha aquatica*, var. *crispa* (Germany), and from *M. viridis*, N. America (Gladstone, *loc. cit.*; Flückiger, Ber. **9**, 473; Beyer, *loc. cit.*; Kremers and Schreiner, Pharm. Rev. **14**, 244; Wallach, Ann. **305**, 223; in Russian oil, see Schimmel's Ber. April, 1898; Ch. Centr. 1898, **1**, 991), and in oil of kuromoji from the Japanese *Lindera sericea* (Kwasnik, Ber. **24**, 81; Arch. Pharm. **230**, 265).

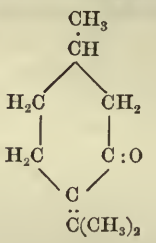
Synthetical Processes.

[A.] From *dipentene* (limonene) [9] by combination with nitrosyl chloride and decomposition with alcoholic potash, whereby the oxime of carvone is produced (Goldschmidt and Zürrer, Ber. **18**, 1732; Wallach, Ann. **245**, 268). The same nitrosochloride is obtained by mixing d- and l-limonene nitrosochlorides (Wallach, Ann. **252**, 124; **270**, 175).

Or limonene tetrabromide (Wallach, Ann. **227**, 280), on heating with methyl alcoholic sodium methoxide, gives bromcarveol methyl ether (*Ibid.* Ann. **281**, 129), and this, by the further action of sodium ethoxide in absolute alcohol, yields carveol methyl ether (*Ibid.* 132). The latter on oxidation with chromic acid in acetic acid solution gives i-carvone.

[B.] *Terpineol* [39] gives a nitrosochloride (Wallach, Ann. **277**, 121), which on heating with sodium ethoxide gives 'oxybishydrocarvoxime' = HO . $C_{10}H_5$: N . OH. The latter yields i-carvone on heating with dilute sulphuric acid (*Ibid.* Ber. **28**, 1773; Wallach and Arny, Ann. **291**, 342).

128. Pulegone.



Natural Sources.

In oil of European pennyroyal from *Mentha pulegium* (Beckmann and Pleissner, Ann. **262**, 1; Bull. Soc. [3] **25**, 110; Tétry, *Ibid.* **27**, 186), and of N. American wild mint from *Mentha canadensis* (Gage, Pharm. Rev. **16**, 412).

Has been found also in oil of American pennyroyal from *Hedeoma pulegioides* (Habliegger, Am. Journ. Pharm. **65**, 417), in oil from the mountain mint, *Pycnanthemum lanceolatum* = *Thymus virginicus* (Alden, Pharm. Rev. **16**, 414), in the oil of *Bystropogon origanifolium* from Teneriffe (Schimmel's Ber. Oct. 1902; Ch. Centr. 1902, **2**, 1208), and in oil of sweet marjoram from *Origanum majorana* (Genvresse and Chablay, Pharm. Centr. **43**, 419; Pharm. Journ. **69**, 335; Journ. Soc. Ch. Ind. **21**, 1347).

The natural product is d-pulegone.

Synthetical Processes.

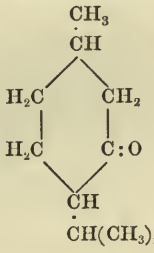
[A.] *Citronellal* [105] on heating with acetic anhydride gives *isopulegol* [42], and this on oxidation with chromic acid in acetic acid yields isopulegone. The latter is transformed into pulegone by contact with barium hydroxide solution at ordinary temperatures (Tiemann and Schmidt, Ber. **29**, 903; **30**, 29;

Tiemann, Ber. **32**, 825; Harries and Roeder, *Ibid.* 3357).

Note:—Isopulegol is formed (with menthoglycol) by agitating citronellal with 5 per cent. sulphuric acid (Barbier and Leser, Comp. Rend. 124, 1308).

[B.] From *isopulegol* [42] as above.

129. Menthone; Methylisopropyl-ketohexamethylene.



Natural Sources.

With menthol [41] in oil of peppermint from *Mentha piperita* and vars. (Moriya, Trans. Ch. Soc. **39**, 82; Andres and Andrejeff, Journ. Russ. Soc. **23**, 26; Ber. **25**, 617; Wallach, Ber. **28**, 1955; Power and Kleber, Arch. Pharm. **232**, 639; Charabot, Bull. Soc. [3] **19**, 117: see also Schimmel's Ber. April, 1895: for occurrence in essence of *Mentha pulegium* see Tétry, Bull. Soc. [3] **27**, 186; in Italian oil of peppermint, Schimmel's Ber. Oct. 1902).

In Bourbon geranium oil (Flatau and Labbé, Bull. Soc. [3] **19**, 788). In oil of *Eucalyptus hæmastoma* (Schimmel's Ber. April, 1888), and in the oil of *Bystropogon origanifolius*, Teneriffe (*Ibid.* Oct. 1902; Ch. Centr. 1902, **2**, 1208). Possibly occurs in oil from 'bucco-leaves' from S. African species of *Barosma* (Gildemeister and Hoffmann, p. 599; also Kondakoff and Bachtschieff, Journ. pr. Ch. [2] **63**, 49: see also under dipentene [**9**, p. 37]).

The natural product is l-menthone. According to Charabot (Ann. Chim. [7] **21**, 207; 279), menthone is probably formed in plants from the oxidation of citronellol.

Synthetical Processes.

[A.] From *menthol* [41] by oxidation with sulphuric acid and potassium dichromate (Moriya, *loc. cit.* 77; Atkinson and Yoshida, Trans. Ch. Soc. **41**, 49; Beckmann, Ann. **250**, 325; **289**, 362).

l-Menthone, on treatment with strong acids or alkalis at ordinary temperatures, or by keeping *per se*, is transformed into d-menthone (Beckmann, Ann. **250**, 334).

[B.] *Citronellol* [38] is said to give menthone among the products of its oxidation (Barbier and Bouveault, Comp. Rend. **122**, 673; 737; 795).

Note:—The citronellol referred to is the 'rhodinol' of Barbier and Bouveault. According to Bouveault *rhodinal* is transformed into menthone by the same process as that by which citronellal is transformed into pulegone (see above). Tiemann and Schmidt on the other hand consider rhodinol and citronellol to be the same compound and the corresponding aldehydes to be also identical (Tiemann and Schmidt, Ber. **29**, 925; Harries and Roeder, Ber. **32**, 355: compare Bouveault, Bull. Soc. [3] **23**, 458; 463).

[C.] From *metacresol* [62] through m-(γ)-cresotic acid (m-homosalicylic = m-hydroxy-p-toluic acid) by the action of sodium and carbon dioxide (Engelhardt and Latschinoff, Zeit. [2] **5**, 623; Biedermann and Pike, Ber. **6**, 324). Dibrom-m-cresotic acid, on heating with sodium in amyl alcohol and oxidation of the product with alkaline permanganate, gives β-methylpimelic acid (Einhorn and Ehret, Ann. **295**, 173). The diethyl ester of the latter condenses under the influence of sodium with the formation of methyl-β-ketohexamethylenecarboxylic ester, and this on treatment with sodium and *isopropyl iodide* [16] gives the isopropyl methyl derivative. The latter on heating with strong alcoholic potash yields a ketone, which is probably methylisopropylketohexamethylene = i-menthone (Einhorn and Klages, Ber. **34**, 3793).

[D.] *Thymol* [67] on distillation with phosphorus pentasulphide gives thiothymol (Fittica, Ber. **6**, 938; Ann. **172**, 325), and this on oxidation with nitric acid yields 3-sulpho-p-toluic acid (*Ibid.* Ann. **172**, 329). The latter on

fusion with potash gives m-(γ)-cresotic acid (Weber, Ber. **25**, 1743). Subsequent steps as above under **C**.

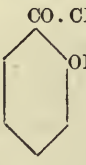
NOTE:—*Toluene* [54] gives 3-sulpho-p-toluic acid through p-nitrotoluene, p-toluidine, p-toluidinesulphonic acid, cyanotoluenesulphonic acid by the diazo-method, the sulphonamide and sulphaminotoluic acid, which on heating gives the imide (methylsaccharin). The latter on evaporating with hydrochoric acid yields the ammonium salt of 3-sulpho-p-toluic acid (Bad. An. Sod. Fab. Germ. Pat. 48583 of 1889; Ber. 22, Ref. 719; Weber, *Ibid.* 25, 1741).

Or p-toluidine can be acetylated, nitrated, and the o-nitro-p-toluidine converted into the nitrile by the diazo-method. The nitrile on reduction gives 3-amino-p-cyanotoluene, and this by hydrolysis 3-amino-p-toluic = homoanthranilic acid (Niementowski, Journ. pr. Ch. [2] 40, 6; 15; Glock, Ber. 21, 2662).

Or the nitrocyano-derivative can be hydrolysed to 3-nitro-p-toluic acid and then reduced to 3-amino-p-toluic acid (Niementowski and Rozánski, Ber. 21, 1997; Noyes, Am. Ch. Journ. 10, 479). The latter gives m-(γ)-cresotic acid by the diazo-method (N. and R. *loc. cit.* 1998: see also under m-cresol [62, pp. 128, 129] for further details).

[**E.**] From *pulegone* [**128**] and *isopropyl alcohol* [**16**]. Pulegone on boiling with formic acid gives methylcyclohexanone = 3-keto-1-methylhexahydrobenzene (see under phenol [**60**; **S**]), and this on treatment with sodium and ethyl acetate gives acetylmethylcyclohexanone (Leser, Bull. Soc. [3] **23**, 370). The potassium derivative of the latter condenses with isopropyl iodide to form acetylmenthone, and this yields menthone on hydrolysis with methyl alcoholic potassium hydroxide (*Ibid.* Comp. Rend. **134**, 1115).

130. Orthohydroxyacetophenone; Ortho-Acetylphenol; 2-Ethanoylphenol.



Natural Source.

In the volatile oil from the wood and bark of *Chione glabra*, W. Indies (Dunstan and Henry, Trans. Ch. Soc. **75**, 66). The methyl ether probably occurs also in the oil (*Ibid.* 71).

Synthetical Processes.

[**A.**] From *cinnamic acid* [Vol. II] through the o-nitro-acid (see under quinol [**71**; **E**] and salicylic aldehyde [**117**; **E**]), the dibromide by bromination, o-nitrophenylpropiolic acid by the action of alkali, and o-nitrophenylacetylene by heating the latter acid with water (Baeyer, Ber. **13**, 2259). o-Aminophenylacetylene obtained by reduction of the nitro-compound (Baeyer and Landsberg, Ber. **15**, 60; Baeyer and Bloem, Ber. **17**, 964) gives o-aminoacetophenone on treatment with sulphuric acid and water (Baeyer and Bloem, *loc. cit.*; Kippenberg, Ber. **30**, 1130), from which o-hydroxyacetophenone can be obtained by the diazo-method (Friedländer and Neudörfer, Ber. **30**, 1080; Dunstan and Henry, *loc. cit.* 71).

Or o-nitrophenylpropiolic acid can be reduced to the amino-acid (Baeyer and Bloem, Ber. **15**, 2147; Richter, *Ibid.* **16**, 679), and this on heating with water gives o-aminoacetophenone (B. and B. *loc. cit.* 2153).

Or from cinnamic acid through phenylpropiolic acid, phenylacetylene, and acetophenone (see under benzoic aldehyde [**114**; **E**]), and then through the o-nitro- and o-amino-ketone (see under salicylic aldehyde [**117**; **D**]), and o-hydroxyacetophenone as above.

[**B.**] From *benzoic* and *acetic acids* [Vol. II] through acetophenone [**114**; **A** and **G**], and then as under salicylic aldehyde [**117**; **D**] and **A** above.

Or from benzoic acid and *zinc methyl* [13] through acetophenone [**114**; **C**], and then as above.

Or from benzoic acid and *acetoacetic ester* [Vol. II] through o-nitro- and o-aminoacetophenone [**117**; **F** and **D**], and then as above under **A**.

[**C.**] From *salicylic acid* [Vol. II] and acetic ester through 2-methoxybenzoylacetic ester, &c., as under salicylic aldehyde [**117**; **G**].

[**D.**] From *coumarin* [Vol. II] through o-coumarilic acid as under salicylic aldehyde [**117**; **H**].

[**E.**] From *orthocoumaric acid* [Vol. II] through dibrom-melilotic acid and o-

coumarilic acid as under salicylic aldehyde [117; I].

[F.] From *styrene* [7] through phenylacetylene and acetophenone (see under benzoic aldehyde [114; B]), and then o-nitroacetophenone, &c., as under A above.

[G.] From *cymene* [6] through *cumic aldehyde* [116] and acid, isopropylbenzene, acetophenone [114; K], and then as above under A.

[H.] *Benzene* [6; I, &c.] becomes a generator of acetophenone, and therefore of the o-hydroxy-ketone, through ethylbenzene and normal or isopropylbenzene, or by interaction with acetyl chloride in presence of aluminium chloride [114; A]. Also through acetanilide and o-aminoacetophenone (see under salicylic aldehyde [117; J]).

131. Piceol; Parahydroxyacetophenone; Para-Acetylphenol.

Natural Source.

Occurs in the form of a glucoside, piceïn, in the needles of *Pinus picea* (Tanret, Comp. Rend. 119, 80; Bull. Soc. [3] 11, 944). The hydrolysis of piceïn is capable of being effected by certain enzymes.

Synthetical Processes.

[A.] From *phenol* [60], *methyl alcohol* [13], and *acetic acid* [Vol. II]. Phenol is converted into anisole (see under anisic aldehyde [120; B]), and the latter into p-acetylanisole by adding acetyl chloride to the solution of anisole in carbon disulphide in presence of aluminium chloride (Gattermann, Ehrhardt, and Maisch, Ber. 23, 1202; Hollcman, Rec. Tr. Ch. 10, 215). p-Acetylanisole is demethylated by the action of hydrogen bromide, giving p-hydroxyacetophenone (Charon and Zamanos, Comp. Rend. 133, 742).

Note:—Phenol and acetyl chloride condense also in carbon disulphide solution under the influence of dry ferric chloride with the formation of p-hydroxyacetophenone (Nencki and Stoeber, Ber. 30, 1769: see also Michael and Palmer, Am. Ch. Journ. 7, 277).

[B.] *Anethole* [68] on oxidation with iodine and mercuric oxide gives p-methoxyhydratropic aldehyde (Bougault, Comp. Rend. 130, 1766; 131, 44; Bull. Soc. [3] 25, 446; Ann. Chim. [7] 25, 514), and this, on oxidation with alkaline silver oxide, yields the corresponding acid (*Ibid.* Comp. Rend. 130, 1767; 131, 44). The latter, on further oxidation by chromic acid mixture, gives p-methoxyacetophenone (*Ibid.* Comp. Rend. 132, 782), which can be demethylated as under A.

Note:—The following synthetical products are generators of p-methoxyacetophenone *via* p-methoxyhydratropic acid:—

Toluene through benzyl chloride and cyanide, from which, by the action of methyl iodide and sodium hydroxide, the nitrile of hydratropic acid is obtained (Meyer, Ann. 250, 123; Oliveri, Gazz. 18, 574). The acid obtained by hydrolysis gives, on nitration, a mixture of o- and p-nitrohydratropic acid and the latter, by reduction, p-aminohydratropic acid (Trinius, Ann. 227, 262; 267). By the diazo-method the amino-acid yields p-hydroxyhydratropic acid (*Ibid.* 268), and this, by methylation, the corresponding p-methoxy-derivative (Bougault, Comp. Rend. 131, 270).

Acetophenone and *hydrogen cyanide* yield a cyanhydrin which, on heating with strong hydriodic acid and red phosphorus, gives hydratropic acid (Janssen, Ann. 250, 136). Subsequent steps as above.

The esters of *phenylacetic* and *oxalic acids* condense under the influence of sodium ethoxide to form the diethyl ester of phenyloxalacetic acid (Wislicenus, Ber. 27, 1092), and this on distillation *in vacuo* gives phenylmalonic ester (*Ibid.* 1093). The latter, with methyl iodide and sodium ethoxide, yields phenylmethylmalonic diethyl ester (Wislicenus and Goldstein, Ber. 28, 815), the acid of which gives hydratropic acid on fusion (*Ibid.* 816).

[C.] *Anisic aldehyde* [120] on heating with acetic anhydride and sodium acetate gives p-methoxycinnamic acid (Perkin, Jahresber. 1877, 792; Journ. Ch. Soc. 31, 408), which combines with bromine to form p-methoxydibromdihydrocinnamic acid = the methyl ether of $1^1 : 1^2$-dibrom-p-hydrocoumaric acid (Eigel, Ber. 20, 2536). The ethyl

ester of the latter acid by the action of alcoholic potash gives p-methoxyphenylpropiolic acid (Reychler, Bull. Soc. [3] **17**, 512), and this on heating with water to 130° yields p-methoxyacetophenone (*Ibid.* 514), which can be demethylated as above.

[**D.**] *Apigenin* [**140**] gives p-hydroxyacetophenone among the products of decomposition by heating with caustic alkali (Vongerichten, Ann. **318**, 131; A. G. Perkin, Trans. Ch. Soc. **71**, 810).

[**E.**] From *cinnamic acid* [Vol. II] through the p-nitro-acid by nitration (see under p-hydroxybenzoic aldehyde [**119**; **B**]). The nitro-acid (ester) on bromination gives p-nitrophenyldibrompropionic acid (ester), and this by the action of alcoholic potash yields p-nitrophenylpropiolic acid (Müller, Ann. **212**, 138; Drewsen, *Ibid.* 154; W. H. Perkin, junr., and Bellenot, Trans. Ch. Soc. **49**, 441). The latter on heating with dilute sulphuric acid gives p-nitroacetophenone (Drewsen, *loc. cit.* 160; Engler and Zielke, Ber. **22**, 203), which reduces to p-aminoacetophenone (Drewsen, *loc. cit.* 162). The latter yields p-hydroxyacetophenone by the diazo-method (Klingel, Ber. **18**, 2691).

[**F.**] From *benzene* [**6**; I, &c.] and *acetic acid* [Vol. II] through aniline, which, on heating with acetic anhydride and zinc chloride, gives p-aminoacetophenone (Klingel, Ber. **18**, 2688; Rousset, Bull. Soc. [3] **11**, 320: see also Köhler, Germ. Pat. 56971 of 1889; Ber. **24**, Ref. 685). From the latter as above under **E**.

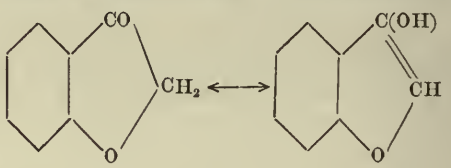
From *benzene* or *toluene* through p-nitrobenzoic aldehyde (see under p-hydroxybenzoic aldehyde [**119**; **E**]). The latter by interaction with *malonic acid* [Vol. II] in presence of aniline or alcoholic ammonia gives p-nitrocinnamic acid (Knoevenagel, Baebenroth, and Wollweber, Ber. **31**, 2612). Subsequent steps through p-nitrophenylpropiolic acid, &c., as above under **E**.

Note:—*Styrene* [7] and all other generators of p-nitrobenzoic aldehyde referred to under p-hydroxybenzoic aldehyde [**119**; **C**, &c.] thus become generators of p-hydroxyacetophenone.

Also from benzene through aniline, p-nitraniline, p-nitrobenzonitrile and acid, and p-nitrobenzoyl chloride. The latter with *sodio-acetoacetic ester* [Vol. II] gives p-nitrobenzoylacetoacetic ester, and this, on boiling with dilute sulphuric acid, yields p-nitroacetophenone (Gevekoht, Ann. **221**, 335). From the latter as above under **E**.

p-Nitrotoluene can also be oxidised to p-nitro-benzoic acid (Glenard and Boudault, Ann. **48**, 344; Beilstein and Wilbrand, Ann. **126**, 255; **128**, 257; G. Fischer, Ann. **127**, 137; **130**, 128; Beilstein and Geitner, Ann. **139**, 335; Körner, Zeit. [2] **5**, 636; Rosenstiehl, *Ibid.* 701). From the latter p-nitrobenzoyl chloride can be obtained by the usual method (Gevekoht, *loc. cit.*).

132. Ketocoumaran; Coumaranone.



Natural Source.

The compound itself has not been found among natural products, but the complex appears to be present in genisteïn, a colouring-matter obtained from dyer's broom, *Genista tinctoria* (A. G. Perkin and Newbury, Trans. Ch. Soc. **75**, 837).

Synthetical Processes.

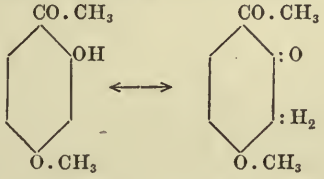
[**A.**] From *o-hydroxyacetophenone* [**130**] by acetylation, bromination, and the action of boiling water in presence of chalk on the acetyl-o-hydroxy-ω-acetophenone bromide (Friedländer and Neudörfer; see under salicylic aldehyde [**117**; **D**]).

[**B.**] From *salicylic aldehyde* [**117**] and *acetic acid* [Vol. II]. Chloracetic acid acts on sodium salicylic aldehyde with the formation of o-aldehydophenoxyacetic acid, $CHO \cdot C_6H_4 \cdot OCH_2 \cdot COOH$ (Rössing, Ber. **17**, 2990). The latter, on oxidation with potassium permanganate, gives salicyloxyacetic acid, $COOH \cdot C_6H_4 \cdot OCH_2 \cdot COOH$ (*Ibid.*

2995), the dialkyl ester of which, on treatment with sodium in benzene solution, yields ketocoumarancarboxylic ester. On treating the ester with alkali ketocoumaran is formed (Friedländer, Ber. **32**, 1868).

[C.] From *phenol* [60] and *acetic acid* [Vol. II] through phenoxyacetic acid by the interaction of chloracetic acid (or ester) and sodium phenoxide (Heintz, Jahresber. **1859**, 361; Hantzsch, Ber. **19**, 1296; Giacosa, Journ. pr. Ch. [2] **19**, 396; Fritzsche, *Ibid.* **20**, 269). Phenoxyacetic acid, on heating with dehydrating agents, gives ketocoumaran (Stoermer, Ber. **30**, 1712; Stoermer and Bartsch, Ber. **33**, 3175).

133. Pæonol; Resacetophenone Methyl Ether; 2-Hydroxy-4-Methoxyacetophenone; Ethanoyl-2 : 4-Phenediol 4-Methyl Ether.



Natural Source.

In the root bark of *Pæonia moutan* from Japan and China (Martin and Yagi, Arch. Pharm. **213**, 335; Nagai, Ber. **24**, 2847).

Synthetical Processes.

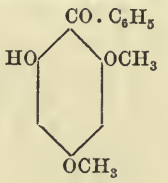
[A.] *Resorcinol* [70] and *acetic acid* [Vol. II] when heated with zinc chloride, or resorcinol alone, when heated with the latter, gives resacetophenone = ethanoyl-2 : 4-phenediol (Nencki and Sieber, Journ. pr. Ch. [2] **23**, 147). The latter is methylated by *methyl iodide* [13] and potassium hydroxide in methyl alcoholic solution (Tahara, Ber. **24**, 2460).

Or from resorcinol and *acetoacetic ester* [Vol. II] through β-methylumbelliferone by treating a mixture in the cold with sulphuric acid, or by heating with zinc chloride (v. Pechmann and Duisberg, Ber. **16**, 2119; Ann. **261**, 169; Schmid, Journ. pr. Ch. [2] **25**, 82; Michael, Am. Ch. Journ. **5**, 434). β-Methylumbelliferone gives resacetophenone on fusion with potash (v. Pechmann and Duisberg, *loc. cit.* 2123).

Or resorcinol and sodio-acetoacetic ester condense in alcoholic solution to give a carboxylic acid which yields β-methylumbelliferone on heating (Michael, Journ. pr. Ch. [2] **35**, 454; **37**, 470; v. Pechmann, Ann. **261**, 169).

Resorcinol and *citric acid* [Vol. II] also give β-methylumbelliferone on heating with sulphuric acid (Wittenberg, Journ. pr. Ch. [2] **24**, 125; v. Pechmann, Ber. **17**, 931).

134. Hydrocotoïn; 2 : 4 : 6-Trihydroxybenzophenone Dimethyl Ether; Benzocotoïn; Benzoylphloroglucinol Dimethyl Ether; 2 : 4-Methoxy-6-Hydroxybenzophenone.



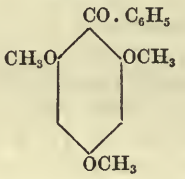
Natural Source.

In coto bark from Bolivia (Jobst and Hesse, **199**, 57). The botanical origin is unknown, but the tree is probably Lauraceous or Monimiaceous.

Synthetical Process.

[A.] From *phloroglucinol* [86], *benzoic acid* [Vol. II] through benzoyl chloride, and *methyl alcohol* [13]. The dimethyl ether of phloroglucinol is prepared by passing hydrogen chloride through a methyl alcoholic solution of phloroglucinol (Will, Ber. **21**, 603). The dimethyl ether is benzoylated by benzoyl chloride in presence of alkali, and the benzoyl-dimethyl ether heated with benzoyl chloride in benzene solution in presence of zinc chloride. The benzoyl-hydrocotoïn thus formed gives hydrocotoïn on hydrolysis (Pollak, Monats. **18**, 736).

135. Methylhydrocotoïn; 2 : 4 : 6-Trimethoxybenzophenone; Benzoylphloroglucinol Trimethyl Ether.



Natural Source.

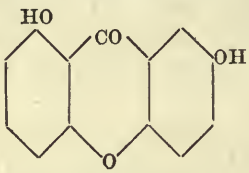
Occurs in paracoto bark (see above under hydrocotoïn) (Jobst and Hesse, Ann. **199**, 53; Ciamician and Silber, Ber. **26**, 799).

Synthetical Process.

[A.] From *hydrocotoïn* [134] and *methyl alcohol* [13] by further methylation with methyl iodide and potassium hydroxide in methyl alcohol (Ciamician and Silber, Ber. **24**, 300; **25**, 1120).

Or directly from *phloroglucinol* [86] through the trimethyl ether (Will, Ber. **21**, 603), and the action of benzoyl chloride on the latter in benzene solution in presence of zinc chloride (Ciamician and Silber, Ber. **27**, 1497).

136. Euxanthone.



Natural Source.

The complex exists in euxanthic acid, the glycuronic congugate acid of euxanthone which occurs in 'purrée' or Indian Yellow, prepared from the urine of cows fed upon mango leaves. Euxanthone is sometimes found in the free state in the colouring-matter, resulting from the decomposition (? bacterial) of euxanthic acid.

Note:—For the constitution of euxanthic acid see Graebe, Ber. **33**, 3360; Graebe, Aders, and Heyer, Ann. **318**, 345.

Synthetical Processes.

[A.] From *resorcinol* [70] and *quinol* [71]. Resorcinol is converted into β-resorcylic acid by heating with aqueous ammonium carbonate or acid potassium carbonate (Brunner and Senhofer, Ber. **13**, 2356; Bistrzycki and Kostanecki, Ber. **18**, 1985). Quinol is converted into its carboxylic acid, gentisic = 2 : 5-phenediolcarboxylic = 2 : 5-dihydroxybenzoic = 5-hydroxysalicylic acid, by a similar process (Senhofer and Sarlaz, Monats. **2**, 448). Gentisic and β-resorcylic acids or resorcinol when heated together with acetic anhydride give euxanthone (Graebe, Ber. **22**, 1405; Kostanecki and Nessler, Ber. **24**, 3983).

[B.] From *resorcinol* [70] and *salicylic acid* [Vol. II]. The latter can be converted into gentisic acid by the following processes:—

By iodising with iodine in presence of alkali, or by the action of iodine on silver salicylate 5-iodosalicylic acid is formed (Lautemann, Ann. **120**, 302; Demole, Ber. **7**, 1437; Birnbaum and Reinherz, Ber. **15**, 458). Or 5-bromsalicylic acid is obtained by the bromination of the acid (Henry, Ber. **2**, 275; Hübner and Heinzerling, Zeit. [2] **7**, 709; Hand, Ann. **234**, 133). The 5-iodo- or bromo-acid gives gentisic acid on fusion with alkali (Lautemann, *loc. cit.* 311; Liechti, Ann. Suppl. **7**, 144; Demole, *loc. cit.* 1438; Goldberg, Journ. pr. Ch. [2] **19**, 371; Miller, Ann. **220**, 124; Rakowski and Leppert, Ber. **8**, 789).

Or salicylic acid on nitration yields 5-nitro-, and the latter on reduction 5-aminosalicylic acid (see under quinol [71; C]). The amino-acid gives gentisic acid by the diazo-method (Goldberg, *loc. cit.*).

[C.] From *resorcinol* [70] and *phenol* [60]. The latter on nitration gives (with o-) p-nitrophenol, and this on heating with *carbon tetrachloride* [1; L] and alcoholic potash yields 5-nitrosalicylic acid (Hasse, Ber. **10**, 2188), which can be transformed into gentisic acid as above under B.

[D.] From *resorcinol* [70] and *benzoic acid* [Vol. II]. The latter can be con-

verted into 5-aminosalicylic acid (see under quinol [71; D]), which gives gentisic acid as above under B.

Benzoic acid can also be converted into gentisic acid through o-nitro- and *anthranilic acid*, o-uraminobenzoic acid, dinitrouraminobenzoic acid, 5-nitro-2-aminobenzoic acid, 5-nitro- and 5-aminosalicylic acid, and then as above under B. Or through 3-brombenzoic acid, the 3-brom-6-nitro- and corresponding amino-acid, 5-bromsalicylic acid, and then as above under B [71; D].

[E.] From *resorcinol* [70] and *anthranilic* (= *2-aminobenzoic*) *acid* [Vol. II]. The latter can be converted into gentisic acid as above under D.

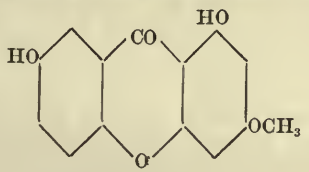
[F.] From *resorcinol* [70] and *gentisin* [137]. The latter gives gentisic acid on fusion with potash [71; L].

[G.] From *resorcinol* [70], *furfural* [126], and *acetone* [106]. The two latter can be made to furnish p-nitrophenol (as under resorcinol [70; H]), from which gentisic acid can be obtained as above under C.

[H.] From *quinol* [71] and *umbelliferone* [Vol. II], the latter yielding β-resorcylic acid on fusion with potash (see under resorcinol [70; E]).

Notes :—β-Resorcylic acid can be obtained also from *toluene* directly [70; B]. Euxanthic acid has been synthesised by the action of acetbromglycuronic acid on the sodium derivative of euxanthone (Neuberg and Niemann, Centr. med. Wiss. 40, 529; Ch. Centr. 1902, 2, 844). For constitution of euxanthone see Kostanecki, Ber. 27, 1989.

137. Gentisin; Methylgentisein; Gentianin; 1 : 7-Hydroxy-3-Methoxyxanthone.



Natural Source.

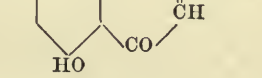
In the root of *Gentiana lutea* from Switzerland and the Tyrol (Trommsdorff, Ann. 21, 134; Leconte, Ann. 25, 202; Baumert, Ann. 62, 106; A. G. Perkin, Trans. Ch. Soc. 73, 672).

Synthetical Processes.

[A.] From *quinol* [71] through gentisic acid (see under euxanthone [136; A]), *phloroglucinol* [86], and *methyl alcohol* (methyl iodide) [13]. Phloroglucinol and gentisic acid, when heated with acetic anhydride, give gentisein, and this yields gentisin on methylation (Kostanecki and Tambor, Monats. 15, 4).

The quinol may be replaced by the other generators of gentisic acid referred to under exanthone [136; B; C; D; E; F; G], viz. *salicylic acid* [Vol. II], *phenol* [60], *benzoic* or *anthranilic acid* [Vol. II], *furfural* [126], and *acetone* [106].

138. Chrysin; 1 : 3-Dihydroxyflavone.



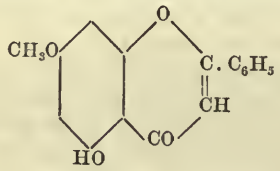
Natural Source.

In the buds of various species of poplar, such as *Populus nigra*, *P. balsamifera*, *P. pyramidalis*, &c. (Piccard, Ber. 6, 884; 7, 888; 10, 176).

Synthetical Processes.

[A.] From *phloroglucinol* [86], *benzoic* and *acetic acids* [Vol. II], *methyl* [13], and *ethyl alcohol* [14]. Phloroglucinol is converted into its trimethyl ether (see under methylhydrocotoïn [135; A]), and the latter condensed with acetyl chloride (by means of aluminium chloride) so as to give phloroacetophenone trimethyl ether (Friedländer and Schnell, Ber. 30, 2152). The latter condenses with ethyl benzoate in presence of sodium ethoxide with the formation of 2 : 4 : 6-trimethoxybenzoylacetophenone, $(CH_3O)_3 . C_6H_2 . CO . CH_2 . CO . C_6H_5$. The latter on heating with strong aqueous hydriodic acid gives chrysin (Emilewicz, Kostanecki, and Tambor, Ber. 32, 2448).

139. Tectochrysin; 1-Hydroxy-3-Methoxyflavone.



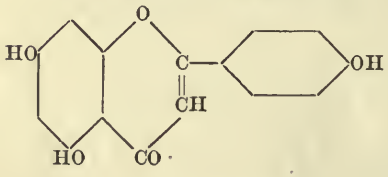
Natural Source.

In poplar buds with chrysin (Piccard, Ber. **6**, 890).

Synthetical Process.

[**A.**] From *chrysin* [**138**] by methylation with methyl iodide and potassium hydroxide (Piccard, Ber. **10**, 176; Emilewicz and Kostanecki, Ber. **32**, 2449).

140. Apigenin; 1 : 3 : 4^1-Trihydroxyflavone.



Natural Source.

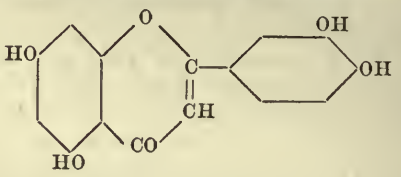
Occurs as glucoside (apiin) in stem, leaves, and seeds of parsley, *Apium petroselinum* (Braconnot, Ann. **48**, 349; Planta and Wallace, Ann. **74**, 262; Lindenborn, Ber. **9**, 1123; Vongerichten, *Ibid.* 1124; **33**, 2334; 2904; Ann. **318**, 121: see also under phloroglucinol [**86**]).

A methyl ether of apigenin (acacetin) is present in the leaves of *Robinia pseudacacia* (A. G. Perkin, Trans. Ch. Soc. **77**, 430).

Synthetical Processes.

[**A.**] From *anisic acid* [Vol. II], *phloroglucinol* [**86**], *acetic acid* [Vol. II], and *methyl* and *ethyl alcohols* [**13**; **14**] as accessories. Anisic ethyl ester is condensed with phloracetophenonetrimethyl ether (see under chrysin [**138**; **A**]) by heating with sodium in xylene solution. The product = 2 : 4 : 6 : 4^1-tetramethoxybenzoylacetophenone, on heating with strong hydriodic acid, gives apigenin (Czajkowski, Kostanecki, and Tambor, Ber. **33**, 1988).

141. Luteolin; 1 : 3 : 3^1 : 4^1-Tetrahydroxyflavone.



Natural Sources.

In weld from *Reseda luteola* (Chevreul, Journ. Chim. Méd. **6**, 157; Berz. Jahresber. **11**, 280; Moldenhauer, Ann. **100**, 180; Schützenberger and Paraf, Bull. Soc. [1] **1861**, 18; Journ. pr. Ch. [1] **83**, 368; Ann. Suppl. **1**, 256; Jahresber. **1861**, 707; Rochleder and Breuer, Zeit. [2] **2**, 602; Hlasiwetz and Pfaundler, Journ. pr. Ch. [1] **94**, 94; A. G. Perkin, Trans. Ch. Soc. **69**, 206; 799; A. G. P. and Horsfall, *Ibid.* **77**, 1314).

Luteolin occurs in the colouring-matter from the flowers of dyer's broom, *Genista tinctoria* (A. G. P. and Newbury, Proc. Ch. Soc. **15**, 179).

A glucoside contained in parsley with apiin is a derivative of luteolin methyl ether (Vongerichten, Ber. **33**, 2334; 2904).

Scoparin from broom, *Spartium scoparium*, may be a glucoside of methyl-luteolin (A. G. Perkin, Proc. Ch. Soc. **16**, 45; Trans. **77**, 423).

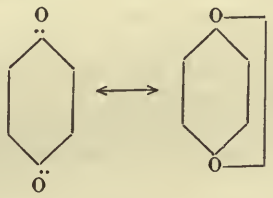
Digitoflavone from *Digitalis* leaves is identical with luteolin (Kiliani and Mayer, Ber. **34**, 3577).

Synthetical Process.

[**A.**] From *phloroglucinol* [**86**], *acetic* and *veratric acids* [Vol. II], *methyl* and *ethyl alcohols* [**13**; **14**]. Phloracetophenonetrimethyl ether (see under chrysin [**138**; **A**]) and ethyl veratrate

are condensed by treatment with sodium so as to form $2:4:6:3^1:4^1$-pentamethoxybenzoylacetophenone. The latter gives luteolin on heating with strong aqueous hydriodic acid (Kostanecki, Rózycki, and Tambor, Ber. **33**, 3415; Diller and Kostanecki, Ber. **34**, 1449).

142. Quinone; Paradioxybenzene.



Natural Sources.

Quinone appears to be among the products of the fermentation of grass, and is probably the result of oxidation by *Bacteria* (Emmerling, Ber. **30**, 1870).

Quinone is formed in albumin (peptone) cultures by *Streptothrix chromogena*, Gasperini (Beyerinck, Centr. Bakter. II, **6**, 1; Ch. Centr. 1900, **1**, 429: see also Furuta, Ch. Centr. 1902, **2**, 385).

The skin secretion of the Millipede, *Iulus terrestris*, possibly contains quinone (Béhal and Phisalix, Comp. Rend. **131**, 1004).

Synthetical Processes.

[A.] From *quinol* [71] by oxidation (Wöhler, Ann. **51**, 152; Nietzki, Ber. **19**, 1468; Clark, Am. Ch. Journ. **14**, 555).

[B.] From *phenol* [60] by oxidation of the p-sulphonic acid (Schrader, Ber. **8**, 760); or through p-nitro- and p-aminophenol, and oxidation of the latter (Schmitt and Siepermann, Journ. pr. Ch. [2] **19**, 317).

[C.] From *furfural* [126] and *acetone* [106] through pyromucic and mucobromic acids, nitromalonic aldehyde, and p-nitrophenol (see under phloroglucinol [86; I] and resorcinol [70; H]).

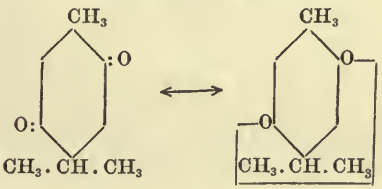
[D.] From *benzene* [6; I, &c.] by the oxidation of many derivatives with open p-position or with easily removed substituents in this position:—

From aniline (Hofmann, Jahresber. **1863**, 415; Nietzki, Ber. **10**, 1934; 2005; **11**, 1004; **19**, 1467; Ann. **215**, 125; Seyda, Ber. **16**, 687; Schniter, Ber. **20**, 2283) by sodium dichromate and sulphuric acid or other oxidising agents. Also by the oxidation of sulphanilic = aniline-p-sulphonic acid (Meyer and Ador, Ann. **159**, 7; Schrader, Ber. **8**, 760).

Or from benzene (or aniline) through p-phenylenediamine and oxidation of the latter (Hofmann, *loc. cit.* 422). Or directly from benzene by combination with chromium oxychloride and decomposition of the product with water (Etard, Ann. Chim. [5] **22**, 270).

The oxidation of aniline by chromic acid mixture is facilitated by electrolytic action (Darmstädter, Germ. Pat. 109012 of 1897; Ch. Centr. 1900, **2**, 151: for electrolytic oxidation in sulphuric acid of benzene to quinone see Kempf, Germ. Pat. 117251 of 1899; Ch. Centr. 1901, **1**, 348).

143. Thymoquinone.



Natural Source.

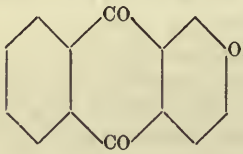
Occurs in wild bergamot oil from *Monarda fistulosa* (Brandel and Kremers, Pharm. Rev. **19**, 200; 244).

Synthetical Processes.

[A.] From *thymol* [67] by oxidation (see under thymoquinol dimethyl ether [83; A]).

[B.] From *carvacrol* [66] by oxidation (83; B).

144. Metahydroxyanthraquinone; 2-Hydroxyanthraquinone.



Natural Source.

In Chay root (*Oldenlandia umbellata*) from N. Burma, Ceylon, Madras Presidency, Malabar and Coromandel coasts (A. G. Perkin and Hummel, Trans. Ch. Soc. **63**, 1177).

Synthetical Processes.

[A.] From *phenol* [**60**] and *phthalic anhydride* (see under benzyl alcohol [**54**; **R**]). A mixture of these gives (with 1-hydroxy-) 2-hydroxyanthraquinone on heating with strong sulphuric acid (Caro and Baeyer, Ber. **7**, 969).

[B.] From *benzoic acid* [Vol. II] through m-nitro-, m-amino-, and m-hydroxybenzoic acid (see under phenol [**60**; **E**]). The latter, when heated with benzoic acid and strong sulphuric acid at 200°, gives m-hydroxyanthraquinone (Liebermann and Kostanecki, Ann. **240**, 263).

[C.] *Anthracene* and *anthraquinone* can be synthesised by various processes:—

Syntheses of Anthracene.

From *toluene* through benzyl chloride (see under benzyl alcohol [**54**; **A**]). The latter gives anthracene on heating with water at 180° (Limpricht, Ann. **139**, 308; Zincke, Ber. **7**, 278), or by the action of aluminium chloride (W. H. Perkin, junr., and Hodgkinson, Trans. Ch. Soc. **37**, 726; Schramm, Ber. **26**, 1706).

Or benzyl chloride and ethyl alcohol give benzyl ethyl ether (Cannizzaro, Jahresber. **1856**, 581), which on heating with phosphorus pentoxide gives (with ethylene) anthracene (Henzold, Journ. pr. Ch. [2] **27**, 518).

Benzyl trichloracetate (from benzyl chloride and *trichloracetic acid*) interacts with *benzene*, in presence of aluminium chloride, to form a compound which gives anthracene on distillation (Delacre, Bull. Soc. [3] **13**, 302).

Dihydroanthracene (furnishing anthracene by oxidation) is probably among the products of the oxidation of toluene by manganese dioxide and sulphuric acid (Weiler, Ber. **33**, 464).

Or from toluene through the o-bromo-derivative and o-brombenzyl bromide (Jackson, Ber. **9**, 932), and the action of sodium on the latter in ethereal solution (Jackson and White, Am. Ch. Journ. **2**, 391; Ber. **12**, 1965).

From *benzene* and *acetylene dibromide* (or *tetrabromide*) by treating a mixture with aluminium chloride or bromide (Anschütz, Ann. **235**, 156; 165; Anschütz and Eltzbacher, Ber. **16**, 623).

Or from benzene and *methylene chloride* [**55**; **E**, p. 117] by the action of aluminium chloride (Friedel, Crafts, and Vincent, Ann. Chim. [6] **11**, 264; Bull. Soc. [2] **40**, 97; **41**, 325). Hexa- and pentachlorethane and perchlorethylene, trichlorethane, and dichlorethyl ether all give anthracene when condensed with benzene by means of aluminium chloride (Mouneyrat, Bull. Soc. [3] **19**, 554; 557; Gardeur, Bull. Acad. Roy. Belg. [3] **34**, 920).

Naphthalene [**12**] can be converted into o-toluic acid (benzyl alcohol [**54**; **R**]), and this, when heated in bromine vapour at 140°, gives phthalide, $C_6H_4<\overset{CO}{CH_2}>O$. The latter, on distillation with lime, yields anthracene (Krczmař, Monats. **19**, 456).

Note:—Toluene thus also becomes a generator of anthracene through o-toluic acid (see under m-cresol [**62**; **A**]).

Phenol [**60**] and benzyl chloride (or *benzyl alcohol* [**54**]) condense to form p-benzylphenol under the influence of zinc chloride or other condensing agents (Paternò, Gazz. **2**, 2; **3**, 121; Paternò and Fileti, *Ibid.* **5**, 382; Liebmann, Ber. **14**, 1844; W. H. Perkin, junr., and Hodgkinson, Trans. Ch. Soc. **37**, 723). p-Benzylphenol gives anthracene among other products on distillation

with phosphorus pentoxide (Paternò and Fileti, *loc. cit.* **3**, 252).

p-Benzylphenol can also be obtained from phenol and *benzoic aldehyde* [**114**]. The latter on treatment with potassium cyanide forms benzoïn (Liebig and Wöhler, Ann. **3**, 276; Zinin, Ann. **34**, 186; Zincke, Ann. **198**, 151). A mixture of benzoïn and phenol gives p-desylphenol on treatment with strong sulphuric acid (Japp and Wadsworth, Trans. Ch. Soc. **57**, 965), and this on fusion with potash yields p-benzylphenol (*Ibid.* 972).

Or *benzoic acid* [Vol. II] and toluene, when heated to 200° with phosphorus pentoxide, give phenyl-o-toluyl ketone (Kollarits and Merz, Ber. **6**, 538: the p-modification is simultaneously formed). The latter yields anthracene on heating with zinc dust (Behr and Van Dorp, Ber. **7**, 17).

Note:—Phenyl-o-toluyl ketone is among the products of the oxidation of toluene by manganese dioxide and sulphuric acid (Weiler, Ber. **33**, 464).

Anthracene is formed by passing the vapours of many synthetical hydrocarbons through red-hot tubes:—Thus, from ethylene and benzene, benzene and styrene, o-benzyltoluene, &c. (Berthelot, Bull. Soc. [2] **7**, 223; **8**, 231; **9**, 295; Ann. **142**, 254; Van Dorp, Ann. **169**, 216: for pyrogenic syntheses of anthracene from benzene and ethylene, from toluene vapour, and from ethylbenzene, see Ferko, Ber. **20**, 660).

Anthracene is among the hydrocarbons formed by passing through a hot tube ethylene (Norton and Noyes, Am. Ch. Journ. **8**. 362), ethylene and diphenyl (Barbier, Comp. Rend. **79**, 121), heptane and octane at 900° (Worstall and Burwell, Am. Ch. Journ. **19**, 815).

Anthracene is among the products formed by the action of dry aluminium chloride on acetylene (Baud, Comp. Rend. **130**, 1319), and by the action at 600–800° of certain metallic carbides, e. g. barium, on the corresponding hydroxides (Bradley and Jacobs, Germ. Pat. 125936 of 1898; Ch. Centr. 1902, **1**, 77).

Styrene on combination with bromine gives $1^1:1^2$-dibromethylbenzene (Blyth and Hofmann, Ann. **53**, 306; Glaser, Ann. **154**, 154; Zincke, Ann. **216**, 288). The same dibromethylbenzene can be obtained by the bromination of ethylbenzene (Radziszewski, Ber. **6**, 493; Friedel and Balsohn, Bull. Soc. [2] **35**, 55). $1^1:1^2$-Dibromethylbenzene gives anthracene by the action of aluminium chloride on its benzene solution (Schramm, Beilstein's 'Handbuch,' 3rd ed. II, 257).

Syntheses of Anthraquinone.

From phthalic anhydride (see under benzyl alcohol [**54**; **R**]) and benzene, a mixture (solution) of these giving, when treated with aluminium chloride, o-benzoylbenzoic acid (Friedel and Crafts, Ann. Chim. [6] **14**, 446; Comp. Rend. **86**, 1368). The latter, on heating *per se* or with phosphorus pentoxide or strong sulphuric acid, yields anthraquinone (Ullmann, Ann. **291**, 24; Behr and Van Dorp, Ber. **7**, 578; Liebermann, *Ibid.* 805; W. H. Perkin, junr., Trans. Ch. Soc. **59**, 1012).

Note:—o-Benzoylbenzoic acid is among the products of oxidation of toluene by potassium permanganate (Weiler, Ber. **33**, 465).

Calcium phthalate gives anthraquinone on dry distillation (Panaotovits, Ber. **17**, 313). Or phthalic acid can be converted into phthaloyl chloride (Müller, Jahresber. **1863**, 393). The latter yields anthraquinone when heated with zinc dust and benzene at 220°, or when treated with aluminium chloride in benzene solution (Piccard, Ber. **7**, 1785; Friedel and Crafts, Ann. Chim. [6] **1**, 523; Bull. Soc. [2] **29**, 49).

Anthraquinone is among the products of the distillation of *calcium benzoate* [Vol. II], and is formed in small quantity by distilling benzoic acid with phosphorus pentoxide (Kekulé and Franchimont, Ber. **5**, 908).

Phenyl-o-toluyl ketone (see above) gives anthraquinone on heating with lead oxide, or on oxidation with manganese dioxide and sulphuric acid (Behr and Van Dorp, Ber. **6**, 754; **7**, 16); also by chlorination at 110°, and decomposition

of the product with water (Thörner and Zincke, Ber. **10**, 1479).

Anthracene is converted into anthraquinone by oxidation (Laurent, Berz. Jahresber. **16**, 366; Ann. Chim. [2] **60**, 220; **72**, 415; Ann. **34**, 287; Anderson, Journ. Ch. Soc. **15**, 44; Ann. **122**, 301; Graebe and Liebermann, Ann. Suppl. **7**, 285; Kopp, Jahresber. **1878**, 1188; Darmstädter, Germ. Pat. 109012 of 1897; Ch. Centr. 1900, **2**, 151).

Anthracene and anthraquinone give m-hydroxyanthraquinone as follows:— Anthracene by the action of bromine gives dibromanthracene bromide (Anderson, *loc. cit.*; Graebe and Liebermann, *loc. cit.* 275), and this on heating at 200° yields tribromanthracene. The latter on oxidation (with chromic acid in acetic acid) gives 2-bromanthraquinone (G. and L. *loc. cit.* 290), and this yields 2-hydroxyanthraquinone on fusion with potash (*Ibid.* Ann. **160**, 141; Suppl. **7**, 290; **212**, 25).

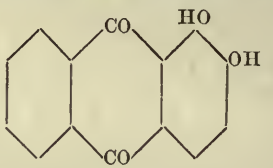
Anthraquinone on sulphonation gives (with disulpho-acid) 2-sulpho-acid (*Ibid.* Ann. **160**, 131), and this yields the 2-hydroxyquinone by potash fusion (*Ibid.* 141; Simon, Ber. **14**, 464; Liebermann, Ann. **212**, 25: see also A. G. and W. H. Perkin, junr., Trans. Ch. Soc. **47**, 680). Or the solution of the sulphonic acid (salt) may be heated with lime and water under pressure at 160° (Meister, Lucius, and Brüning, Germ. Pat. 106505 of 1898; Ch. Centr. 1900, **1**, 741).

Or the 2-sulphonic acid heated with excess of aqueous ammonia at 190° gives 2-aminoanthraquinone (Perger, Ber. **12**, 1567: see also Bourcart, *Ibid.* 1418), and this yields the 2-hydroxyquinone by the diazo-method (Perger, *loc. cit.* 1569).

By the action of nitric acid on dibromanthracene (Claus and Hertel, Ber. **14**, 978), or on anthraquinone (Böttger and Petersen, Ann. **166**, 147), the α-nitro-quinone is formed, and this on reduction with potassium sulphydrate gives the α-amino-quinone (*Ibid.* 149: see also Claus and Hertel, *loc. cit.* 979). The latter yields the m-hydroxyquinone by the diazo-method (B. and P. *loc. cit.* 151).

[D.] From *alizarin* [145] by treatment with alkaline stannite (Liebermann and Fischer, Ber. **8**, 975). Or through α-alizarinamide by heating alizarin with aqueous ammonia at 200° (Liebermann, Ann. **183**, 207), and elimination of the NH_2-group by the diazo-method (*Ibid.* 208).

145. Alizarin; 1 : 2-Dihydroxyanthraquinone.



Natural Sources.

Occurs as the glucoside ruberythric acid ($C_{26}H_{28}O_{14}$) in madder from the root of *Rubia tinctoria* (Robiquet and Colin, Ann. Chim. [2] **34**, 225; Runge, Journ. pr. Ch. **5**, 362; Schunck, Ann. **66**, 174; 201; **81**, 336; **87**, 344; Phil. Mag. [4] **5**, 410; 495; **12**, 200; 270; Journ. pr. Ch. **59**, 465; Debus, Ann. **66**, 351; Wolff and Strecker, Ann. **75**, 1; Rochleder, Ber. **3**, 295; Ann. **80**, 321; **82**, 205; Wartha, Ber. **3**, 545; 673; Willigk, Ann. **82**, 339; Rosenstiehl, Ann. Chim. [5] **18**, 235; Comp. Rend. **88**, 1194; Wurtz, Comp. Rend. **96**, 465; Liebermann, Ber. **20**, 2241; Bergami, *Ibid.* 2247).

Alizarin occurs also in Chay root from *Oldenlandia umbellata* (see under m-hydroxyanthraquinone [144]; A. G. Perkin and Hummel, Trans. Ch. Soc. **63**, 1167).

Synthetical Processes.

[A.] From *catechol* [69] and *phthalic anhydride* (see under benzyl alcohol [54; R]), a mixture of these compounds giving alizarin when heated with strong sulphuric acid (Baeyer and Caro, Ber. **7**, 972).

[B.] *Anthracene* [144; C] is chlorinated or brominated, and the product oxidised to dichlor- or dibromanthra-

quinone. The halo-quinone gives alizarin on fusion with alkali (Graebe and Liebermann, Ann. Suppl. **7**, 300; Ber. **3**, 359; Bull. Soc. [2] **11**, 516).

Or *anthraquinone* is sulphonated, and the monosulphonic acid (see under m-hydroxyanthraquinone [**144**; **C**]) fused with alkali and potassium chlorate (G. and L. *loc. cit.*; Perkin, Journ. Ch. Soc. **23**, 133; Ber. **9**, 281). The latter is the technical process.

α-Nitroanthraquinone, α-dinitro-, and diaminoanthraquinone give alizarin on fusion with alkali (Böttger and Petersen, Ber. **4**, 227; Ann. **160**, 145; **166**, 147; Meister, Lucius, and Brüning, Jahresber. **1873**, 1122; Claus, Ber. **15**, 1514).

Or anthraquinonesulphonic acid gives on nitration a mixture of two nitrosulphonic acids (Claus, *loc. cit.*); the α-acid yields alizarin on fusion with alkali. Or the nitrosulphonic acid can be reduced to the corresponding amino-acid (Claus, *loc. cit.* 1519), and this converted into 1-hydroxyanthraquinone-2-sulphonic acid by the diazo-method (Lifschütz, Ber. **17**, 900). The latter gives alizarin on alkaline fusion (*Ibid.* 901).

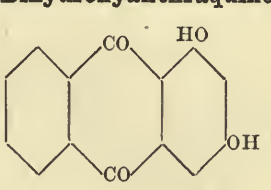
[**C.**] *m-Hydroxyanthraquinone* [**144**] (and the isomeric 1-hydroxyquinone simultaneously formed from phenol and phthalic anhydride) gives alizarin on alkaline fusion.

[**D.**] *Gallic acid* [Vol. II] on heating with strong sulphuric acid gives rufigallic acid = 1 : 2 : 3 : 5 : 6 : 7-hexahydroxyanthraquinone (Robiquet, Ann. **19**, 204; Wagner, Ch. Centr. 1861, 47; Löwe, Journ. pr. Ch. **107**, 296; Jaffé, Ber. **3**, 694; Klobukowski and Noelting, Ber. **8**, 819; **9**, 1256; **10**, 880; Widmann, Ber. **9**, 856). The latter yields alizarin on reduction with sodium amalgam (Widmann, *loc. cit.*; Bull. Soc. [2] **24**, 359).

[**E.**] From *vanillin* [**121**] and *benzene* [**6**; **1**, &c.] through the following processes:—Acetvanillin (Tiemann and Nagai, Ber. **11**, 647; Pschorr and Sumuleanu, Ber. **32**, 3405) on nitration and hydrolysis of the product gives o-nitrovanillin, and this on methylation yields the methyl ether. The latter on oxidation by alkaline permanganate gives o-nitroveratric acid, the nitro-acid o-aminoveratric acid by reduction, and hemipic acid (through the nitrile) by the diazo-method, followed by hydrolysis of the nitrile (Pschorr and Sumuleanu, *loc. cit.* 3411). Hemipic acid in benzene solution under the influence of aluminium chloride gives hydroxymethoxybenzoylbenzoic acid, and this, by the action of strong sulphuric acid, yields alizarin methyl ether, which gives alizarin by demethylation on heating with strong hydriodic acid at 127° (Lagodzinski, Ber. **28**, 1427).

[**F.**] From *hystazarin* [**147**] by heating with strong sulphuric acid to 200–205° (Liebermann and Hohenemser, Ber. **35**, 1778).

146. Purpuroxanthin; Xanthopurpurin; 1 : 3-Dihydroxyanthraquinone.



Natural Source.

Occurs with alizarin and purpurin in madder root (Schützenberger and Schiffert, Bull. Soc. [2] **4**, 12). The carboxylic acid also is present in madder (Schunck and Römer, Ber. **10**, 172).

Synthetical Processes.

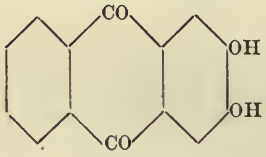
[**A.**] From *benzoic acid* [Vol. II] through the 3 : 5-disulphonic acid (Barth and Senhofer, Ann. **159**, 217), the 3 : 5-dihydroxy-acid (*Ibid.* 222), and the action of strong sulphuric acid on a mixture of the latter with benzoic acid at 105–110° (Noah, Ber. **19**, 332; Ann. **241**, 266: anthrachrysone = 1 : 3 : 5 : 7-tetrahydroxyanthraquinone is simultaneously formed in this process).

[**B.**] From *purpurin* [**149**] by reduction with phosphorus iodide and water,

stannous chloride, sodium stannite, or phosphorus and water (Schützenberger and Schiffert, Bull. Soc. [2] **4**, 12; Rosenstiehl, Ann. Chim. [5], **18**, 224; Comp. Rend. **79**, 764; Liebermann and Fischer, Ann. **183**, 213).

Or purpurin on heating with aqueous ammonia gives an amide (Stenhouse, Ann. **130**, 337; Liebermann, Ann. **183**, 212), which yields purpuroxanthin by the diazo-method (Liebermann, *loc. cit.* 213).

147. Hystazarin; 2 : 3-Dihydroxyanthraquinone.



Natural Source.

The methyl ether occurs in Chay root from *Oldenlandia umbellata* (see under m-hydroxyanthraquinone [144]; A. G. Perkin and Hummel, Trans. Ch. Soc. **67**, 822).

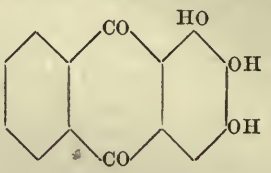
Synthetical Processes.

[A.] *Catechol* [69] and *phthalic anhydride* [54; R] give (with alizarin) hystazarin when heated at 140–150° with strong sulphuric acid (Liebermann, Ber. **21**, 2501; Schöller, *Ibid.* 2503).

Or *veratrole* (see under methyl-eugenol [81; A]) on condensation with phthalic anhydride by means of aluminium chloride gives 3 : 4-dimethoxybenzoylbenzoic acid, which, on heating with strong sulphuric acid, yields hystazarin dimethyl ether, and finally, by demethylation, free hystazarin (Lagodzinski and Lorétan, Ber. **28**, 118; Liebermann and Hohenemser, Ber. **35**, 1778).

Note :—The monomethyl ether has not been synthesised.

148. Anthragallol; 1 : 2 : 3-Trihydroxyanthraquinone.



Natural Source.

The three isomeric dimethyl ethers occur in Chay root (A. G. Perkin and Hummel, Trans. Ch. Soc. **63**, 1168; **67**, 819).

Synthetical Processes.

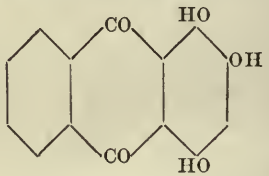
[A.] From *pyrogallol* [84] and *phthalic anhydride* [54; R] by heating a mixture of the two compounds with strong sulphuric acid (Seuberlich, Ber. **10**, 39).

[B.] From *benzoic* and *gallic acids* [Vol. II] by heating a mixture with strong sulphuric acid (*Ibid.*).

[C.] From *alizarin* [145] through β-nitro- and β-aminoalizarin (Schunck and Römer, Ber. **12**, 584; 588 : see also Rosenstiehl, Bull. Soc. [2] **26**, 63; Brunner and Chuard, Ber. **18**, 445). Bromanthragallol from β-aminoalizarin gives a sulphonic acid on heating with sulphurous acid, and this yields anthragallol on heating with sulphuric acid (Bayer & Co., Germ. Pat. 125575; Journ. Ch. Soc. **82**, Abst. I, 383).

Note :—The dimethyl ethers have not been synthesised.

149. Purpurin; 1 : 2 : 4-Trihydroxyanthraquinone.



Natural Source.

Occurs with alizarin, purpuroxanthin, &c., in madder root, probably as an unstable glucoside (Colin and Robiquet, Ann. Chim. [2] **48**, 69; **51**, 110;

Gaulthier de Claubry and Persoz, Ann. Chim. [2] **48**, 69; **51**, 110; Runge, *Ibid.* **63**, 282; Schiel, Ann. **60**, 74; Debus, Ann. **66**, 351; **86**, 117; Wolff and Strecker, Ann. **75**, 1; Rochleder, Ann. **80**, 321; **82**, 205; Stenhouse, Proc. Roy. Soc. **12**, 633; **13**, 145; Kopp, Jahresber. **1861**, 938; Schützenberger, Bull. Soc. [2] **4**, 12; Jahresber. **1864**, 542; Auerbach, Ber. **4**, 979; Schünck and Römer, Ber. **10**, 551).

The carboxylic acid also occurs in madder (Schützenberger and Schiffert, Bull. Soc. [2] **4**, 13; Rosenstiehl, Comp. Rend. **84**, 561; Liebermann, Ber. **10**, 1618).

Synthetical Processes.

[**A.**] From *phenol* [**60**] and *phthalic anhydride* [**54**; **R**]. The phenol is converted into p-chlorphenol (see under resorcinol [**70**; **C**]), and this, when heated with phthalic anhydride and strong sulphuric acid, gives (with 1 : 4-dihydroxyanthraquinone) a small quantity of purpurin (Liebermann and Giesel, Ber. **10**, 608). The 1 : 4-dihydroxy-quinone (quinizarin) yields purpurin on oxidation with sulphuric acid and manganese dioxide (Baeyer and Caro, Ber. **8**, 152).

[**B.**] From *quinol* [**71**] and *phthalic anhydride* through quinizarin by heating a mixture of these two compounds with strong sulphuric acid (Grimm, Ber. **6**, 506; Liebermann, Ann. **212**, 11), and then as above under **A**.

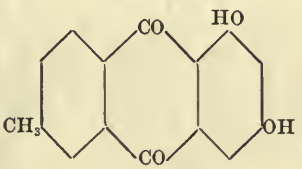
[**C.**] From *alizarin* [**145**] by oxidation with manganese dioxide and sulphuric acid (De Lalande, Comp. Rend. **79**, 669; Ber. **7**, 1545; Jahresber. **1874**, 486). Or by heating with strong sulphuric acid to 225° (Liebermann and Hohenemser, Ber. **35**, 1781).

Or alizarin on nitration of the diacetate gives α-nitro- = 4-nitroalizarin (Perkin, Ber. **8**, 780; Journ. Ch. Soc. 1876, **2**, 578; Jahresber. **1877**, 587; Schunck and Römer, Ber. **12**, 587; Brasch, Ber. **24**, 1612), and this on reduction with sodium amalgam or ammonium sulphide yields α-aminoalizarin (Perkin, *loc. cit.*; Brasch, *loc. cit.*). The latter gives purpurin by the diazo-method (Brasch, *loc. cit.* 1614: see also Meister, Lucius, and Brüning, Germ. Pat. 97688 of 1897; Ch. Centr. 1898, **2**, 696).

[**D.**] From *purpuroxanthin* [**146**] by fusion with caustic potash (Noah, Ber. **19**, 333).

[**E.**] *Anthraquinone* [**144**; **C**] gives purpurin by brominating to α-dibrom- and finally to tribromanthraquinone (Graebe and Liebermann, Ann. Suppl. **7**, 289; Diehl, Ber. **11**, 181). The latter yields purpurin on fusion with potash at 200° (Diehl, *loc. cit.* 184).

150. Methylpurpuroxanthin; 1 : 3-Dihydroxy-6-Methylanthraquinone.



Natural Source.

In the colouring-matter 'mangkoudu' from the root bark of *Morinda umbellata* from Java and the Malay Peninsula, and from E., S., and S. W. India (A. G. Perkin and Hummel, Trans. Ch. Soc. **65**, 863).

Synthetical Process.

[**A.**] From *benzoic acid* [Vol. II] through 3 : 5-dihydroxybenzoic acid (see under purpuroxanthin [**146**; **A**]) and *toluene* [**54**; **A**, &c.] through p-toluic acid (see under o-cresol [**61**; **A**]). A mixture of the two acids gives methylpurpuroxanthin on heating with strong sulphuric acid (Marchlewski, Trans. Ch. Soc. **63**, 1142).

CARBOHYDRATES AND GLUCOSIDES.

151. Dihydroxyacetone; Propanediolone.

$HO.CH_2.CO.CH_2.OH$

Natural Sources.

A product of fermentation of glycerol by the sorbose bacterium (Bertrand, Comp. Rend. **126**, 842; 984; Bull. Soc. [3] **19**, 502; Bertrand and Sazerac, Comp. Rend. **132**, 1504). According to Emmerling (Ber. **32**, 541) the sorbose bacterium is *Bacterium xylinum* of A. J. Brown (Trans. Ch. Soc. **49**, 432). Other micro-organisms are capable of acting upon glycerol in a similar way (Bertrand, Comp. Rend. **133**, 887).

Glucose appears to give dihydroxyacetone among the products of its fermentation by *Bacillus roseus vini* (Bordas, Joulin, and Raczkowski, Comp. Rend. **126**, 1050), and the same *Bacillus* produces the dihydroxyketone from glycerol (*Ibid.* 1443).

Synthetical Processes.

[A.] From *formic aldehyde* [91] and *methyl alcohol* [13] through nitroisobutylglycerol and dihydroxyacetoneoxime (see under glycerol [48; L]).

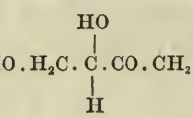
[B.] From *citric acid* [Vol. II] through acetonedicarboxylic acid and diaminoacetone [48; M].

[C.] From *hippuric acid* [Vol. II] through diaminoacetone [48; N].

[D.] *Glycerol* [48] gives 'glycerose' on oxidation with nitric acid or by electrolysis (Van Deen, Jahresber. **1863**, 501; Stone, Am. Ch. Journ. **15**, 656; Fischer and Tafel, Ber. **20**, 1088), by oxidation with platinum black (Grimaux, Comp. Rend. **104**, 1276; Bull. Soc. [2] **45**, 481; **49**, 251; Emmerling, Ber. **32**, 542), with sodium hypobromite or bromine and lead glycerate (Fischer and Tafel, *loc. cit.* 3384; **21**, 2634; **22**, 106), or with hydrogen peroxide in presence of ferrous sulphate (Fenton and Jackson, Trans. Ch. Soc. **75**, 5). Glycerol gives glycerose on oxidation by quinone in the presence of light (Ciamician and Silber, Ber. **34**, 1532).

Glycerose is a mixture of dihydroxyacetone with glyceric aldehyde, the former predominating (Fischer and Tafel, Ber. **20**, 3384; see also Piloty, Ber. **30**, 3162; Wohl and Neuberg, Ber. **33**, 3099).

152. d-Erythrulose; Butanetriolone.



Natural Source.

A product of fermentation of erythritol by the sorbose bacterium (Bertrand, Comp. Rend. **126**, 762; **130**, 1330; 1472; Bull. Soc. [3] **19**, 347; **23**, 681).

Synthetical Processes.

[A.] From *erythritol* [50] by oxidation with nitric acid (Fischer and Tafel, Ber. **20**, 1088), with platinum black (Grimaux, Comp. Rend. **104**, 1276; Bull. Soc. [2] **45**, 481; **49**, 251), or with hydrogen peroxide and ferrous sulphate (Fenton and Jackson, Trans. Ch. Soc. **75**, 7; Neuberg, Ber. **35**, 2627).

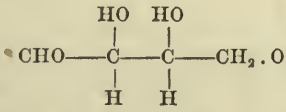
Note:—The synthetical product is i-erythrulose. The ketose character of the synthetical sugar, and therefore its identity with the biochemical sugar, has only been proved (apart from optical properties) in the case of the product obtained by the last method, viz. hydrogen peroxide and ferrous sulphate (Neuberg, *loc. cit.*). Other synthetical tetroses (probably aldoses) have been obtained, but not from biochemical sources. In order to complete the history of these compounds the synthetical processes are given below.

Other Syntheses of Tetroses.

[B.] From *tartaric acid* [Vol. II] through glycollic aldehyde (see under furfural [126; E]). The latter in contact with dilute alkali at 0° undergoes aldol condensation with the formation of erythrose (Fischer and Landsteiner, Ber. **25**, 2553; Jackson, Trans. Ch. Soc. **77**, 131: see also Fischer, Ber. **27**, 3200; Neuberg, Ber. **35**, 2630).

NOTE:—The generators of glycollic aldehyde referred to under furfural [126; F; G, &c.] thus become generators of erythrose. These are:—*acetal* [93]; *ethyl alcohol* [14]; *ethylene*.

[C.] From *d-gluconic acid* [Vol. II] through *d-arabinose* [153] by oxidising the calcium salt with bromine in presence of lead carbonate or with hydrogen peroxide and ferric acetate (see under **153**; **B**). d-Arabinose on further oxidation with bromine and water gives d-arabonic acid, and this on oxidation as above yields d-erythrose (Ruff, Ber. **32**, 3672). The erythrose has the constitution:—



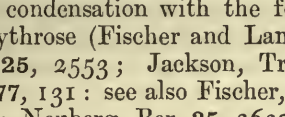
[D.] *Dextrose* [154] gives an oxime which on treatment with acetic anhydride yields the nitrile of pentacetylgluconic acid (see under **153**; **A**). The nitrile gives d-arabinose on hydrolysis with acids (*Ibid.*). Subsequent steps as above under **C**.

[E.] From *glycerol* [48] through *acroleïn* [101], which, on treatment with hydrogen chloride in alcoholic solution, gives the diethylacetal of β-chlorpropionic aldehyde (Alsberg, Jahresber. 1864, 495; Wohl, Ber. **31**, 1797). The latter yields acroleïn-acetal on treatment with potassium hydroxide (*Ibid.* 1798), and the acetal, on heating with dilute sulphuric acid, gives (racemic) glyceric aldehyde (*Ibid.* 2394), of which the oxime on heating with aqueous caustic alkali yields glycollic aldehyde (Wohl and Neuberg, Ber. **33**, 3106). Subsequent steps as above under **B**.

NOTE:—A conversion of l-arabinose into a tetrose is possible through the following steps:—l-arabinoseoxime; tetra-acetylarabonic nitrile; tetrose (Wohl, Ber. **26**, 743).

l-Arabinose has been converted through l-arabonic acid into l-erythrose by oxidising the calcium arabonate with hydrogen peroxide in presence of a ferrous salt. An isomeric tetrose (l-threose) is obtained by similar processes from l-xylose through l-xylonic acid (Ruff, Ber. **34**, 1362). The l-arabinose and l-xylose employed in these processes are not synthetical products.

153. d-Arabinose; Pentanetetrolal.



NATURAL SOURCE.

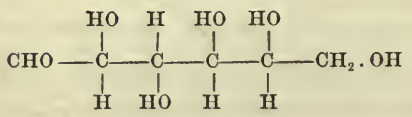
A pentose has been found in the urine in a case of morphinism (Salkowski and Jastrowitz, Centr. med. Wiss. 1892, Nos. 19 and 32) which, according to Neuberg (Ber. **33**, 2243), is racemic arabinose, and may therefore be considered to contain the d-arabinose complex. (For behaviour of the stereoisomeric arabinoses in the animal body see Neuberg and Wohlgemuth, Ber. **34**, 1745.) This urine pentose is synthesised in the organism (Neuberg, Ber. **35**, 1472: for the separation of d-arabinose from the racemic compound by l-menthylphenylhydrazine see Neuberg, Ber. **36**, 1192).

SYNTHETICAL PROCESSES.

[A.] From *dextrose* [154], the oxime of which on treatment with sodium acetate and acetic anhydride gives the cyanacetate = pentacetylgluconitrile. The latter on hydrolysis yields d-arabinose. Or the nitrile, on treatment with ammoniacal silver oxide solution, gives the pentose in combination with acetamide (Wohl, Ber. **26**, 730: see also Neuberg and Wohlgemuth, Zeit. physiol. Ch. **35**, 31).

[B.] From *d-gluconic acid* [Vol. II] by oxidation with bromine in presence of lead carbonate, or with hydrogen peroxide in presence of basic ferric acetate (Ruff, Ber. **31**, 1573; **32**, 553; **33**, 1799; **35**, 2360, note).

154. Dextrose; d-Glucose; Grape Sugar; Starch Sugar; Hexanepentolal.



NATURAL SOURCES.

Widely distributed throughout the vegetable kingdom, being found in the sap of plants and in most fruits and flowers. It is generally accompanied by lævulose and sometimes by certain C_{12}-sugars, especially saccharose.

Honey contains from 32 to 42 per cent. of dextrose (Dubrunfaut and Soubeiran, Jahresber. **1849**, 464; Roeders, *Ibid.* **1863**, 574; Brown, 'Analyst,' 1878, 257: see also König and Karsch, Zeit. anal. Ch. **34**, 1; Beckmann, *Ibid.* **35**, 263; v. Raumer, *Ibid.* **41**, 333).

Manna, an exudation from the manna ash (*Ornus europæa* and *O. rotundifolia*), contains from 2–3 per cent. of dextrose (Tanret, Bull. Soc. [3] **27**, 947).

A honey-like exudation from *Euonymus japonica*, produced by insect punctures, contains dextrose (Maquenne, Bull. Soc. [3] **21**, 1082).

The sugar from mahwa-flowers from *Bassia latifolia* consists of 'invert sugar' (v. Lippmann, Ber. **35**, 1448).

Crocin and picrocrocin from the saffron plant, *Crocus sativa*, contain the dextrose complex (Kastner, Ch. Centr. 1902, **2**, 383).

The natural products known as glucosides, which are found in such large numbers of plants, are esters, in which generally some sugar, and most frequently glucose, plays the part of a polyhydric alcohol (see Beilstein's 'Handbuch,' III, 565, and 'Die Glykoside' by Van Rijn, Berlin, 1900).

Saccharose (cane-sugar) is resolved by the majority of yeasts into dextrose and lævulose. Moulds such as *Aspergillus niger* and *Penicillium glaucum* exert the same action (Gayon, Comp. Rend. **86**, 52; Duclaux, 'Chimie biologique,' 1883; Fernbach, Thèse, 1890: for two last see J. R. Green's 'Fermentation,' p. 115).

Penicillium duclauxi as well as *P. glaucum* can invert cane-sugar (Bourquelot; J. R. Green, *loc. cit.*). *Monilia candida* can also hydrolyse saccharose (Fischer and Lindner, Ber. **28**, 3037). *Mucor racemosus* is said to be capable of inverting saccharose (Fitz, Ber. **17**, 1196; Brefeld, Landw. Jahrb. **5**, 308, as quoted by Fitz). Saccharose is not hydrolysed by *Saccharomyces apiculatus* (Fischer and Lindner, *loc. cit.* 3039).

Monilia javanica, one of the fungi present in the ferment 'raggi' used for preparing arrack in Java (see under ethyl alcohol [14]), can invert saccharose (Went and Prinsen Geerligs, Bot. Zeit. 1895, p. 143). The ferment 'koji' used in Japan for preparing 'saké' is also capable of inverting saccharose (Kellner, Mori, and Nagaoka, Zeit. physiol. Ch. **14**, 297; Kozai, Centr. Bakter. II, **6**, 385).

The enzymes of various yeasts, &c., which are capable or incapable of hydrolysing polysaccharides have been investigated by Kalanthar (Zeit. physiol. Ch. **26**, 88).

Certain bacteria (*Clostridium*, *Cladothrix*, and *Sarcina*) are capable of inverting saccharose (Laxa, Centr. Bakter. II, **6**, 286; Ch. Centr. 1900, **1**, 1298). This sugar is inverted in bouillon by *Bacillus megatherium*, *B. fluorescens liquefaciens*, and *Proteus vulgaris* (Fermi and Montesano, Centr. Bakter. II, **1**, 482; 542; Ch. Centr. 1895, **2**, 712). The sugar *Bacteria* of Marshall Ward and J. R. Green can invert saccharose (Proc. Roy. Soc. **65**, 79). So also can the gum-producing *Bacillus levaniformans* (Greig-Smith and Steel, Journ. Soc. Ch. Ind. **21**, 1381) and the sugar-gelatinising *Clostridium gelatinosum* (Laxa, Zeit. Zuckerind. **26**, 122; Journ. Fed. Inst. **8**, 639). *Streptococcus hornensis* probably inverts saccharose (Boekhout, Centr. Bakter. II, **6**, 161).

Maltose is fermentable only by those yeasts which contain the enzyme maltase (*Sacch. cerevisiæ* and *octosporus*), and not by those containing invertin (*Sacch. marxianus*). It is thus probable that the hydrolysis of maltose to dextrose precedes fermentation (Fischer, Ber. **28**, 1433: see also Maquenne's work for

general summary; 'Les Sucres,' Paris, 1900, p. 646). *Sacch. apiculatus* does not directly ferment maltose (Amthor, Zeit. physiol. Ch. **12**, 558). The 'koji' ferment (see above) produces dextrose from maltose (Kozai, Centr. Bakter. II, **6**, 385).

Lactose or milk-sugar is hydrolysed into dextrose and galactose (Bouchardat, Ann. Chim. [4] **27**, 68; Kent and Tollens, Ann. **227**, 221). The lactic bacteria can effect this hydrolysis (Von Freudenreich, Centr. Bakter. II, **6**, 332).

Frohberg yeast is capable of hydrolysing the biose trehalose (Fischer, Ber. **28**, 1432; Kalanthar, Zeit. physiol. Ch. **26**, 88). Trehalose is slowly fermented by certain yeasts, such as Saatz (surface and sedimentary), Frohberg (surface), Logos, *Sacch. ellipsoideus* and *pastorianus*, and by *Monilia candida* with the formation of dextrose; other species (*Sacch. apiculatus* and *pombé*) are without action (Bau, Ch. Centr. 1899, **2**, 130).

Certain mould-fungi such as *Aspergillus niger*, *Penicillium glaucum*, and *Volvaria speciosa* contain an enzyme, by virtue of which they hydrolyse trehalose with the formation of dextrose (Bourquelot, Comp. Rend. **116**, 826; Bull. Soc. Mycol. **9**, 189). *Bacillus fluorescens liquefaciens* slowly hydrolyses trehalose (Emmerling and Reiser, Ber. **35**, 702).

Strophanthin from the seeds of *Strophanthus kombe* yields on hydrolysis (with strophantidin) a carbohydrate, 'strophantobiose methyl ether,' which on further hydrolysis gives mannose, rhamnose, and dextrose (Feist, Ber. **33**, 2095).

Raffinose (melitriose) is hydrolysed by *Aspergillus niger* with the formation of melibiose and finally dextrose and galactose (Gillot, Bull. Acad. Roy. Belg. 1899, 211; Ch. Centr. 1899, **2**, 129).

Melibiose is not affected by surface yeast, but is resolved into dextrose and d-galactose, and finally fermented by sedimentary yeast (Bau, Woch. Brau. **16**, 397; Fischer and Lindner, Ber. **28**, 3035). The resolution of raffinose by feeble ferments was observed by Berthelot (Comp. Rend. **109**, 548), and the product identified as melibiose by Scheibler and Mittelmeier (Ber. **22**, 3118).

Gentianose (? a triose), contained in gentian root, is hydrolysed by dilute sulphuric acid or the enzyme of *Aspergillus niger* into dextrose (2 mols.) and lævulose (1 mol.). The gentiobiose obtained (with lævulose) by partial hydrolysis gives dextrose (2 mols.) on complete hydrolysis (Bourquelot and Hérissey, Comp. Rend. **132**, 571; **135**, 399).

Melezitose, a triose found in the mannas from *Pinus larix*, &c., is resolved by hydrolysing agents (dilute acids or the enzyme of *Aspergillus niger*) into dextrose and the biose turanose, the latter giving dextrose as a final product of hydrolysis (*Ibid.* Journ. Pharm. [6] **4**, 385; Alekhine, Ann. Chim. [6] **18**, 532).

Starch is saccharified with the production of dextrin, maltose, and dextrose by the mould-fungi used in making the Javanese 'raggi' (see under ethyl alcohol [**14**] for full references). The species chiefly concerned are *Chlamydomucor oryzæ* and *Rhizopus oryzæ*. The ferment ('koji') used in the above process can produce dextrose from raffinose (Kozai, Zeit. Bakter. II, **6**, 385). The mould-fungi concerned in the production of the Japanese 'saké' can also saccharify starch (see under ethyl alcohol [**14**] for references).

The ferments concerned in the production of the Japanese 'awamori' comprise, among others, the starch-saccharifying *Aspergillus luchuensis* of Inui (Journ. Imp. Coll. Sci. Tokio, 1901, **15**; Journ. Fed. Inst. **8**, Abst. 529).

The mould-fungus *Mucor erectus* can resolve starch into dextrose among other carbohydrates (see under ethyl alcohol [**14**]). *Mucor* (*Amylomyces*) *rouxii* of Calmette, which is contained in Chinese yeast, is capable of hydrolysing starch (see under ethyl alcohol [**14**] for references: for industrial formation of dextrose by *Mucor* or *Aspergillus* see Calmette's Fr. Pat., Journ. Fed. Inst. **7**, 392). *Mucor* β- and γ-*Amylomyces*,

found on Japanese and Tonquin rice respectively, are starch saccharifying moulds (Sitnikoff and Rommal, Journ. Fed. Inst. 7, 112). Chinese yeast from Cambodia contains *Mucor cambodia*, which also can saccharify starch (Chrzaszcz, Zeit. Bakter. II, 7, 326).

A *Monilia* (? *M. sitophila*, Saccardo) found on earth-nuts in Java can saccharify starch (Went, Centr. Bakter. II, 7, 544; 591; also Journ. Ch. Soc. 80, II, Abst. 412).

Bacillus anthracis can produce sugar (? dextrose) from starch (Maumus, Comp. Rend. Soc. Biol. 1893, 107). Starch is slowly hydrolysed by *Bacillus fluorescens liquefaciens* (Emmerling and Reiser, Ber. 35, 702). Dextrose is among the products of hydrolysis of starch by *Bacillus suaveolens* (Sclavo and Gosio, Bied. Centr. 20, 419; Journ. Ch. Soc. 60, Abst. 1284).

Dextrose is present as a normal constituent of the blood of man and animals, and of the lymph, chyle, and urine (Miura, Zeit. Biol. 32, 279; Seegen, Ber. 21, Ref. 849; Abeles, *Ibid.* 850; Pickardt, Zeit. physiol. Ch. 17, 217; Bence Jones, Journ. Ch. Soc. 14, 22; Baisch, Zeit. physiol. Ch. 19, 338; 20, 249; Quinquaud, Comp. Rend. Soc. Biol. 41, 285: for occurrence in normal blood of hen see Saito and Katsuyama, Zeit. physiol. Ch. 32, 231). It has been found also in the aqueous humour of the eye (Pautz, Zeit. Biol. 31, 212), in aqueous extract of liver (Seegen and Kratschmer, Pflüger's Arch. 22, 206; 24, 52), in muscle (Panormoff, Zeit. physiol. Ch. 17, 596), and in the cerebrospinal fluid (Nawratzki, Du Bois-Reymond's Arch. 1897, p. 136; Ch. Centr. 1897, 1, 1237).

The source of dextrose in the animal body is probably glycogen, the latter giving dextrose on hydrolysis (Berthelot and De Luca, Comp. Rend. 49, 213; Ann. Chim. [3] 58, 448; Külz and Vogel, Zeit. Biol. 23, 100; 108).

Sugar is present in considerable quantity in the blood and urine in cases of diabetes. The sugar is ordinary dextrose (Thénard, 1806; Chevreul, Ann. Chim. [1] 95, 319; Bouchardat, Comp. Rend. 6, 337; Peligot, *Ibid.* 7, 106; Ann. Chim. [2] 67, 113; Le Goff, Comp. Rend. 127, 817; Patein and Dufau, *Ibid.* 128, 375).

Dextrose occurs in the urine in cases of diaceturia (Kobert, Ch. Centr. 1900, 2, 920), and is formed by muscular fibre and in the liver after death (Cadéac and Maignon, Comp. Rend. 134, 1443).

Synthetical Processes.

[A.] From *formic aldehyde* [91] or *glycerol* [48] through α-acrose, α-acrosazone, α-acrosone, i-fructose, i-mannitol, i-mannose, i-mannonic acid, and d-mannonic acid (see under mannitol [51; A]). The latter acid on heating with quinoline at 140–150° is converted (partially) into *d-gluconic acid* [Vol. II], which can be separated from unaltered mannonic acid by removing the latter as brucine salt. d-Gluconic acid gives dextrose = d-glucose on reduction with sodium amalgam in acid solution (Fischer, Ber. 23, 799; 2611).

[B.] From *acetone* [106] through *acroleïn* [101] and α-acrose (see under mannitol [51; G]).

[C.] From *tartaric acid* [Vol. II] through glycollic aldehyde and α-acrose [51; G].

Note :—Other generators of glycollic aldehyde, viz. *acetal* [93], *ethyl alcohol* [14], and *choline* [Vol. II], are referred to under furfural [126; F; G; H].

[D.] *Sorbitol* [52] gives dextrose on oxidation with dilute potassium permanganate solution (Vincent and Delachanal, Comp. Rend. 108, 354), with bromine and water (*Ibid.* 111, 51: see also Fischer, Ber. 23, 3686), or with hydrogen peroxide and ferrous sulphate (Fenton, Trans. Ch. Soc. 75, 10).

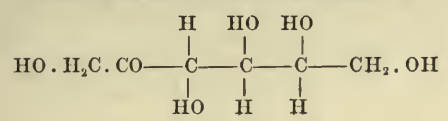
[E.] *Lævulose* [155], under the influence of dilute caustic alkali, gives (with mannose and 'glutose') dextrose (Lobry de Bruyn and Van Eckenstein, Rec. Tr. Ch. 14, 156; 203; 16, 274; 282; Ber. 28, 3078). The salts of weak organic acids at 100° and (to a less extent) those of mineral acids in aqueous solution are also capable of transforming lævulose into dextrose

when the former is in excess (*Ibid.* **14**, 162; 203; Prinsen Geerligs, Ch. Centr. 1898, **1**, 712).

[F.] *Mannose* [**156**], under the influence of dilute alkali as above, gives dextrose with lævulose and other sugars (Lobry de Bruyn and Van Eckenstein, *loc. cit.* **14**, 98; 156; 203; **16**, 257; 274; Ber. **28**, 3078).

[G.] *d-Gluconic acid* [Vol. II] lactone gives glucose on reduction with sodium amalgam in acid solution (Fischer, Ber. **22**, 2204; **23**, 804: also **A** above).

155. Lævulose; d-Fructose; Fruit Sugar; Hexanepentolone.



Natural Sources.

Occurs throughout the vegetable kingdom associated with dextrose. It accompanies dextrose also in honey (see under dextrose for references).

The sweet pods of the 'mesquit tree,' *Prosopis dulcis*, from N. and S. America contain over 5 per cent. of lævulose, but no dextrose (Steel, Rep. Aust. Assoc. 1898, p. 946). Invert sugar is contained in the mahwa-flowers from *Bassia latifolia* (see under dextrose). Manna (see under dextrose) contains 2·5–3·4 per cent. of lævulose, arising probably from the hydrolysis of manneotetrose (see below: Tanret, Bull. Soc. [3] **27**, 947).

The yeasts, moulds, and *Bacteria* capable of hydrolysing or 'inverting' saccharose may be regarded as biochemical producers of lævulose from the C_{12}-sugar (see under dextrose). Yeast allowed to infuse in chloroform water gives a l-sugar, apparently lævulose (Salkowski, Zeit. physiol. Ch. **13**, 506).

Saccharose is fermented by *Leuconostoc mesenteroides* with the formation of dextran and lævulose (Van Tieghem, Jahresber. d. Agrikulturch. **1879**, 544).

Lævulose is produced from mannitol by *Bacterium aceti* and *B. xylinum* (A. J. Brown, Trans. Ch. Soc. **49**, 182; **51**, 638). *B. aceti* of Hansen resembles *B. aceti* of Brown in its action on mannitol (Seifert, Ch. Centr. 1897, **2**, 871).

The sorbose bacterium (= *B. xylinum* according to Emmerling) produces lævulose from mannitol (Vincent and Delachanal, Comp. Rend. **125**, 716; Bertrand, *Ibid.* **126**, 763). Mannitol is not oxidised by *Bacterium pasteurianum*, and is only converted slowly into lævulose by *B. kützingianum* (Seifert, Ch. Centr. 1897, **2**, 871; Bied. Centr. **27**, 123; Journ. Ch. Soc. **74**, II, 399; Mayer, Journ. Fed. Inst. **4**, 666).

Raffinose (melitriose) is hydrolysed by high fermentation yeasts to melibiose and lævulose, while low fermentation yeasts produce dextrose, lævulose, and d-galactose. The yeasts investigated were Frohberg and Saatz, *Saccharomyces cerevisiæ*, *S. ellipsoideus*, *S. pastorianus*, *S. logos*, *S. marxianus*, *S. anomalus*, *Schizosacch. pombé*, and the kéfir ferment. *S. apiculatus* does not resolve raffinose (Bau, Ch. Centr. 1898, **2**, 682; Journ. Fed. Inst. **4**, 644).

Raffinose is inverted and finally completely assimilated by *Aspergillus niger* (Gillot, Bull. Acad. Roy. Belg. 1899, p. 211). In a solution of raffinose in presence of a mineral acid *Penicillium glaucum* also causes inversion (*Ibid.* 1900, p. 99).

Gentianose, from gentian root, gives lævulose on hydrolysis (see under dextrose for reference).

Inulin, a carbohydrate related to starch and found in many plants as a reserve material, is resolved by the enzyme known as inulase into lævulose. (According to Tanret, Bull. Soc. [3] **9**, 227, some dextrose is also formed by ordinary hydrolysis.) Inulase is found in *Aspergillus niger* (see J. R. Green's 'Fermentation,' Chap. VI; also Bourquelot, Comp. Rend. **116**, 1143), as well as in association with inulin in various tubers, bulbs, &c.

Lævomannan, a complex polysaccharide obtained from the ivory-nut (*Phytelephas macrocarpa*), gives lævulose and mannose on hydrolysis (Baker and

Pope, Proc. Ch. Soc. **16**, 72; Trans. **77**, 696).

Graminin, a reserve carbohydrate obtained from *Arrhenatherum bulbosum*, appears to be a polysaccharide of lævulose (Harlay, Comp. Rend. **132**, I, 423).

Manneotetrose ($C_{24}H_{42}O_{21}$), a sugar contained in 'manna,' is resolved by *Aspergillus*, by enzymes, and by hydrolysing agents generally into lævulose and manninotriose, $C_{18}H_{32}O_{16}$. The latter contains the dextrose and galactose complexes (Tanret, Comp. Rend. **134**, 1586; Bull. Soc. [3] **27**, 947).

A l-sugar has been found in urine, and this is probably lævulose (Külz, Zeit. Biol. **27**, 228; Cotton, Bull. Soc. [2] **33**, 546). According to Bretet (Ch. Centr. 1898, **1**, 67), this sugar occurs in diabetic urine. In certain pathological cases lævulose occurs in the urine, serum, ascitic and pleural fluids (Neuberg and Strauss, Zeit. physiol. Ch. **36**, 227).

Synthetical Processes.

[A.] *Dextrose* [154] is converted into the osazone by phenylhydrazine, the osazone reduced by zinc dust and acetic acid to isoglucosamine, and the latter decomposed by nitrous acid. Or the osazone is (more conveniently) heated with fuming hydrochloric acid and converted into the glucosone. The latter gives lævulose on reduction (see under sorbitol [52; C]; also Fischer and colleagues, Ber. **19**, 1920; **20**, 2569; **21**, 2631; **22**, 94; **23**, 370; 2121).

Dextrose gives lævulose among other sugars under the influence of caustic alkaline solutions (Lobry de Bruyn and Van Eckenstein; see under dextrose [154; E]).

Dextrose gives glucosone when oxidised by hydrogen peroxide and ferrous sulphate (Morrell and Crofts, Trans. Ch. Soc. **75**, 786; **81**, 666), and this can be reduced to lævulose as above.

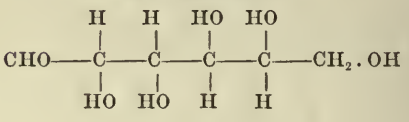
[B.] From *d-mannose* [156] through the osazone and osone, and then as above (see under sorbitol [52; C]).

Lævulose is formed with other sugars by the action of alkali on mannose (Lobry de Bruyn and Van Eckenstein, Rec. Tr. Ch. **14**, 98; 156; 203; **16**, 257; 274; Ber. **28**, 3078).

[C.] *Mannitol* [51], on oxidation by air in presence of platinum black, or by potassium permanganate or nitric acid, gives a mixture of mannose and lævulose (Gorup-Besanez, Ann. Chim. [3] **62**, 489; Iwig and Hecht, Ber. **14**, 1760; Dafert, Ber. **17**, 227; *Ibid.* Ref. 479; Fischer, Ber. **20**, 831; Fischer and Hirschberger, Ber. **21**, 1805); also by oxidation with nitroso-camphor (Cazeneuve, Comp. Rend. **109**, 185).

The oxidation of mannitol by bromine water and sodium carbonate solution also yields lævulose (Fischer, Ber. **23**, 3686).

156. d-Mannose; Seminose; Hexanepentolal.



Natural Sources.

An anhydride of mannose occurs in the leaves of *Amorphophallus konjac* = *rivieri*, and mannose itself has been extracted from the stalk (Tsukamoto, Bull. Imp. Coll. Agric. Tokio, **2**, 406; Journ. Ch. Soc. **72**, Abst. 275: see also Tsuji, *Ibid.* **70**, 44; Kinoshita, *Ibid.* 60).

Mannose occurs in ordinary cane-sugar molasses, but it appears to result from the heating of the 'invert sugar' with lime (Lobry de Bruyn, Rec. Tr. Ch. **14**, 125; **16**, 257; 274).

The sugar contained in orange-peel is possibly mannose (Flatau and Labbé, Bull. Soc. [3] **19**, 408).

The mannans or mannosides found in many plants contain the mannose complex. Among such sources are salep mucilage from the tubercles of the root of *Orchis morio* (Gans and Tollens, Ber. **21**, 2150; Ann. **249**, 245; Fischer and Hirschberger, Ber. **22**, 369; Hérissey, Comp. Rend. **134**, 721), and the reserve material contained in many nuts, seeds, and berries, of which

the following are given by Reiss (Ber. **22**, 612):—Palmaceæ (*Phytelephas macrocarpa*; *Phœnix dactylifera*; *Chamærops humilis* = *Trachycarpus excelsa*; *Lodoicea seychellarum*; *Elaïs guineensis*): Liliaceæ (*Allium cepa*; *Asparagus officinalis*): Iridaceæ (*Iris pseudacorus*): Loganiaceæ (*Strychnos nux vomica*): Rubiaceæ (*Coffea arabica*). (See also Schulze and Steiger, Ber. **20**, 290; Zeit. physiol. Ch. **14**, 227; Schulze, Ber. **22**, 1192; **23**, 2579; Zeit. physiol. Ch. **16**, 422.)

The nut of *Phytelephas macrocarpa*, used as 'vegetable ivory,' is a particularly rich source of mannan (Reiss, *loc. cit.*; Fischer, Ber. **22**, 1155; Fischer and Hirschberger, *Ibid.* 3218). The complex carbohydrate from this nut, which gives mannose (and galactose) on hydrolysis, is a 'mannogalactan' (Baker and Pope, Proc. Ch. Soc. **16**, 72; Trans. **77**, 696).

The reserve carbohydrates of the seeds of lucern (*Medicago sativa*) and of *Trigonella fœnum-græcum* are mannogalactans (Bourquelot and Hérissey, Comp. Rend. **130**, 731).

The carbohydrate of the albumins of the St. Ignatius bean (*Strychnos ignatii*) and of *S. nux vomica* is a mixture of mannan and galactan (Bourquelot and Laurent, *Ibid.* 1411; **131**, 276). The reserve carbohydrate of the seeds of *Trifolium repens* is a mannogalactan (Hérissey, *Ibid.* **130**, 1719); also that of the seeds of the American bean, *Gleditschia triacanthos* (Goret, *Ibid.* **131**, 60).

The carbohydrate obtained by Wroblewski (Ber. **31**, 1134) from the 'invertin' of yeast may be mannose (Salkowski, Zeit. physiol. Ch. **31**, 304).

The Japanese Alga, 'nori' (*Porphyra laciniata*), gives d-mannose (with i-galactose) on hydrolysis (Oshima and Tollens, Ber. **34**, 1422).

A reserve carbohydrate found in the bulb of *Lilium candidum* and *L. auratum*, and probably in *L. bulbiferum*, *L. croceum*, *L. dauricum*, *L. lancifolium*, *L. longiflorum*, and *L. martagon*, gives mannose on hydrolysis (Parkin, Proc. Cambridge Phil. Soc. **11**, 139).

The seeds of *Phœnix canariensis* contain mannans in sufficient quantity to serve as a convenient source of mannose on hydrolysis (Bourquelot and Hérissey, Comp. Rend. **133**, 644).

Reserve carbohydrates contained in the seeds of *Aucuba japonica* and *Ruscus aculeatus* are mannans (Champenois, Comp. Rend. **133**, 885; Dubat, *Ibid.* 942). The endosperm of the germinating date contains a mannan (Grüss, Ber. deutsch. bot. Gesell. **20**, 36; Woch. Brau. **19**, 243; Ch. Centr. 1902, **1**, 1227). Asparagus seeds contain a mannan (Peters, Arch. Pharm. **240**, 53); so also do the seeds of *Œnanthe phellandrium* (Champenois, Journ. Pharm. **15**, 228).

The reserve carbohydrates of the seeds of the Palmaceous plants, *Areca catechu*, *Astrocaryum vulgare*, *Œnocarpus bacaba*, *Erythea edulis*, and *Metroxylon sagu*, contain mannans (Liénard, Comp. Rend. **135**, 593). The presence of mannan in the seeds of *Trachycarpus excelsa* and of *Rohdea japonica*, and in the wood of *Cryptomeria*, has been shown by Kimoto (Bull. Imp. Coll. Agric. Tokio, **5**, 253: see also Reiss as quoted above).

Mannans have been found in coffee berries and coco and palm nuts (Schulze, Ber. **23**, 2582; **24**, 2277, &c.); in carob seeds from *Ceratonia siliqua* (Effront, Comp. Rend. **125**, 38; 116; 309; Van Eckenstein, *Ibid.* 719; Bourquelot and Hérissey, *Ibid.* **129**, 228; 339; 391; 614); (probably) in gum ammoniacum (Frischmuth, Ch. Centr. 1898, **1**, 36), and in stalks of rye (Ritthausen, *Ibid.*).

The carbohydrate 'strophanthobiose methyl ether' resulting from the hydrolysis of strophanthin contains the mannose complex (Feist, Ber. **33**, 2095: see also under dextrose [**154**]).

Mannose-yielding compounds are contained in the seeds of *Diospyros kaki* and in the root of *Amorphophallus konjac* = *rivieri* (Loew and Ishii; Loew and Tsuji, as quoted by Tollens, 'Kohlenhydrate,' II, 229); in ergot of rye (Voswinkel, Ch. Centr. 1891, **2**, 766); in various woods (Weld, Lindsey, and Tollens, Ber. **23**, 2990; Ann. **267**, 341); in ligneous tissue of gymnosperms (Bertrand, Bull. Soc. [3] **7**, 468; Comp. Rend. **114**, 1492; **129**, 1025); in cryptogams

(Winterstein, Zeit. physiol. Ch. **21**, 152); and in gum extracted from yeast by lime or alkali (Hessenland, Zeit. d. Ver. f. Rübenzuckerindustrie, 1892, p. 671; Salkowski, Ber. **27**, 497; Zeit. physiol. Ch. **13**, 506).

The woody tissue of cycads and conifers and (to a small extent) that of *Ephedra distachya* contains mannose-yielding compounds (Bertrand, Comp. Rend. **129**, 1025).

Note :—For general distribution of mannan in the wood of the sugar maple and throughout the vegetable kingdom see Storer in the Bulletin of Bussey Institution, III, No. 2, 1902.

Synthetical Processes.

[A.] From *formic aldehyde* [91] through *a*-acrose, &c., as under mannitol [51; A]. d-Mannonic acid gives d-mannose on reduction with sodium amalgam in acid solution (*loc. cit.*; also Fischer, Ber. **22**, 2204).

[B.] From *glycerol* [48] through *a*-acrose, &c., as under mannitol [51; B].

[C.] From *mannitol* [51] with lævulose by oxidation (see under lævulose [155; C]). Also by oxidation with hydrogen peroxide and ferrous sulphate (Fenton and Jackson, Trans. Ch. Soc. **75**, 8).

[D.] From *tartaric acid* [Vol. II] through glycollic aldehyde and *a*-acrose (see under mannitol [51; G]).

[E.] *Dextrose* [154] gives mannose (with lævulose, glutose, and *ϕ*-fructose) under the influence of alkali or lead hydroxide (Lobry de Bruyn and Van Eckenstein, Rec. Tr. Ch. **16**, 257; 274).

[F.] *Lævulose* [155] gives mannose with other sugars under the same conditions as above (*Ibid.* **14**, 156; 203; **16**, 274; 282; Ber. **28**, 3078).

157. Salicin; Saligenin Glucoside.

$$HO.CH_2.C_6H_4.O(C_6H_{11}O_5)$$

Natural Sources.

In bark and leaves of *Salix helix*, *S.* '*præcox*,' *S. pentandra*, and other species. Occurs also in bark and leaves of *Populus tremula*, *P. tremuloides*, &c. (Tischhauser, Ann. **7**, 280), and in flower buds of *Spiræa ulmaria* (Buchner, Ann. **88**, 224).

Occurs also in castoreum (Wöhler, Ann. **67**, 360).

Note :—For full references and list of species see under saligenin [55].

Synthetical Process.

[A.] From *salicylic aldehyde* [117] and *dextrose* [154]. The latter is converted into acetchlorglucose [$C_6H_7OCl(C_2H_3O_2)_4$] (Colley, Comp. Rend. **70**, 401; Ann. Chim. [4] **21**, 363: see also Königs, Ber. **21**, 2207; Fischer and E. F. Armstrong, Sitz. Pr. Akad. 1901, **13**, 316; F. v. Arlt, Monats. **22**, 144; Skraup and Kremann, *Ibid.* 375; F. and E. F. A., Ber. **34**, 2885). Salicylic aldehyde and acetchlorglucose in presence of potassium ethoxide give the glucoside helicin (Michael, Am. Ch. Journ. **1**, 309; Comp. Rend. **89**, 355; Ber. **12**, 2260; **14**, 2100; **15**, 1922: see also Schiff, Ber. **14**, 2559).

Helicin on reduction with sodium amalgam or zinc and sulphuric acid gives salicin (Lisenko, Zeit. [1] **1864**, 577; Michael, Am. Ch. Journ. **5**, 172).

158. Populin; Benzoylsalicin.

$$(C_7H_5O_2)CH_2.C_6H_4.O(C_6H_{11}O_5)$$

Natural Sources.

In bark, leaves, and buds of *Populus tremula*, *P. nigra*, *P. pyramidalis*, and *P. balsamifera* (Braconnot, Ann. Chim. [2] **44**, 296; Berz. Jahresber. **11**, 286; Biot and Pasteur, Comp. Rend. **34**, 606; Piria, Ann. Chim. [3] **34**, 278; **44**, 366; Ann. **81**, 245; **96**, 375; Piccard, Ber. **6**, 890; Hallwachs, Ann. **101**, 372; v. Lippmann, Ber. **12**, 1648; Herberger, Arch. Pharm. **46**, 104; **47**, 250).

Synthetical Process.

[A.] From *salicin* [157] and *benzoic acid* [Vol. II] by heating the glucoside with benzoic anhydride (Schiff, Ann. **154**, 5).

159. Methylarbutin; Glucoside of p-Methoxyphenol.

$CH_3O.C_6H_4.O(C_6H_{11}O_5)+H_2O$

Natural Sources.

Occurs with arbutin in the leaves of the red bearberry, *Arctostaphylos uva-ursi*, and in all the plants which contain arbutin (Hlasiwetz and Habermann, Ann. **177**, 334; Schiff, Ann. **206**, 159: see also under quinol [**71**]).

Synthetical Process.

[**A.**] From *quinol methyl ether* [**73**] and *dextrose* [**154**] by the interaction of acetchlorglucose (see above under salicin [**157**; **A**]) and potassium-quinol methyl ether (Michael, Am. Ch. Journ. **5**, 178; Ber. **14**, 2097).

SULPHUR COMPOUNDS.

160. Carbon disulphide.

CS_2

Natural Sources.

Schizophyllum lobatum, a fungus found in Java on fallen branches of *Pedocarpus* and on dead bamboo, when cultivated in sugar-peptone infusion gives carbon disulphide or some compound from which the CS_2-complex is easily split off (Went, Ber. deut. bot. Gesell. 1896, p. 939; Ch. Centr. 1896, **2**, 939).

Carbon disulphide occurs in mustard oil, resulting possibly from the decomposition of sinigrin or of the allyl isothiocyanate (Gadamer, Arch. Pharm. **235**, 53).

Synthetical Processes.

[**A.**] By heating carbon in sulphur vapour (Lampadius, 1796; Clement and Desormes, Ann. Chim. **42**, 121; Vauquelin and Robiquet, *Ibid.* **61**, 145; Berthollet, Thénard, and Vauquelin, *Ibid.* **72**, 252; Berzelius and Marcet, Schweigger's Journ. **9**, 284; Gilbert's Ann. **28**, 427; 453; **48**, 177; Ann. Chim. **83**, 252; Pogg. Ann. **6**, 144; Zeise, Schweigger's Journ. **26**, 1; **41**, 98; 170; **43**, 160; Couerbe, Ann. Chim. [2] **61**, 225; Kolbe, Ann. **45**, 53; **49**, 143; Pelouze and Fremy, 'Traité d. Chim.' 4me éd. I, 923; Sidot, Bull. Soc. [2] **13**, 323; Comp. Rend. **69**, 1303; Journ. Pharm. [4] **13**, 239: for manufacture in the electric furnace see Taylor, Trans. Amer. Electroch. Soc. **1**, 115; Journ. Soc. Ch. Ind. **21**, 1236; also Eng. Pat. 16556 of 1902).

[**B.**] From *methane* [**1**] through carbon tetrachloride by extreme chlorination (Dumas, Ann. **33**, 187). The latter gives carbon disulphide on heating with phosphorus pentasulphide at 200° (Rathke, Ann. **152**, 200).

[**C.**] From *ethyl alcohol* [**14**] through chloroform by distillation with bleaching powder (see under methane [**1**; **D**]). By chlorination chloroform gives carbon tetrachloride (Regnault, Ann. **33**, 332; Friedel and Silva, Bull. Soc. [2] **17**, 537), which can be treated as above under **B**.

[**D.**] From *acetone* [**106**] through chloroform (Liebig, Ann. **1**, 199), and then as above.

[**E.**] From *acetic aldehyde* [**92**] through chloral by chlorination (Pinner, Ber. **4**, 256; Wurtz and Vogt, Zeit. [2] **7**, 679). Chloral is decomposed by alkali with the formation of chloroform (Liebig, *loc. cit.*).

[**F.**] From *acetic acid* [Vol. II] through the trichloro-acid by chlorination (Dumas, Ann. **32**, 101). Trichloracetic acid gives chloroform on heating with aqueous alkali (*Ibid.* 113; Ann. Chim. [2] **56**, 115).

[**G.**] From *methyl alcohol* [**13**] through methyl chloride (Dumas and Peligot, Ann. **15**, 17; Ann. Chim. **61**, 193; Groves, Journ. Ch. Soc. **27**, 641). The latter can be chlorinated to carbon tetrachloride (Damoiseau, Comp. Rend. **92**, 42), and treated as under **B**.

[H.] From *trimethylamine* [Vol. II] through methyl chloride by heating the hydrochloride to 326° (Vincent, Journ. Pharm. [4] **30**, 132; Jahresber. **1878**, 1135), and then as above under **G**.

[I.] From *formic acid* [Vol. II] and *methyl alcohol* [13] through methyl formate (Volhard, Ann. **176**, 133). The latter on extreme chlorination gives perchlormethyl formate (Hentschel, Journ. pr. Ch. [2] **36**, 100; 214; 305), and this decomposes in contact with aluminium chloride with the formation of carbon tetrachloride (*Ibid.* 308).

[J.] *Allyl isothiocyanate* [166] gives carbon disulphide among the products obtained by heating with water at 100-105° (Gadamer, Arch. Pharm. **235**, 53).

[K.] From *gallic acid* [Vol. II] through trichlor-*aa*-glyceric acid by the action of hydrochloric acid and potassium chlorate (Schreder, Ann. **177**, 282). The trichloro-acid gives chloroform by the action of alkali in the cold.

[L.] From *salicylic acid* [Vol. II] through trichlor-*aa*-glyceric acid as above.

[M.] From *phenol* [60] through trichlor-*aa*-glyceric acid as above.

[N.] *Benzene* [6; I, &c.] by the action of potassium chlorate and sulphuric acid gives trichlorphenomalic acid, $CCl_3 . CO . CH : CH . CO_2H$ (Carius, Ann. **142**, 129; Kekulé and Strecker, Ann. **223**, 170; Anschütz, Ann. **254**, 152), and this yields chloroform (with maleïc acid) on heating with barium hydroxide solution. Subsequent steps as under **B**.

161. Methyl Mercaptan; Methanethiol; Methyl Sulphydrate.

$CH_3 . SH$

Natural Sources.

Among the products of anaerobic putrefaction of albumin (Nencki and Sieber, Monats. **10**, 526). The *Bacilli* known to produce this compound from serum albumin are *Bacillus magnus*, *B. spinosus*, *B. liquefaciens*, and the anthrax *Clostridium*.

Occurs among the products of putrefaction of fish (Mörner, Zeit. physiol. Ch. **22**, 514) and of elastin by anaerobic micro-organisms (Zoja, *Ibid.* **23**, 236). Also among the products of intestinal decomposition of albumin (Hammarsten, 'Lehrbuch,' 3rd ed. 277) and, possibly, in urine after taking asparagus (*Ibid.* 480; Nencki, Arch. exp. Path. **17**).

A bacterium found in the urine of a patient suffering from pneumonia and albuminaria caused production of methyl mercaptan (Karplus, Virch. Arch. **131**, 210; Journ. Ch. Soc. **64**, II, 335).

Bacillus esterificans isolated from putrefying litmus solution and *Bac. præpollens* from the intestinal contents decompose peptone infusions with the production of mercaptan (? methyl) among other products (Maassen, Ch. Centr. 1899, **2**, 1058).

A mercaptan (? methyl) is among the products of the anaerobic putrefaction of milk by *Bacillus putrificus* and by the *Bacilli* of malignant œdema and of symptomatic anthrax (Bienstock, Ch. Centr. 1901, **1**, 1209).

Synthetical Processes.

[A.] From *methyl alcohol* [13]. Sodium methyl sulphate is distilled with potassium hydrosulphide (Gregory, Ann. **15**, 239; Obermeyer, Ber. **20**, 2918; Klason, *Ibid.* 3407).

[B.] From *thiocyanic acid* [174] and *methyl alcohol* [13]. Potassium thiocyanate on distillation with calcium methyl sulphate gives methyl thiocyanate (Cahours, Ann. Chim. [3] **18**, 261; Ann. **61**, 95). The latter on heating to 180° yields (with the isothiocyanate) methyl thiocyanurate (Hofmann, Ber. **13**, 1349), and this on heating with ammonia gives (with melamine) methyl mercaptan (Hofmann, Ber. **18**, 2758; Obermeyer, Ber. **20**, 2919).

[C.] *Methyl sulphide* [163] gives methyl thiocyanate on heating with cyanogen bromide (Cahours, Jahresber. **1875**, 257). The latter is obtained by the action of bromine on *hydrogen cyanide* [172] or its salts (Serullas, Berz. Jahresber. **8**, 94; Ann. Chim.

[2] **34**, 100; **35**, 294; 315; Langlois, Ann. Suppl. **1**, 384; Ann. Chim. [3] **61**, 482; Scholl, Beilstein's 'Handbuch,' I, 1434).

[D.] From *benzene* [6; I, &c.] and *carbon disulphide* [160] through aniline and phenyl mustard oil by the usual methods (Hofmann, Jahresber. **1858**, 349; Ber. **2**, 453; **15**, 986; Weith and Merz, Zeit. [2] **5**, 589; Rathke, Ber. **3**, 861; Rudneff, Journ. Russ. Soc. **10**, 184; Werner, Trans. Ch. Soc. **59**, 400). The mustard oil is reduced by aluminium amalgam to diphenylthiourea and (through thioformaldehyde) methyl mercaptan (Gutbier, Ber. **34**, 2033).

162. Normal Butyl Mercaptan; n-Butanethiol.

$CH_3 . CH_2 . CH_2 . CH_2 . SH$

Natural Source.

Occurs in the secretion of the Philippine badger, *Mydaus marchei* (Beckmann, Pharm. Centr. 1896 [n. f.], **17**, 557).

Note:—The secretion contains also n-butyl sulphide, probably a product of oxidation of the mercaptan (*Ibid.* 558).

Synthetical Process.

[A.] From *n-butyl alcohol* [17] and potassium hydrosulphide as above under methyl mercaptan [161; A] (Saytzeff and Grabowsky, Ann. **171**, 251; **175**, 348). Or by the interaction of the n-butyl haloid and potassium hydrosulphide, or by distillation of the alcohol with phosphorus pentasulphide (general method; see Kekulé, Ann. **90**, 311).

163. Methyl Sulphide.

$(CH_3)_2S$

Natural Source.

In American oil of peppermint (Schimmel's Ber. Oct. 1896; Kleber, Pharm. Rev. **14**, 269; Gerber, Mon. Sci. [4] **11**, 880).

Synthetical Processes.

[A.] From *methane* [1] through methyl chloride by chlorination (Berthelot, Ann. Chim. [3] **52**, 97), and interaction of the latter with potassium sulphide (Regnault, Ann. Chim. [2] **71**, 391; Ann. **34**, 26).

[B.] From *methyl alcohol* [13] through methyl chloride (Dumas and Peligot, Ann. Chim. **61**, 193; Groves, Journ. Ch. Soc. **27**, 641), and then as above. Or by heating sodium methyl sulphate with potassium sulphide (Klason, Ber. **20**, 3407).

[C.] From *trimethylamine* [Vol. II] through methyl chloride by heating the hydrochloride of the base to 326° (Vincent, Journ. Pharm. [4] **30**, 132; Jahresber. **1878**, 1135).

164. Ethyl Sulphide.

$(C_2H_5)_2S$

Natural Source.

Occurs in urine of dogs (Abel, Zeit. physiol. Ch. **20**, 253).

Synthetical Process.

[A.] From *ethyl alcohol* [14] through ethyl chloride or ethyl potassium sulphate, and the interaction of these with potassium sulphide (Regnault, Ann. Chim. [2] **71**, 387; Loir, Comp. Rend. **26**, 195; Riche, Ann. Chim. [3] **43**, 297: see also Döbereiner, Ann. **4**, 172, and Finckh, Ber. **27**, 1239).

Notes:—*Vinyl sulphide*, $(CH_2 : CH)_2S$, the chief constituent of the oil of *Allium ursinum* (Semmler, Ann. **241**, 92), does not appear to have been synthesised, but could no doubt be prepared from vinyl bromide and potassium sulphide by the general method.

Allyl sulphide, $(CH_2 : CH . CH_2)_2S$, which is generally stated to be a constituent of oil of garlic, &c. (Wertheim, Ann. **51**, 289; **55**, 297; Pless, Ann. **58**, 36), according to Semmler (Arch. Pharm. **230**, 434) does not exist in this oil, and is therefore most probably absent from the other plant oils in which it is supposed to have been found.

165. Secondary Butyl Isothiocyanate or Thiocarbimide; Oil of Spoonwort.

$CH_3 . CH_2 . CH(CH_3) . NCS$

Natural Source.

In oil of spoonwort or scurvy-grass, *Cochlearia officinalis* (Hofmann, Ber. **2**, 102; **7**, 508; Gadamer, Arch. Pharm. **237**, 92). According to Gadamar (*loc. cit.*) it probably exists as glucoside in the plant.

Synthetical Processes.

[A.] From *n-butyl alcohol* [17] and *carbon disulphide* [160]. The alcohol is converted into n-butylene through n-butyl iodide (Linnemann, Ann. **161**, 196) and the action of alcoholic potash on the latter (Lieben and Rossi, Ann. **158**, 164; Saytzeff, Journ. pr. Ch. [2] **3**, 88; Grabowsky and Saytzeff, Ann. **179**, 330). n-Butylene combines with hydrogen iodide to form 2-iodobutane = secondary butyl iodide (Wurtz, Ann. **152**, 23; Saytzeff, Ber. **3**, 870). The latter, by the action of ammonia, gives the amine = 2-aminobutane (Hofmann, Ber. **7**, 513), and this on combination with carbon disulphide in alcoholic or ethereal solution, precipitation of the product [di-(sec.)-butyldithiocarbamate] with mercuric chloride, and decomposition of the mercury compound by boiling with water yields the isothiocyanate (Hofmann, Ber. **7**, 512).

[B.] *Isobutyl alcohol* [18] by the action of hot zinc chloride gives a mixture of two butylenes, of which one is pseudobutylene = symmetrical dimethylethylene (Nevolé, Bull. Soc. [2] **24**, 122; Le Bel and Greene, Am. Ch. Journ. **2**, 23; Bull. Soc. [2] **29**, 306; Faworsky and Desbout, Journ. pr. Ch. [2] **42**, 152; J. Wislicenus and Schmidt, Ann. **313**, 210: see also Nef, Ann. **318**, 28). The latter combines with hydrogen iodide to form secondary butyl iodide, which can be converted into the amine and treated with *carbon disulphide* [160], &c., as above under **A**.

Isobutyl alcohol also gives pseudobutylene (with isobutylene) by the action of sulphuric acid (Konowaloff, Bull. Soc. [2] **34**, 333; Puchot, Ann. Chim. [5] **28**, 508), or by pyrogenic contact decomposition by plumbago crucible material (Ipatieff, Ber. **35**, 1061).

Isobutyl chloride gives all three butylenes on pyrogenic decomposition by passing over heated lime (Nef, Ann. **318**, 22).

Note:—For conversion of pseudobutylene into methylethyl ketone see under methylacetyl carbinol [44; D]. The ketone is convertible into secondary butyl alcohol and amine as below under **K**.

[C.] From *methyl alcohol* [13], *glycerol* [48], and *carbon disulphide* [160]. Methyl alcohol is converted into methyl iodide, and glycerol into allyl iodide (see under isobutyl alcohol [18; D]). A mixture of the two iodides on treatment with sodium gives (by isomeric transformation?) pseudobutylene (Wurtz, Bull. Soc. [2] **8**, 265; Ann. **144**, 235; Grosheintz, Bull. Soc. [2] **29**, 201), which can be converted into 2-iodobutane, &c., as above.

[D.] From *acetic aldehyde* [92] and *carbon disulphide* [160]. Aldehyde is convertible by the action of sulphuretted hydrogen into a solid trithioaldehyde, $C_6H_{12}S_3$ (Weidenbusch, Ann. **66**, 158; Pinner, Ber. **4**, 258; Klinger, Ber. **9**, 1893; **11**, 1024; Böttinger, Ber. **11**, 2205; Friedel and Crafts, Ann. **124**, 114; Baumann and Fromm, Ber. **22**, 2602; **24**, 1464; Fromm, Ber. **32**, 2650), and this gives pseudobutylene on heating with copper (Eltekoff, Ber. **10**, 1904).

Or from aldehyde, *ethyl alcohol* [14], and carbon disulphide. Zinc ethyl and aldehyde combine to form a compound, which is decomposed by water with the formation of 2-butanol (Wagner, Ann. **181**, 261). Subsequent steps as below under **G**.

Or aldehyde combines with hydrogen chloride to form ethylidene oxychloride = 1 : 1¹-dichlorether (Lieben, Comp. Rend. **46**, 662; Ann. **106**, 336; Kessel, Ann. **175**, 44; Geuther, Ann. **218**, 16), which by the action of zinc ethyl gives secondary butyl ether. The latter on

heating with hydriodic acid at 130° yields 2-iodobutane (Kessel, *loc. cit.*).

[E.] From *angelic* or *tiglic acid* [Vol. II] and *carbon disulphide* [160] through brom-methylethylacetic acid = 3-brombutane-2-carboxylic acid by combination of either of the isomeric acids with hydrogen bromide (Pagenstecher, Ann. **195**, 109). Pseudobutylene is among the products of decomposition of the bromo-acid by alkali (*Ibid.* 113).

Or the acids can be combined with hydrogen iodide (Schmidt, Ann. **208**, 254; J. Wislicenus, Talbot, and Henze, Ann. **313**, 207); the products give the stereo-isomeric pseudobutylenes on treatment with alkali (W. T. and H. *loc. cit.*: see also Ch. Centr. 1897, **2**, 261).

[F.] From *ethyl alcohol* [14] and *carbon disulphide* [160]. The alcohol is converted into ether, and the latter into 1 : 2-dichlorether (Malaguti, Ann. **32**, 15; Ann. Chim. [2] **70**, 338; [3] **16**, 5; 19; Lieben, Ann. **111**, 121; **123**, 130; **133**, 287; **141**, 236; **146**, 180; **150**, 87). By the interaction of dichlorether and *zinc ethyl* ethylchlorether = 2-ethyl-1-chlorbutyl ether is obtained, and this on heating with hydriodic acid at 140° gives 2-iodobutane (Lieben, Ann. **150**, 96). Subsequent steps as above under **A**.

Or from ethyl alcohol through *ethylene glycol* [45]. The latter can be converted into the iodhydrin = iodethyl alcohol (Simpson, Proc. Roy. Soc. **10**, 119; Butleroff and Ossokin, Ann. **144**, 42; **145**, 257), which by the action of zinc ethyl gives 2-butanol (B. and O. Ann. **145**, 263). Subsequent steps as below under **G**.

Note:—Generators of ethylene thus become, with carbon disulphide, generators of secondary butyl isothiocyanate.

[G.] From *methyl* and *ethyl alcohols* [13; 14], *formic acid* [Vol. II], and *carbon disulphide* [160]. A mixture of methyl and ethyl iodides with formic ethyl ester is treated with zinc, and the product decomposed by water so as to give 2-butanol = secondary butyl alcohol (Saytzeff, Ann. **175**, 374). The alcohol can be converted into the corresponding iodide (= 2-iodobutane) by the usual methods, and the latter into the amine and isothiocyanate as before.

[H.] From *erythritol* [50] and *carbon disulphide* [160]. Erythritol on heating with hydriodic acid gives 2-iodobutane (De Luynes, Bull. Soc. [2] **2**, 3; Ann. **125**, 252). Subsequent steps as above under **A**.

[I.] *Thiocyanic acid* [174] can be converted into secondary butyl thiocyanate by interaction of the potassium salt and *secondary butyl iodide* (see above under **G**). The alkyl thiocyanate is probably convertible into the isothiocyanate by the action of heat (general method: see Hofmann, Ber. **13**, 1350).

[J.] *Isovaleric acid* [Vol. II] gives a small quantity of pseudobutylene among the products of the dry distillation of the calcium salt (Dilthey, Ber. **34**, 2119). Subsequent steps as above under **B**, &c.

[K.] From *acetoacetic acid* (*ester*) [Vol. II] and *methyl alcohol* [13] through methylethyl ketone (see under methylacetyl carbinol [44; **B**]). The ketone gives secondary butyl alcohol on reduction (Norris and Green, Am. Ch. Journ. **26**, 293: for electrolytic reduction see Elbs and Brand, Zeit. Elektroch. **8**, 783). The alcohol with *carbon disulphide* gives the mustard oil as above under **G**.

Note:—The generators of methylethyl ketone referred to under methylacetyl carbinol [44, p. 95] thus become, with carbon disulphide, generators of secondary butyl mustard oil:—*acetic* and *propionic acids*; *acetic* and *butyric acids*; *zinc methyl* and *propionyl chloride*; *zinc ethyl* and *acetyl chloride*; *ethyl iodide* and *acetic anhydride*, &c.

[L.] From *isoamyl alcohol* [22] and *carbon disulphide* [160]. The alcohol gives pseudobutylene among the products of pyrogenic contact decomposition by passing the vapour through a hot iron tube (Wurtz, Ann. **104**, 249; Butleroff, Ann. **145**, 277; Ipatieff, Ber. **35**, 1053). From pseudobutylene as above under **B**.

[M.] From *n-propyl alcohol* [15] through n-hexane (see under n-hexyl alcohol [23; **A**]) and *carbon disulphide*. Hexane gives, among other products, n- and pseudobutylenes when mixed with air and passed over heated platinum (v. Stepski, Monats. **23**, 773).

[N.] From *mannitol* [51] through hexane (see under n-hexyl alcohol [23; B]) and *carbon disulphide*, and then as above.

Note :—All generators of n-hexane referred to under n-hexyl alcohol [23] thus become, with carbon disulphide, generators of this mustard oil. n-Hexyl alcohol itself is a generator of hexane through n-hexyl iodide and reduction of the latter.

166. Allyl Isothiocyanate or Thiocarbimide; Mustard Oil.

$CH_2 : CH . CH_2 . NCS$

Natural Sources.

Occurs as glucoside, potassium myronate or sinigrin, in black mustard from the seeds of *Sinapis nigra* and *S. juncea*. (For references see Gildemeister and Hoffmann's 'Die aetherischen Oele,' p. 533; Gadamer, Arch. Pharm. **235**, 44; Ber. **30**, 2322.)

A glucoside (probably sinigrin) is contained in horse-radish root, *Cochlearia armoracia* (Hubatka, Ann. **47**, 153; Sani, Schimmel's Ber. April 1894; Gadamer, Arch. Pharm. **235**, 577).

The root of garlic-mustard (*Sisymbrium alliaria*) gives an oil on distillation which apparently contains allyl mustard oil (Wertheim, Ann. **52**, 52; Pless, Ann. **58**, 38).

The plant and seeds of penny-cress, *Thlaspi arvense*, give an oil which, according to Pless (*loc. cit.* 36), contains allyl mustard oil. The recent work of Semmler (Arch. Pharm. **230**, 434) throws doubt on the existence of allyl mustard oil in these two last plants. According to Ritthausen (Journ. pr. Ch. [2] **24**, 273) sinigrin (potassium myronate) occurs in the seeds of turnip, *Brassica rapa*.

According to Bokorny (Ch. Zeit. **24**, 771; 817; 832) *Iberis amara*, *I. umbellata*, and *I. sempervirens*, scurvy-grass (*Cochlearia officinalis*), winter cabbage (*Brassica oleracea*), and radish (*Raphanus sativus*), contain some glucoside which yields mustard oil (? allyl) under the influence of myrosin. (For occurrence of mustard oil in seeds of Cruciferæ see also Jörgensen, Ch. Centr. 1898, **2**, 927; 1899, **2**, 781).

Note :—Many mustard oils which were at one time thought to contain allyl have by later investigation been proved to be isothiocyanates of other radicles.

Synthetical Process.

[A.] From *glycerol* [48] through allyl iodide (see under isobutyl alcohol [18; D]) and *thiocyanic acid* [174], by the distillation of potassium or silver thiocyanate with allyl iodide (Zinin, Ann. **95**, 128; Berthelot and De Luca, Ann. Chim. [3] **44**, 495; Comp. Rend. **41**, 21). The normal ester produced at first is transformed into the mustard oil by the action of the heat (Oeser, Ann. **134**, 7; Billeter, Ber. **8**, 464; Gerlich, Ann. **178**, 89).

Note :—Sinigrin when hydrolysed at 0° by myrosin (the mustard seed enzyme) gives, with allyl mustard oil, a trace of allyl thiocyanate (E. Schmidt, Ber. 10, 187). The latter can be synthesised from ammonium thiocyanate and allyl bromide in alcoholic solution at 0° (Gerlich, *loc. cit.* 85), or from allyl iodide and potassium hydrosulphide through allyl mercaptan, the lead compound of the latter giving allyl thiocyanate on treatment with cyanogen chloride in ethereal solution (Billeter, *loc. cit.*).

167. Crotonyl Isothiocyanate or Thiocarbimide; Crotonyl Mustard Oil.

$C_4H_7 . NCS =$
$CH_2 : CH . CH_2 . CH_2 . N : C : S$ (?)

Natural Sources.

This mustard oil is apparently contained in the oil-cake from rape seed (Jörgensen, Ch. Centr. 1899, **2**, 781; Landw. Versuchs-Sta. **52**, 269, &c.); also in the seeds of *Brassica glauca*, *B. dichotoma*, &c. (*Ibid.* Ch. Centr. 1898, **2**, 928), and *B. napus* (Sjollema, Rec. Tr. Ch. **20**, 237).

Synthetical Processes.

[A.] From *isobutyl alcohol* [18] through isobutylene bromide (see under isobutyl alcohol [18; A] and tertiary butyl alcohol [19; B]), and *carbon*

disulphide [160]. On heating the isobutylene bromide with alcoholic ammonia at 100°, a product containing a crotonylamine is formed (Hofmann, Ber. 7, 515; 12, 992). The latter is heated with carbon disulphide in alcoholic solution, and the product (the crotonylamine salt of crotonyldithiocarbamic acid) treated with an aqueous solution of mercuric chloride, silver nitrate, or ferric chloride, and then boiled (*Ibid.* Ber. 7, 516; 8, 108; Ann. Chim. Physiol. [7] 17, 262: see also for general method Rudneff, Ber. 12, 1023; Hecht, Ber. 23, 282; Ponzio, Gazz. 26, 323).

[B.] From *crotonic aldehyde* [102] through crotonyl alcohol by reduction (Lieben and Zeisel, Monats. 1, 825; Charon, Ann. Chim. [7] 17, 223; Comp. Rend. 128, 737). The alcohol combines with hydrogen bromide to form α-brom-β-butylene = crotonyl bromide, and this by interaction with potassium or *ammonium thiocyanate* [174] gives crotonyl isothiocyanate (*Ibid.*).

Note:—The generators of isobutylene referred to under isobutyl alcohol [18; B; C, &c.] thus become, with carbon disulphide, generators of crotonyl mustard oil. These are *isovaleric acid* [Vol. II]; *glycerol* and *acetone* [48; 106]; *acetic acid* and *acetone*; *amyl alcohol* of fusel oil [22]. *Tertiary butyl alcohol* [19] is also a generator of isobutylene (see under isobutyl alcohol [18; A]).

The identity of the synthetical mustard oil with the natural product requires confirmation. According to Sjollema (*loc. cit.*) the crotonyl mustard oil from *Brassica napus* is not identical with either Hofmann's or Charon's compounds.

168. Angelyl Isothiocyanate or Thiocarbimide; Angelyl Mustard Oil.

$C_5H_9 . NCS$

Natural Source.

Said to have been obtained from rape seed oil-cake (Jörgensen as above under 167).

Synthetical Processes.

[A.] From *amyl alcohol* of fusel oil [22] through 'isoamylene' (see under acetone [106; E]) and *carbon disulphide* [160]. The amylene is converted into angelylamine by heating the bromide with alcoholic ammonia, and the amine into the mustard oil by the general method as described above under 167; A (Hofmann, Ber. 8, 106; 12, 991).

Note:—The identity of the natural with the synthetical product has not been established.

169. Benzyl Isothiocyanate or Thiocarbimide; Benzyl Mustard Oil.

$C_6H_5 . CH_2 . NCS$

Natural Sources.

Occurs in the ethereal oil of the Capuchin cress, *Tropæolum majus*, and of the garden cress, *Lepidium sativum*; also as the glucoside, glucotropæolin, in seeds of the same plants (Gadamer, Arch. Pharm. 237, 111; 507; Ber. 32, 2335; Beyerinck, Centr. Bakter. II, 6, 72).

Synthetical Processes.

[A.] From *benzoic acid* [Vol. II] and *carbon disulphide* [160]. Ammonium benzoate is converted into benzonitrile (Fehling, Ann. 49, 91; Laurent and Gerhardt, Jahresber. 1849, 327; Wöhler, Ann. 192, 362; Anschütz and Schultz, Ann. 196, 48; Buckton and Hofmann, Ann. 100, 155; Gerhardt, 'Traité, &c.,' IV, 762; Henke, Ann. 106, 276; Henry, Ber. 2, 307: see also under benzoic aldehyde [114; C]), and the latter reduced to benzylamine (Mendius, Ann. 121, 144; Spica, Gazz. 10, 515; Bamberger and Lodter, Ber. 20, 1709). Or benzonitrile and *ethyl alcohol* [14] and hydrogen chloride condense to the hydrochloride of benzimidoethyl ether (Pinner, Ber. 16, 353: general synthesis), and this by interaction with ammonia gives an amidine which, on reduction by sodium amalgam in acid solution, yields benzylamine (Henle, Ber. 35, 3044).

Benzylamine and carbon disulphide

give the mustard oil by the general method (Hofmann, Ber. **1**, 201).

Benzamide, from ammonium benzoate or from benzoyl chloride and ammonia, gives benzylamine among the products of its electrolytic reduction in sulphuric acid (Baillie and Tafel, Ber. **32**, 71).

Ethyl benzoate yields benzonitrile by interaction with sodamide (Titherley, Trans. Ch. Soc. **81**, 1527).

Benzoic acid also gives benzonitrile through benzoyl chloride, and the interaction of the latter with benzamide (Sokoloff, Gerhardt's 'Traité, &c.,' I, 383), or with *potassium thiocyanate* [174] or cyanate (Limpricht, Ann. **99**, 117; Schiff, Ann. **101**, 93). Also by the interaction of cyanogen bromide and potassium benzoate (Cahours, Ann. **108**, 319; Ann. Chim. [3] **52**, 200), of benzoic acid and potassium thiocyanate (Letts, Ber. **5**, 673) or lead thiocyanate (Krüss, Ber. **17**, 1767).

Also from benzoic and *acetic acids via* acetophenone and mandelic acid (see under benzoic aldehyde [114; G]), and then through phenylbrom- and phenylamino-acetic acid and benzylamine, &c., as below under **B**.

Benzoyl chloride and *methylamine* [Vol. II] give methylbenzamide (Van Romburgh, Rec. Tr. Ch. **4**, 388), which, by the action of phosphorus pentachloride, yields an imidochloride (v. Pechmann, Ber. **28**, 2367). Benzenylmethylimidochloride on heating decomposes into methyl chloride and benzonitrile (*Ibid.* **33**, 611). The latter can be reduced to benzylamine as above.

[**B.**] From *benzoic aldehyde* [114] and *carbon disulphide* [160]. Benzaldoxime by the action of acetic anhydride gives benzonitrile (Lach, Ber. **17**, 1571). Also by the action of monopersulphuric acid (Caro's reagent: Bamberger and Scheutz, Ber. **34**, 2023). Subsequent steps as above.

Or benzaldoxime gives benzylamine directly on reduction with sodium amalgam and acetic acid (Goldschmidt, Ber. **19**, 3232).

Or the oxime ('syn-' or 'anti-') by the action of chlorine in chloroform solution gives benzhydroximic chloride (Werner and Buss, Ber. **27**, 2197), which, by interaction with hydroxylamine, yields benzenyloxyamidoxime, $C_6H_5 . C(:N . OH) . NH . OH$, and this gives benzonitrile when treated with acetic anhydride (Ley, Ber. **31**, 2127).

Or benzaldehyde cyanhydrin (from the aldehyde and *hydrogen cyanide* [172]) with alcoholic ammonia gives the nitrile of phenylaminoacetic acid, from which the acid can be obtained by hydrolysis (Tiemann, Ber. **13**, 383). The acid yields benzylamine on dry distillation (Tiemann and Friedländer, Ber. **14**, 1969). Or the cyanhydrin hydrolyses to mandelic acid (Winckler, Ann. **18**, 310; Müller, Ber. **4**, 980; Wallach, Ann. **193**, 38), and this combines with hydrogen bromide to form phenylbromacetic acid (Glaser and Radziszewski, Zeit. [2] **4**, 142). The latter gives phenylaminoacetic acid on heating with aqueous ammonia (Stöckenius, Ber. **11**, 2002).

Benzoic aldehyde with aqueous ammonia yields 'hydrobenzamide' (Laurent, Ann. **21**, 130; Rochleder, Ann. **41**, 89), and the latter gives benzylamine (with toluene) by reduction in alcoholic solution with sodium (O. Fischer, Ber. **19**, 748).

Benzoic aldehyde phenylhydrazone reduces to benzylamine (and aniline) with sodium amalgam and acetic acid (Tafel, Ber. **19**, 1928), or by electrolysis (Tafel and Pfeffermann, Ber. **35**, 1510).

Benzoic aldehyde and *glycin* [Vol. II] give benzylamine when heated to 130° (Curtius and Lederer, Ber. **19**, 2463; Erlenmeyer, junr., Ber. **30**, 1528).

Benzylamine is among the products formed by heating benzoic aldehyde with *ammonium formate* [Vol. II] (Leuckart and Bach, Ber. **19**, 2128).

[**C.**] *Hippuric acid* [Vol. II] gives benzonitrile on heating *per se* or with zinc chloride (Limpricht and Uslar, Ann. **88**, 133; Gössmann, Ann. **100**, 74). Subsequent steps through benzylamine and with *carbon disulphide* as before.

[**D.**] From *phenylacetic acid* [Vol. II] through the bromo-acid (Radziszewski, Ber. **2**, 208), the phenylamino-acid as above under **B**, and benzylamine with *carbon disulphide* as before.

[E.] *Styrene* [7] gives phenylchloracetic acid and mandelic acid (see under benzoic aldehyde [114; B]). Subsequent steps through benzylamine with *carbon disulphide* as above under B.

[F.] From *phenol* [60] and *carbon disulphide* [160]. Phenol and *potassium cyanide* [172] give benzonitrile (see under benzoic aldehyde [114; H]).

[G.] From *cymene* [6] and *carbon disulphide*. Cymene gives acetophenone [114; K]. Then as above under A.

[H.] From *benzene* [6; I, &c.] or *toluene* [54] and *carbon disulphide* [160]. All generators with these hydrocarbons of acetophenone or benzonitrile referred to under benzoic aldehyde [114; A] become generators of benzylamine and, with carbon disulphide, of benzyl mustard oil.

Aniline (from nitrobenzene) on diazotisation with nitrous acid and interaction of the diazo-compound with *nitromethane* (see under hydrogen cyanide [172; J, &c.]) gives, among other products, phenylnitromethane = 1^1-nitrotoluene (Bamberger, Schmidt, and Levinstein, Ber. **33**, 2053). The latter reduces to benzylamine (Konowaloff, Ber. **28**, 1861). Toluene also on nitration with nitric acid of 1·12 sp. gr. at 100° yields phenylnitromethane (*Ibid. loc. cit.*; Journ. Russ. Soc. **31**, 254).

NOTE:—For other methods of formation of phenylnitromethane see Gabriel, Ber. 18, 1254; Cohn, Ber. 24, 3867.

Benzylamine is obtained from benzyl chloride and alcoholic ammonia (Cannizzaro, Ann. **134**, 128; Suppl. **4**, 24; Mason, Trans. Ch. Soc. **63**, 1313; Limpricht, Ann. **144**, 305: see also Seelig, Ber. **23**, 2971; Dhommée, Comp. Rend. **133**, 636); also from benzyl chloride and *potassium cyanide* [172] through benzyl cyanide and hydrolysis of the latter to phenylacetamide (Purgotti, Gazz. **20**, 173; 593), which gives benzylamine by action of bromine in presence of potassium hydroxide (Hofmann, Ber. **18**, 2738; Hoogewerff and Van Dorp, Rec. Trav. Ch. **5**, 253).

Or benzyl chloride or iodide interacts with silver nitrite to form phenylnitromethane (Holleman, Rec. Tr. Ch. **13**, 405; Hantzsch and Schultze, Ber. **29**, 700; Van Raalte, Rec. Tr. Ch. **18**, 383), which can be reduced to benzylamine as above.

Or benzyl chloride or bromide and silver cyanate give benzyl isocyanate (Letts, Journ. Ch. Soc. **25**, 446; Ber. **5**, 91; Strakosch, Ber. **5**, 692; Ladenburg and Struve, *Ibid.* **10**, 46). Silver cyanate is obtained from potassium cyanate by double decomposition (Mendius, Jahresber. **1860**, 17); the potassium salt is obtained by the oxidation of *potassium cyanide* or *ferrocyanide* [172] (Wöhler, Berz. Jahresber. **3**, 78; **4**, 92; Pogg. Ann. **1**, 117; Liebig, Ann. **38**, 108; **41**, 289; Kolbe, Ann. **64**, 237; Clemm, Ann. **66**, 382; Wurtz, Ann. Chim. [3] **42**, 44; Lea, Jahresber. **1861**, 789; Bell, Ch. News, **32**, 100; Gattermann, Ber. **23**, 1224; Volhard, Ann. **259**, 378; H. Erdmann, Ber. **26**, 2438; Reychler, Bull. Soc. [3] **9**, 427).

Benzyl isocyanate gives benzylamine on decomposition by caustic alkali (Cannizzaro, Ann. **134**, 128; Strakosch, Ber. **5**, 692: see also Letts, *Ibid.* 91).

Benzylamine can be obtained also from benzyl chloride and acetic acid through benzylacetamide (Rudolph, Ber. **12**, 1297), and decomposition of the latter with alcoholic potash (*Ibid.*).

Or from benzyl chloride and *formic aldehyde* [91] through the aldehyde or through 'trioxymethylene' and the base, hexamethylenamine, formed by the action of ammonia on the aldehyde or on trioxymethylene (Butleroff, Ann. **115**, 322; Wohl, Ber. **19**, 1842; Grassi-Cristaldi and Motta, Gazz. **29**, 43). The compound of hexamethylenamine and benzyl chloride gives benzylamine on decomposition with alcoholic hydrochloric acid (Delépine, Comp. Rend. **124**, 292; Bull. Soc. [3] **17**, 294).

[I.] *Naphthalene* [12] is a generator of benzonitrile through phthalic acid and phthalimide (see under benzoic aldehyde [114; J]).

[J.] From *cumic aldehyde* [116] through isopropylbenzene and acetophenone, &c. [114; K].

170. Phenylethyl Isothiocyanate, Thiocarbimide, or Mustard Oil.

$C_6H_5.CH_2.CH_2.NCS$

Natural Sources.

Occurs in the ethereal oil of the water-cress, *Nasturtium officinale*, and the winter-cress, *Barbarea præcox*. The glucoside (gluconasturtiin) exists as potassium salt in the seeds of these plants (Gadamer, Ber. **32**, 2339; Arch. Pharm. **237**, 507). According to Bertram and Walbaum (Journ. pr. Ch. [2] **50**, 557), this mustard oil is contained in the ethereal oil from the roots of *Reseda*.

Synthetical Processes.

[A.] From *toluene* [**54**; **A**, &c.] and *potassium cyanide* [**172**] through benzyl cyanide (see under benzyl mustard oil [**169**; **H**]) and *carbon disulphide* [**160**]. Benzyl cyanide on reduction gives ω-phenylethylamine (Spica and Colombo, Gazz. **5**, 124; Bernthsen, Ann. **184**, 304; Spica, Jahresber. **1879**, 440; Ladenburg, Ber. **19**, 783). The amine gives the mustard oil by the general method (Neubert, Ber. **19**, 1825).

The nitrile of symmetrical triphenylglutaric acid, obtained by the condensation of benzyl cyanide with *benzoic aldehyde* [**114**] by means of sodium ethylate (Meyer, Ann. **250**, 156), gives ω-phenylethylamine on reduction with sodium in alcoholic solution (Henze, Ber. **31**, 3065).

Or benzyl chloride can be combined with the sodium compound of *chlormalonic ester* [Vol. II] (Conrad and Bischoff, Ann. **209**, 219) so as to give benzyl chlormalonate (Conrad, *loc. cit.* 243). The latter, on treatment with potassium or barium hydroxide, gives benzyltartronic acid (*Ibid.* 245), and this yields phenyl-α-lactic acid on heating at 160–180° (*Ibid.* 247). Subsequent steps as below under **D**.

Also from *benzene* [**6**; I, &c.] through ethylbenzene (see under phlorol [**64**; **A**]). The compound of the latter with chromium oxychloride is decomposed by water with the formation of α-toluic aldehyde (Etard, Ann. Chim. [5] **22**, 248), the oxime of which (Dollfus, Ber. **25**, 1917) gives phenylethylamine on reduction (Bischler and Napieralski, Ber. **26**, 1905). Ethylbenzene also yields α-toluic aldehyde among the products of its oxidation by potassium persulphate (Moritz and Wolffenstein, Ber. **32**, 434).

Or from ethylbenzene through styrene bromide (see under styrene [**7**; **A**]), and then as below under **B**.

[B.] *Styrene* [**7**] gives ethylbenzene (see under phlorol [**64**; **B**]), which, with *carbon disulphide* [**160**], yields the mustard oil as above under **A**.

Or styrene can be combined with bromine, and the bromide converted into the glycol (see under benzoic aldehyde [**114**; **B**]). The latter on heating with 20 per cent. sulphuric acid gives α-toluic aldehyde (Zincke, Ber. **11**, 1402; Ann. **216**, 301; also Tiffeneau, Comp. Rend. **134**, 1505), which can be converted into phenylethylamine as above under **A**.

Or styrene, by the action of iodine in presence of mercuric oxide, gives an iodo-derivative, which yields α-toluic aldehyde on treatment with silver nitrate (Bougault, Comp. Rend. **131**, 529).

[C.] From *tartaric* or *racemic* acid [Vol. II], and *n-propyl alcohol* [**15**], and *carbon disulphide* [**160**], through pyroracemic acid and propionic aldehyde, ethylisophthalic acid, ethylbenzene, &c. (see under phlorol [**64**; **J**]).

Note:—Generators of pyroracemic acid are given under benzyl alcohol [**54**; **F**; **I**; **M**, &c.].

[D.] From *benzoic aldehyde* [**114**], *alcohol* [**14**], *acetic acid* [Vol. II], and *carbon disulphide* [**160**]. Chloracetic ester and benzoic aldehyde on treatment with sodium in alcoholic solution give the ester of β-phenyloxyacrylic = phenylglycidic acid (Erlenmeyer, Ann. **271**, 153). The latter yields α-toluic aldehyde on distillation with dilute sulphuric acid (Baeyer, Ber. **13**, 304: see also Glaser, Ann. **147**, 100). Phenylglycidic acid decomposes at ordinary temperatures into α-toluic aldehyde and carbon dioxide (Erlenmeyer, Ber. **13**, 308).

Or phenylglycidic acid (ester) by the action of sodium amalgam gives phenyl-α-lactic acid (Plöchl, Ber. **16**, 2823), and the latter yields α-toluic aldehyde on heating *per se* at 130° or with dilute sulphuric acid at 200° (Erlenmeyer, Ber. **13**, 304). Subsequent steps as above under **A**.

Or from benzoic aldehyde and *hydrogen cyanide* [**172**] through the nitrile of mandelic acid (see under benzyl mustard oil [**169**; **B**]). This nitrile, according to Fileti (Schiff, Ber. **12**, 297; 1700), can be reduced to phenylethylamine.

[**E.**] From *cinnamic acid* [Vol. II] and *carbon disulphide* [**160**]. Cinnamic acid can be converted into phenyl-α-chlorlactic acid by combination with hypochlorous acid (Glaser, Ann. **147**, 79; Erlenmeyer and Lipp, Ann. **219**, 185). Phenyl-α-chlorlactic acid on treatment with cold alcoholic potash gives β-phenyloxyacrylic acid (Glaser, *loc. cit.* 98), which can be treated as above under **D**. Or the phenyl-α-chlorlactic acid yields α-toluic aldehyde directly on distillation with sodium carbonate solution (Forrer, Ber. **17**, 982).

Or cinnamic acid can be combined with bromine, and the phenyldibrompropionic acid converted by boiling with water into phenyl-α-bromlactic acid (Glaser, *loc. cit.* 84; Erlenmeyer, Ber. **13**, 310). The latter gives β-phenyloxyacrylic acid on treatment with alkali (Glaser, *loc. cit.* 98).

Or cinnamic acid on combination with a hypobromite and treatment of the product with alkali gives α-oxyphenylpropionic lactone, which, on heating in a partial vacuum or with water, yields α-toluic aldehyde (H. Erdmann, Eng. Pat. 8248, April, 1899; Journ. Soc. Ch. Ind. **19**, 273).

Sodium cinnamate on treatment with iodine chlorhydride gives phenyliodhydracrylic = α-iodo-β-phenyl-β-hydroxypropionic acid, and this on heating with water yields α-toluic aldehyde (Erlenmeyer and Rosenhek, Ber. **19**, 2464; Erlenmeyer, Ann. **289**, 276).

Or from cinnamic acid through phenylglyceric acid (see under benzoic aldehyde [**114**; **E**]). The latter gives phenyl-β-chlorlactic acid or the corresponding bromo-acid by treatment with hydrochloric or hydrobromic acid (Leschhorn, Ann. **271**, 153; Lipp, Ber. **16**, 1290). The phenyl-β-chlor- (or bromo-) acid yields α-toluic aldehyde on distillation with dilute alkali (Erlenmeyer and Lipp, Ann. **219**, 182). Phenylglyceric acid gives α-toluic aldehyde directly on heating to 160° (Lipp, Ber. **16**, 1288).

[**F.**] From *benzoic* and *acetic acids* [Vol. II] through acetophenone (see under benzoic aldehyde [**114**; **A** and **G**]), dypnone, and ethylbenzene (see under phlorol [**64**; **K**]), and then as above under **A**.

[**G.**] *Cymene* [**6**] can be converted into acetophenone through cumic acid and isopropylbenzene = cumene (see under benzoic aldehyde [**114**; **K**]).

[**H.**] From *phenylacetic* (*a-toluic*) and *formic acids* [Vol. II] by distilling a mixture of the calcium salts (Cannizzaro, Ann. **119**, 254), and treating the α-toluic aldehyde thus formed as above under **A**.

[**I.**] *β-Phenylpropionic acid* [Vol. II] is converted into its amide (Hofmann, Ber. **18**, 2740), and the latter into ω-phenylethylamine by the action of bromine in presence of potassium hydroxide (*Ibid.*; also Hoogewerf and Van Dorp, Rec. Tr. Ch. **5**, 254).

[**J.**] *Phenylalanine* [Vol. II] gives ω-phenylethylamine on rapid heating (Erlenmeyer and Lipp, Ann. **219**, 202: see also Schulze and Barbieri, Journ. pr. Ch. [2] **27**, 346; Ber. **14**, 1788; **16**, 1713).

171. Parahydroxybenzyl Isothiocyanate, Thiocarbimide, or Mustard Oil.

Natural Source.

Occurs in the oil of white mustard from the seeds of *Sinapis alba*. The glucoside contained in the seeds is sin-

albin (Robiquet and Boutron-Charlard, Journ. Pharm. [2] **17**, 279; Will and Laubenheimer, Ann. **199**, 150; Gadamer, Arch. Pharm. **235**, 83; Ber. **30**, 2327–2334).

Synthetical Processes.

[A.] From *toluene* [54] and *carbon disulphide* [160]. Paranitrobenzyl chloride (see under p-hydroxybenzoic aldehyde [119; E]) is converted into a phthalimide derivative (see under benzoic aldehyde [114; J]) by interaction with potassium phthalimide (Gabriel, Ber. **20**, 2224), and this derivative converted into p-nitrobenzylamine by heating with hydrochloric acid at 190–200°. The nitro-amine gives p-aminobenzylamine on reduction, and the latter p-hydroxybenzylamine by the diazo-method. The mustard oil is obtained from the base by the usual method (Salkowski, Ber. **22**, 2143).

p-Nitrobenzylamine can also be obtained from *benzylamine* (see under benzyl mustard oil [169; A to end]) by acetylation, nitration of the benzyl-acetamide, and reduction of the p-nitro-derivative (Amsel and Hofmann, Ber. **19**, 1284). The generators of benzylamine, viz. *benzoic acid* and *acetic aldehyde*, *hippuric* and *phenylacetic acids*, and *styrene*, thus become, with carbon disulphide, generators of p-hydroxybenzyl mustard oil.

CYANOGEN COMPOUNDS.

172. Hydrogen Cyanide; Hydrocyanic or Cyanhydric Acid; Prussic Acid; Formonitrile.

H.CN

Natural Sources.

Occurs to a considerable extent in the free state or in very loose combination in all parts of *Pangium edule*, Java (Greshoff, Ber. **23**, 3549). Also in *Hydnocarpus inebrians* = *H. wightiana?* and *H. alpinus* (*Ibid.* 3550). The sweet and bitter cassava contain hydrogen cyanide, especially the skin (Francis, 'Analyst,' **2**, 4; Carmody, 'Bulletin of Miscellaneous Information,' Trinidad; 'Nature,' **63**, 500: for occurrence of hydrogen cyanide in *Pangium edule* and in bitter almonds see also Marco Soave, Journ. Ch. Soc. **80**, II, Abst. 332).

The hydrogen cyanide complex is contained in the glucoside amygdalin (for occurrence see under benzoic aldehyde [114]). The complex exists in plants belonging to the Amygdalaceæ, Asclepiads, Bixaceæ, Tiliaceæ, Sapotaceæ, Sapindaceæ, Papilionaceæ, Convolvulaceæ, Euphorbiaceæ, Linaceæ, and Aroideæ (Greshoff). Traces of free hydrogen cyanide have been found among Saxifrages, in young shoots of certain species of *Ribes*, viz. *R. rubrum*, *R. nigrum*, and *R. aureum*. The seed embryo of *Eriobotyra japonica* contains ·04 per cent. of hydrogen cyanide.

The complex exists in a compound occurring in many wild Rosaceæ and in an amygdalin-like compound found in the young green parts of the Ranunculaceous *Aquilegia vulgaris*. No hydrogen cyanide could be found in the Aroideæ, *Arum maculatum*, *A. italicum*, *Arisarum vulgare*, *Amorphophallus rivieri*, or *Dieffenbachia seguine* (Hébert, Bull. Soc. [3] **17**, 664; **19**, 310). R. Fischer, contrary to the statement of Greshoff, was unable to find hydrogen cyanide in *Mitchella repens* (Pharm. Rev. **16**, 98).

Amygdalin, or some glucoside yielding hydrogen cyanide on hydrolysis, is present in the leaves of *Indigofera galegoïdes* (Van Romburgh, Schimmel's Ber. Oct. 1894; April, 1896).

The distribution of hydrogen cyanide in various parts of *Prunus laurocerasus* has been investigated by Van der Ven (Ch. Centr. 1898, **2**, 678). The opening buds of *Prunus lauro-*

cerasus and *P. padus* contain a glucoside which yields hydrogen cyanide (Verschaffelt, Proc. K. Akad. Wetensch. Amsterdam, **5**, 31; Journ. Ch. Soc. **82**, II, Abst. 523).

The herb *Spiræa aruncus*, the herb and flowers of *S. sorbifolia*, and the leaves of *S. japonica* give hydrogen cyanide on distillation with water (Wicke, Ann. **83**, 175). Amygdalin, or some similar compound yielding hydrogen cyanide on hydrolysis, is present in the seeds of many species of *Vicia*, and absent in others (Bruyning and Van Haarst, Rec. Tr. Ch. **18**, 468).

Compounds containing the hydrogen cyanide complex are present in the flowers of peach, blackthorn, and mountain ash, in the stem-bark and root of the latter, in the stem-bark of Portugal laurel, and in the root of *Manihot* (Euphorbiaceæ).

The glucoside lotusin contained in *Lotus arabicus* from Egypt and N. Africa gives hydrogen cyanide on hydrolysis or zymolysis (Dunstan and Henry, Proc. Roy. Soc. **67**, 224; **68**, 374; Phil. Trans. B, **194**, 515). Cyanogenetic glucosides are contained also in the young plants of *Sorghum vulgare*, in *Manihot utilissima*, *Linum usitatissimum*, *Lotus australis*, and *Phaseolus lunatus*, the Lima bean (Dunstan and Henry, Proc. Roy. Soc. **70**, 153; Phil. Trans. 1902, A, 399; 'Nature,' **68**, 287; Brünnich, Trans. Ch. Soc. **83**, 788).

In the animal kingdom hydrogen cyanide is said to have been obtained from *Chilognatha* (Myriopods).

Synthetical Processes.

[**A.**] From carbon, hydrogen, and nitrogen through *acetylene* [methane, **1**; **A**], which combines with nitrogen under the influence of the electric spark (Berthelot, Comp. Rend. **67**, 1141; Ann. **150**, 60; Dewar, Proc. Roy. Soc. **29**, 188; **30**, 85). Hydrogen cyanide is also formed from acetylene and nitrogen or ammonia in the electric furnace (Hoyermann, Ch. Zeit. **26**, 70). Acetylene and nitric oxide when mixed and exploded by the electric spark give hydrogen cyanide (Huntingdon, Germ. Pat. 93852 of 1896; Ch. Centr. 1897, **2**, 1166). Acetylene gives among the products of its oxidation by fuming nitric acid a crystalline compound ($C_6H_4O_3N_4$), which yields hydrogen cyanide on heating above 120° (Baschieri, Atti Real. Accad. Linc. [5] **9**, 391). Acetylene when exploded with oxygen in the presence of nitrogen gives hydrogen cyanide (Mixter, Sill. Journ. [4] **9**, 5; **10**, 299).

Hydrogen cyanide is formed by heating wood charcoal with nitric acid (Burls, Evans, and Desch, Ch. News, **68**, 75).

Ammonia (two molecules) and nitrous oxide (one molecule), when mixed and passed over heated carbon, give hydrogen cyanide (Roeder and Grünwald, Germ. Pat. 132909 of 1901; Ch. Centr. 1902, **2**, 235).

Cyanides or cyanamides are formed by passing nitrogen, ammonia, or nitric oxide and steam over the carbides of the metals of the alkalis or alkaline earths heated to a high temperature. Calcium cyanamide is formed directly from nitrogen by heating lime and carbon in the electric furnace with access of atmospheric air (Caro and Frank, Germ. Pat. 88363 of 1895; Ber. **29**, Ref. 816; *Ibid.* No. 92587 of 1895; Ch. Centr. 1897, **2**, 654; No. 95660 of 1896; Ch. Centr. 1898, **1**, 813; No. 108971 of 1898; Ch. Centr. 1900, **1**, 1120; Nos. 116087 and 116088 of 1898; Ch. Centr. 1900, **2**, 1222; also the patents of Erlwein and Frank and of Bradley and Jacobs referred to below).

Potassium cyanide is formed by the combination of strongly heated carbon and nitrogen in presence of potassium carbonate or hydroxide (Desfosses, Ann. Chim. **38**, 158; Journ. Pharm. **12**; Fownes, 'Athenæum,' 1841, p. 625; Journ. pr. Ch. **26**, 412; Lewis Thompson, Berz. Jahresber. **21**, 80; Bunsen and Playfair, Rep. Brit. Assoc. 1845, 185; Journ. pr. Ch. **42**, 397; Delbrück, Ann. **64**, 296; Journ. pr. Ch. **41**, 161; Wöhler, Jahresber. **1850**, 550; Rieken, Ann. **79**, 77; Marguerite and Sour-

deval, Comp. Rend. **50**, 1100; Hempel, Ber. **23**, 3390; De Lambilly, Journ. Soc. Ch. Ind. **11**, 604; 1006; Young, Eng. Pat. 24856 of 1893: for technical production of cyanides from atmospheric nitrogen or ammonia and carbon in presence of fused alkali see also Pfleger's Germ. Pats. 88115 of 1894 and 89594 of 1895; Ber. **29**, Ref. 748 and 1197; Stassfurter Ch. Fab., Eng. Pats. 9350, 9351, and 9352 of 1900; Journ. Soc. Ch. Ind. **20**, 77: for production of cyanides from atmospheric nitrogen and fused alkali in presence of carbon and iron see Victor Alder's Germ. Pats. 12351 of 1880; Ber. **14**, 1126; 18945 of 1881; Ber. **15**, 1776; also Täuber, Ber. **32**, 3152: for production of barium cyanide from barium carbide and atmospheric nitrogen in the electric furnace see Bradley and Jacobs, Eng. Pat. 7558 of 1900; for manufacture of calcium cyanide and cyanamide by means of the electric furnace from calcium carbide and nitrogen see Erlwein and Frank, Amer. Pat. 708333 of 1902; Journ. Soc. Ch. Ind. **21**, 1232; Erlwein, Zeit. angew. Ch. **16**, 533: for production of hydrogen cyanide from metallic cyanides see Feld's Eng. Pat. 24904 of 1901; Journ. Soc. Ch. Ind. **21**, 1553).

Potassium cyanide is formed by passing carbon monoxide and nitrogen over a fused mixture of potassium carbonate and carbon (Possoz and Boissière, Wagner's Jahresber. **1855**, 83, from the 'London Journ. of Arts,' **1845**, 380), or by passing carbon monoxide and ammonia through a fused mixture of potassium hydroxide and carbon (Young and Macfarlane, Eng. Pat. 3092 of 1892).

Sodamide gives sodium cyanide when heated in an atmosphere of carbon monoxide (Beilstein and Geuther, Ann. **108**, 91; Conroy, Journ. Soc. Ch. Ind. **15**, 9).

Fused sodium in contact with carbon gives sodium cyanide when heated in an atmosphere of ammonia, sodamide and cyanamide being formed as intermediate products (Castner, Eng. Pats. 12218 and 12219 of 1894: see also Deutsch. Gold- u. Silber-Scheide-Anstalt, &c., Germ. Pat. 126241 of 1900; Ch. Centr. 1901, **2**, 1184; Eng. Pats. 21820 of 1900 and 3329 of 1901; Journ. Soc. Ch. Ind. **20**, 1113 and **21**, 345; also Darling, Journ. Franklin Inst. Jan. 1902). Barium cyanide is formed by passing carbon monoxide over heated barium nitride (Maquenne, Comp. Rend. **114**, 221).

Ammonium cyanide is formed when ammonia is passed over heated carbon (Kuhlmann, Ann. **38**, 62; Journ. pr. Ch. **16**, 482; Lance, Comp. Rend. **124**, 819; Lance and De Bourgade, Germ. Pat. 100775 of 1897; Ch. Centr. 1899, **1**, 766; Eng. Pat. 26326 of 1897: for production of ammonium cyanide by passing ammoniacal gases over heated 'contact' surfaces see Besenfelder's Germ. Pat. 120264 of 1900; Ch. Centr. 1901, **1**, 1125; 122144 of 1900; *Ibid.* **2**, 379: for earlier work on the production of cyanides from ammonia and carbon see also Clouet, Ann. Chim. **11**, 30; Bonjour, Scherer's Journ. **2**, 621; Schröder, *Ibid.* 626; 628; Langlois, Journ. pr. Ch. **23**, 232; Berz. Jahresber. **22**, 84; Ann. **38**, 64: for historical summary to 1842 see Erdmann and Marchand, Journ. pr. Ch. **26**, 411. Scheele obtained potassium cyanide from a fused mixture of 'tartar' and coal or graphite and ammonium chloride, 'Sämmtliche phys. u. chem. Werke,' Hermbstädt, Vol. II, p. 345).

Potassium cyanide is formed when ammonia is passed into a heated mixture of carbon and potassium carbonate or hydroxide (Desfosses, *loc. cit.*; Kuhlmann, *loc. cit.*; Grüneberg, Flemming, and Siepermann, Eng. Pat. 13697 of 1889; Beilby, Eng. Pat. 4820 of 1891; Siepermann, Eng. Pat. 13754 of 1893; Riepe, Germ. Pat. 105051 of 1898; Ch. Centr. 1899, **2**, 1080).

Sodium cyanide is formed by passing ammonia over a heated mixture of sodium carbonate and zinc with or without carbon (Hood and Salamon, Eng. Pat. 21239 of 1893). Alkaline cyanides are formed by passing ammonia over a mixture of alkaline sulphide and charcoal at a red heat (Grossmann, Eng. Pat. 24011 of 1899; also Germ. Pat. 121555 of 1900; Ch. Centr. 1901, **2**, 68). Ammonium chloride and borax

on ignition give a boron nitride which, on fusion with potassium carbonate and carbon, yields potassium cyanide (Moïse, Germ. Pat. 91708 of 1895; Ch. Centr. 1897, **2**, 156).

Cyanogen is formed on passing electric sparks between carbon poles in an atmosphere of nitrogen (Morren, Comp. Rend. **48**, 342), and this combines with hydrogen under the influence of the silent electric discharge (Boillot, Comp. Rend. **76**, 1132), or on heating the mixed gases to 500–550° (Berthelot, Bull. Soc. [2] **33**, 2; Ann. Chim. [5] **18**, 380). An aqueous solution of cyanogen is found to contain hydrogen cyanide among other products after long keeping (Wöhler, Pogg. Ann. **15**, 627).

Phospham (Gerhardt, Ann. Chim. [3] **18**, 188; **20**, 225; Liebig and Wöhler, Ann. **11**, 139; Pauli, Ann. **101**, 41; Salzmann, Ber. **7**, 494; Besson, Comp. Rend. **114**, 1264), on heating with an alkaline carbonate and carbon or iron, gives a cyanide or ferrocyanide respectively (Vidal, Germ. Pat. 95340 of 1897; Ch. Centr. 1898, **1**, 542).

[B.] *Carbon disulphide* [**160**] and ammonia combine to form ammonium thiocyanate (Zeise, Ann. **47**, 36; Millon, Jahresber. **1860**, 237; Zeit. [1] **1861**, 64; Gélis, Jahresber. **1861**, 340; **1863**, 746; Schwartz, Wagner's Jahresber. **1869**, 269; Schulze, Journ. pr. Ch. [2] **47**, 518; Claus, Ann. **179**, 112: for combination in presence of sulphites and hydrosulphites see Goldberg and Siepermann, Germ. Pats. 83435 of 1895, and 87813 of 1896; Ber. **28**, Ref. 950; **29**, Ref. 744: for historical summary and patented processes see further N. Caro, Ch. Ind. **13**, 244; **14**, 287; Conroy, Journ. Soc. Ch. Ind. **15**, 10: for production of thiocyanates from carbon disulphide and ammonia in presence of lime or magnesia see Hood and Salamon, Germ. Pat. 72644 of 1892; Ber. **27**, Ref. 281; British Cyanides Co., Germ. Pat. 81116 of 1894; Ber. **28**, Ref. 667; Albright and Hood, Germ. Pat. 85492 of 1895; Ber. **29**, Ref. 314: for technical production of thiocyanates see also Tscherniac and Günzburg, Ding. poly. Journ. **245**, 214; Journ. Soc. Ch. Ind. **1**, 150; Nafzger, Journ. Soc. Ch. Ind. **5**, 324; Gasch, *Ibid.* 379; Crowther and Rossiter, *Ibid.* **13**, 887; Brock, &c., *Ibid.* 1195; Albright and Hood, *Ibid.* **14**, 657).

Thiocyanates can by various processes of oxidation or reduction be converted into cyanides or ferrocyanides (Péan, Jahresber. **1858**, 585; Gélis, Wagner's Jahresber. **1862**, 283; **1863**, 321; Fleck, *Ibid.* **1863**, 323; Alander, Ding. poly. Journ. **226**, 318; Tscherniak and Günsburg, Jahresber. **1878**, 1123; Wagner's Jahresber. **1878**, 500; **1879**, 471; **1880**, 386; **1882**, 510; Playfair, Eng. Pat. 7764 of 1890; Journ. Soc. Ch. Ind. **11**, 14; Lüttke, Germ. Pat. 89607 of 1895; Ber. **29**, Ref. 1197; United Alkali Co., Germ. Pat. 97896 of 1895; Ch. Centr. 1898, **2**, 837: for electrolytic oxidation see Parker, Eng. Pats. 17447 of 1888 and 2383 of 1889 and also Journ. Soc. Ch. Ind. **9**, 67; 291: for oxidation by hydrogen peroxide see Raudnitz, Zeit. Biol., Jubelband, **42**, 91; Ch. Centr. 1901, **2**, 1234: for historical summary from the technological point of view see Caro and Conroy as above; also for Raschen's process of oxidation by nitric acid, Conroy, Journ. Soc. Ch. Ind. **18**, 432: see further Raschen, &c., Journ. Soc. Ch. Ind. **14**, 1046; Goerlich and Wichmann, *Ibid.* 657; Beringer, Eng. Pat. 18565 of 1899; Raschen, Norman, and Luxton and the United Alkali Co., Eng. Pat. 12180 of 1900; Journ. Soc. Ch. Ind. **20**, 809: for *reduction* of thiocyanates to cyanides by hydrogen see Sestini and Funaro, Gazz. **12**, 184; Conroy, Heslop, and Shores, Journ. Soc. Ch. Ind. **20**, 320; British Cyanides Co., Germ. Pat. 132294 of 1901; Ch. Centr. 1902, **2**, 80: for reduction of copper and other thiocyanates see Rossiter, Crowther, and Albright, Eng. Pats. 4403 and 6226 of 1901; Journ. Soc. Ch. Ind. **21**, 173; 345).

Cyanides are formed also from thiocyanates by heating the latter with calcium carbide or in an atmosphere of acetylene (Conroy, Heslop, and Shores, *loc. cit.*; Sandmann, Zeit. angew. Ch. **15**, 543).

[C.] From *benzene* [**6**; I, &c.], the

nitro-derivatives of which give hydrogen cyanide among the products of the action of alkali (Hübner and Post, Ber. **5**, 408). From benzene *via* nitrobenzene, phenylhydroxylamine, and nitrosobenzene. The latter gives hydrogen cyanide among the products of the action of alkali (Bamberger, Ber. **33**, 1939).

Or from benzene through trichlorphenomalic acid (see under carbon disulphide [**160**; **N**]) and chloroform, and then as under **E** below.

Or from *toluene* [**54**; **A**, &c.] through o-nitrotoluene and o-toluidine, the latter giving hydrogen cyanide by the action of sodium hypochlorite (Meigen and Normann, Ber. **33**, 2714).

[**D.**] From *phenol* [**60**], hydrogen cyanide being among the products of the action of alkali on the nitro-derivatives (Hübner and Post, as above: see also Wedekind and Häussermann, Ber. **35**, 1133).

From phenol and *ethyl alcohol* [**14**] through coumarone (see under phlorol [**64**; **C**]) and nitrocoumarone (see under salicylic aldehyde [**117**; **A**]). The latter gives hydrogen cyanide among the products of its decomposition by sodium ethylate (Stoermer and Kahlert, Ber. **35**, 1640).

[**E.**] From *ethyl alcohol* [**14**] through chloroform (see under methane [**1**; **D**]). Hydrogen cyanide is formed by passing ammonia and chloroform vapour through a hot tube, or by heating chloroform and alcoholic ammonia to 180–190° (Heintz, Ann. **100**, 369; Cloëz, Jahresber. **1858**, 345). Also by the action of caustic potash on chloroform in presence of aqueous ammonia (Hofmann, Ann. **144**, 116).

Alcohol also gives hydrogen cyanide among the products of its oxidation by nitric acid, possibly through the formation of an oximido-compound (Gill and Meusel, Zeit. [2] **5**, 66; Hantzsch, Ann. **222**, 65).

Or from alcohol through glyoxal by oxidation with nitric acid (Debus, Ann. **102**, 20; **107**, 199; **110**, 316; **118**, 253). The oxime (glyoxime) gives cyanogen on heating with acetic anhydride (Lach, Ber. **17**, 1573), and this can be converted into hydrogen cyanide as above under **A**.

Note:—The following compounds thus become, through chloroform, generators of hydrogen cyanide (see under carbon disulphide [**160**; **D**; **E**; **F**; **K**; **L**; **M**]):—

Acetone [**106**]; *aldehyde* [**92**]; *acetic*, *gallic*, or *salicylic acid* [Vol. II]; *phenol* [**60**]. The last three through trichlor-*aa*-glyceric acid and chloroform.

[**F.**] From *formic aldehyde* [**91**], the polymeric oxime of which gives hydrogen cyanide on sudden heating (Scholl, Ber. **24**, 577). Or formoxime yields hydrogen cyanide on dehydration by phosphorus pentoxide (Dunstan and Bossi, Trans. Ch. Soc. **73**, 360).

[**G.**] From *isobutyric aldehyde* [**94**] through the *a*-brom-paraldehyde by bromination (Franke, Monats. **21**, 205). The latter gives an oxime which, by the action of acetic anhydride, yields a resinous nitrile which is decomposed by sodium carbonate into hydrogen cyanide and acetone (*Ibid.* 210: see also under acetone [**106**; **DD**]).

[**H.**] *Dextrose*, *lævulose* [**154**; **155**], and many sugars give hydrogen cyanide among the products of their oxidation by nitric acid (Hantzsch, Ann. **222**, 65: for production from saccharose see Burls, Evans, and Desch, Ch. News. **68**, 75).

[**I.**] From *formic acid* [Vol. II] by heating the dry ammonium salt (Pelouze and Döbereiner, Ann. **2**, 90), or by distilling this salt or formamide with phosphorus pentoxide (Lorin, Ann. **132**, 255; Hofmann, Journ. pr. Ch. **91**, 61; Journ. Ch. Soc. **16**, 74). By distilling ammonium formate (or formamide) into heated potash potassium cyanide is formed (Glock, Germ. Pat. 108152 of 1899; Ch. Centr. 1900, **1**, 1115).

Or phospham, when heated with formic acid, gives at 150–200° hydrogen cyanide (Vidal, Germ. Pat. 101391 of 1898; Ch. Centr. 1899, **1**, 960; also Eng. Pat. 4227 of 1898; Journ. Soc. Ch. Ind. **18**, 398).

[**J.**] From *acetic acid* [Vol. II], dry sodium acetate giving the cyanide (15 p.c.) on heating with a nitrite (Warren, Ch. News, **72**, 40; Kerp, Ber. **30**, 610: see also Roussin, Comp. Rend. **47**, 875).

According to Kerp (*loc. cit.* 611) free hydrogen cyanide is also evolved.

Or potassium chloracetate, by the action of a nitrite, yields nitromethane (Preibisch, Journ. pr. Ch. [2] **8**, 316). The latter, by the action of alkalis, gives 'methazonic acid' (Lecco, Ber. **9**, 705; Dunstan and Goulding, Trans. Ch. Soc. **77**, 1262), which, on heating with acids or alkalis or by oxidation with potassium permanganate, yields hydrogen cyanide (D. and G., *loc. cit.* 1264).

A solution of copper acetate heated with ammonia gives cuprous cyanide (Vittenet, Bull. Soc. [3] **21**, 261).

Acetic acid and *methyl alcohol* [13] give dimethylacetoacetic methyl ester, which, on treatment with nitric acid, yields a compound decomposable by alkali with the formation of hydrogen cyanide among other products (W. H. Perkin, junr., Proc. Ch. Soc. **17**, 204).

[K.] From *propionic acid* [Vol. II] by heating dry sodium propionate with a nitrite as above (Kerp, *loc. cit.* 611).

[L.] From *tartaric acid* [Vol. II] as above, potassium sodium tartrate or neutral sodium tartrate being fused with nitrite. Free hydrogen cyanide is also evolved (Warren, *loc. cit.*; Kerp, *loc. cit.* 611).

Or indirectly from tartaric acid through 'nitrotartaric acid' (Dessaignes, Ann. **82**, 362; Demole, Ber. **10**, 1789; Kekulé, Ann. **221**, 245). The latter [or the 'dioxytartaric' acid obtained from it by the action of ethyl nitrite (Kekulé, *loc. cit.* 247), or by decomposition by aqueous sodium carbonate and acetate (Thiele and Dralle, Ann. **302**, 291, note)] gives glyoxal on heating with acid sodium sulphite in aqueous solution (Hinsberg, Ber. **24**, 3236). Subsequent steps through glyoxime and cyanogen, &c., as above under **E**.

Note:—Dioxytartaric acid can also be obtained from tartaric acid through its oxidation product, dihydroxymaleïc acid (see under furfural [126; E]), and further oxidation of the latter by bromine and water (Fenton, Trans. Ch. Soc. 67, 48; 73, 71).

[M.] From *oxalic acid* [Vol. II] by heating the ammonium salt alone or with phosphorus pentoxide, &c. (Dumas, Ann. **10**, 295; Bertagnini, Ann. **104**, 176; Storch, Ber. **19**, 2459). The cyanogen thus formed can be converted into hydrogen cyanide as above under **A**.

[N.] From *lactic acid* [Vol. II] through 'nitrolactic acid' (Henry, Ber. **3**, 532), the latter undergoing spontaneous decomposition with evolution of hydrogen cyanide (*Ibid.*).

[O.] From *acetic aldehyde* [92] through glyoxal by oxidation with nitric acid (Liubavin, Ber. **8**, 768; Journ. Russ. Soc. **7**, 249; **13**, 496; Ber. **10**, 1366; De Forcrand, Bull. Soc. [2] **41**, 242; Spiegel, Ch. Zeit. **19**, 1423), and then through the oxime and cyanogen as above under **E**.

[P.] From *catechol* [69], which gives dioxytartaric acid when acted upon by nitrous gas in ethereal solution (Barth, Monats. **1**, 869). Subsequent steps as above under **L**.

[Q.] *Protocatechuic acid* [Vol. II] gives dioxytartaric acid when treated as above (Gruber, Ber. **12**, 514).

[R.] *Quinone* [142] gives hydrogen cyanide when oxidised by nitric acid in excess (Kerp, Ber. **30**, 612).

[S.] From *glycocoll* [Vol. II], which gives hydrogen cyanide when heated with dilute sulphuric acid and manganese dioxide (Watts's Dict., Morley and Muir, II, 627). Or glycin ethyl ester, by the action of nitrous acid, gives ethyl diazoacetate (Curtius, Journ. pr. Ch. [2] **38**, 401). The latter, on treatment with sodium ethylate, yields the sodium derivative of ethyl isodiazoacetate. Free ethyl isodiazoacetate gives hydrogen cyanide among the products of its decomposition by heat (Hantzsch and Lehmann, Ber. **34**, 2506).

[T.] From *methylamine* [Vol. II] by the action of heat on the vapour (Wurtz, Ann. Chim. [3] **30**, 454), or by combustion of the moist vapour (Tollens, Zeit. [2] **2**, 516). Hydrogen cyanide is also among the products of oxidation of methylamine by monopersulphuric acid (Bamberger and Seligman, Ber. **35**, 4299).

[U.] *Trimethylamine* [Vol. II], when the vapour is passed through a red-hot

tube, gives hydrogen and ammonium cyanides (Willm, Bull. Soc. [2] **41**, 449).

[V.] From *methane* [1] and nitrogen, which give ammonium cyanide under the influence of the silent electric discharge (Figuier, Bull. Soc. [2] **46**, 61).

[W.] From *succinic acid* [Vol. II] through acetylenedicarboxylic acid (see under methane [1; T]). The silver salt of the latter on treatment with strong nitric acid is decomposed with the formation of silver cyanide.

[X.] From *fumaric acid* [Vol. II] through dibromsuccinic acid and acetylenedicarboxylic acid (see under methane [1; U]), and then as above.

[Y.] From *methyl alcohol* [13] through methyl iodide and nitromethane (Bewad, Journ. Russ. Soc. **24**, 126; V. Meyer, Ann. **171**, 32). From the latter through methazonic acid as above under J. Nitromethane is also among the products of interaction of dimethyl sulphate and a nitrite (Kaufler and Pomeranz, Monats. **22**, 492).

[Z.] From *ethylamine* [Vol. II], hydrogen cyanide being among the products of pyrogenic decomposition (Muller, Bull. Soc. [2] **45**, 438).

[AA.] From *malonic acid* [Vol. II] and *ethyl alcohol* [14]. Ethyl malonate on nitration gives a nitromalonic ester, and this on heating with water at 160° yields hydrogen cyanide among other products (Wahl, Comp. Rend. **132**, 1050).

[BB.] From *glycerol* [48] through allyl alcohol (see under ethyl alcohol (14; G]). The latter gives glyoxal by 'contact' oxidation over heated platinum (Trillat, Comp. Rend. **133**, 822). From glyoxal as above under E.

[CC.] From *coumarin* [Vol. II] through coumarone (see under phlorol [64; D]), and then through nitrocoumarone as above under D.

[DD.] From *salicylic aldehyde* [117] and *acetic acid* [Vol. II] through coumarone (see under phlorol [64; E]), and then as above under D.

[EE.] From *cinnamic acid* [Vol. II] through coumarone (see under phlorol [64; F]), and then as above.

[FF.] From *lysine* [Vol. II], hydrogen cyanide being among the products of oxidation by barium permanganate (Zickgraf, Ber. **35**, 3401).

[GG.] *Urea* [Vol. II] gives zinc cyanide on heating with zinc dust (Aufschläger, Monats. **13**, 268).

Organic Cyanides.

NOTE:—The cyanides of allyl, benzyl, and phenylethyl which, chiefly on the authority of Hofmann (Ber. 7, 518; 520; 1293), are included among the products contained in the oils of black and white mustard seed and of various cresses, are now known not to occur as such in the plants, but to result as secondary products of decomposition of the corresponding mustard oils (Gadamer, Arch. Pharm. 237, 111; Ber. 32, 2336; Ter Meulen, Rec. Tr. Ch. 19, 37).

173. Isocyanacetic Acid.

$CN.CH_2.COOH$

NATURAL SOURCE.

This acid, on the authority of Calmels (Bull. Soc. [2] **42**, 266), is said to have been found in toads.

SYNTHETICAL PROCESSES.

[A.] From *acetic acid* [Vol. II] by the interaction of the bromo-acid and *silver cyanide* [172] (Calmels, *loc. cit.*).

[B.] From *glycocoll* [Vol. II] by the action of *chloroform* [1; D] in presence of caustic potash (*Ibid.*).

174. Thiocyanic Acid; Sulphocyanic Acid.

NC.SH

NATURAL SOURCES.

Allyl thiocyanate is possibly present in traces with the isothiocyanate in allyl mustard oil (see latter [166] for natural sources: also Schmidt, Ber. **10**, 187; Gildemeister and Hoffmann, 'Die aetherischen Oele,' p. 538).

Potassium thiocyanate occurs in the urine of man, dogs, horses, and cattle, and also in saliva and gastric juice. (For occurrence in urine see Munk, Virchow's

Arch., **69**, 354; Gscheidlen, Pflüger's Arch. **14**, 401: in saliva, submaxillary and sublingual, Gscheidlen, *loc. cit.*; Oehl, Canstatt's Jahresber. d. Med. **1**, 120; Krüger, Zeit. Biol. **37**, 6; Ch. Centr. 1899, **1**, 53; Grober, Ch. Centr. 1901, **1**, 839: in gastric juice, Kehling, Zeit. physiol. Ch. **18**, 397; Nencki, Ber. **28**, 1318; Nencki and Sieber, Zeit. physiol. Ch. **32**, 291: in nasal and conjunctival secretions, Muck, Ch. Centr. 1900, **2**, 1157: for method of identification in urine, blood, bile, &c., see Bruylants, Journ. Pharm. [5] **18**, 104; 153.)

Synthetical Processes.

[**A.**] From *carbon* through cyanogen (see under hydrogen cyanide [**172**; **A**]). Cyanogen passed over heated potassium polysulphide gives thiocyanate (Wöhler, Pogg. Ann. **3**, 181). Nitrogen passed over a strongly ignited mixture of potassium carbonate (containing sulphate) and charcoal gives a trace of potassium thiocyanate (Erdmann and Marchand, Journ. pr. Ch. **26**, 414). Or cyanogen chloride interacts with ammonia to form cyanamide (Cloëz and Cannizzaro, Ann. **78**, 229), which can be treated as below under **E**. Nitrogenous organic matter (such as *urea*) fused with potassium polysulphide gives potassium thiocyanate (Aufschläger, Zeit. anal. Ch. **35**, 315).

Or carbon dioxide passed over heated sodamide gives cyanamide (Beilstein and Geuther, Ann. **108**, 93; Drechsel, Journ. pr. Ch. [2] **16**, 203). Ammonium carbonate or carbamate heated with sodium also yields cyanamide (Fenton, Trans. Ch. Soc. **41**, 263). Subsequent steps as below under **E**.

Ammonium thiocyanate is produced by the electrolysis of a solution of ammonium hydrosulphide with gas-retort carbon electrodes (Millot, Comp. Rend. **103**, 153; Bull. Soc. [2] **46**, 246).

[**B.**] From *hydrogen cyanide* [**172**] by combination with ammonium polysulphide (Liebig, Ann. **61**, 126). Or metallic cyanides or ferrocyanides [**172**; **A**] give thiocyanates on heating with sulphur or alkaline sulphides (Porret, Gilb. Ann. **53**, 184; Berzelius, Berz. Jahresber. **1**, 48; Wiggers, Ann. **29**, 319; Liebig, Ann. **50**, 349; **51**, 288; **61**, 126; Henneberg, Ann. **73**, 230; Löwe, Jahresber. **1853**, 407; Babcock, Zeit. [2] **2**, 666; Fröhde, Pogg. Ann. **119**, 317: for production of potassium thiocyanate by the fusion of carbon, sulphur, and ammonium sulphate with potassium hydroxide see Fleck, Ding. poly. Journ. **169**, 209: for production of potassium thiocyanate by the interaction of potassium thiosulphate and cyanide see Dobbin, Ch. News, **77**, 131).

[**C.**] From *carbon disulphide* [**160**] and ammonia as under hydrogen cyanide [**172**; **B**].

[**D.**] From *ethyl alcohol* [**14**] and nitric acid, &c., through mercury fulminate (see under benzoic aldehyde [**114**; **A**]). The latter gives ammonium thiocyanate when acted upon by sulphuretted hydrogen (Ber. **8**, 1178).

[**E.**] *Urea* [Vol. II] on heating with sodium or by distillation with quicklime gives cyanamide (Fenton, Trans. Ch. Soc. **41**, 262; Emich, Monats. **10**, 332). The latter on treatment with sulphuretted hydrogen or (better) ammonium sulphide yields thiourea (Baumann, Ber. **6**, 1375; **8**, 26), and this on heating with water at 140° or *per se* at 160–170° becomes converted into ammonium thiocyanate (Haller, Bull. Soc. [2] **45**, 706).

[**F.**] *Guanidine* [Vol. II] is converted into the nitroso-derivative (Thiele, Ann. **273**, 133). The latter on heating with water gives cyanamide (*Ibid.* 136), which can be treated as above under **E**.

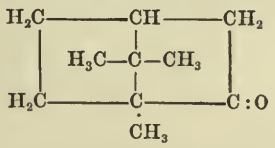
Note:—For the liberation of free thiocyanic acid from its salts see Wöhler, Gilbert's Ann. **69**, 271; Hermes, Zeit. [2] **2**, 417; Journ. pr. Ch. **97**, 465; Zimmermann, Ann. **199**, 1; Klason, Journ. pr. Ch. [2] **35**, 403.

APPENDIX

While the foregoing pages were passing through the press several additional syntheses of natural products have been accomplished. In order to make the present volume as complete as possible, these and other recent discoveries bearing upon the synthetical processes dealt with in the text, together with a few corrections, have been included in this appendix.

CAMPHOR AND TERPENE GROUP.

175. Camphor; 1 : 7 : 7-Trimethyl-1 : 2 : 2-Bicyclo-2-Heptanone.



Natural Sources.

Camphor (d-modification) is obtained from *Cinnamomum camphora* = *Laurus camphora*, which grows in the eastern districts of Central China, in South China, in the Malay Archipelago, in the islands of Formosa and Hainan, and in the S. Japan islands, Kiushiu and Shikoku. l-Camphor occurs in the oil of *Matricaria* (*Pyrethrum*) *parthenium*, common feverfew, which is cultivated in Germany (Dessaignes and Chautard, Journ. pr. Ch. **45**, 45; Chautard, Jahresber. **1863**, 555). Oil of tansy, from *Tanacetum vulgare*, appears also to contain l-camphor (Schimmel & Co., as quoted by Gildemeister and Hoffmann, 'Die aetherischen Oele,' p. 889: see also Persoz, Comp. Rend. **13**, 436; Ann. **44**, 313; Journ. pr. Ch. **25**, 55; Vohl, Arch. Pharm. **124**, 16).

Ordinary (d-) camphor has been found also in oil of spike from *Lavandula spica* (Kane, Journ. pr. Ch. **15**, 163; Dumas, Ann. **6**, 248; Lallemand, Ann. **114**, 197; Bruylants, Journ. Pharm. [4] **30**, 139). Its occurrence in oil of sage from *Salvia officinalis* (Muir, Trans. Ch. Soc. **37**, 678) could not be confirmed by Schimmel & Co. (Ber. Oct. 1895, p. 40). It occurs in oil of sassafras bark to the extent of 6·8 per cent. (Power and Kleber, Pharm. Rev. 1896; Ch. Centr. 1897, **2**, 42), in oil of sweet basil from *Ocimum basilicum* (Bertram and Walbaum, Arch. Pharm. **235**, 176), and in Siam cardamom oil from *Amomum cardamomum* (Schimmel's Ber. Oct. 1897; Ch. Centr. 1898, **1**, 258). Small quantities have been found also in the oil of cinnamon root, Ceylon (Trommsdorff, 'Handb. d. Pharm.' 1827, p. 666; Dumas and Peligot, Ann. **14**, 50; Schimmel's Ber. Oct. 1892), and in oil of rosemary from *Rosmarinus officinalis* (Lallemand, Ann. **114**, 197; Montgolfier, Bull. Soc. [2] **25**, 17; Bruylants, Journ. Pharm. [4] **29**, 508; Pharm. Journ. [3] **10**, 327; Jahresber. **1879**, 944; Haller, Comp. Rend. **108**, 1308). The camphor from this last source is a mixture of the d- and l-modifications (Montgolfier, *loc. cit.*).

Note:—The oil from the leaves of the camphor tree has been examined by Schimmel & Co. (Ber. Oct. 1892) and by Hooper (Pharm. Journ. 56, 21). For determination of camphor in camphor oils see Löhr, Ch. Zeit. 25, 292. For the mode of formation of camphor in the plant see Tschirch and Shirasawa, Arch. Pharm. 240, 257.

Synthetical Processes.

[A.] From *malonic* and *oxalic acids* [Vol. II], *acetone* [106], and *methyl* and *ethyl alcohols* [13; 14]. Acetone is converted into mesityl oxide (see under acetone [106; S, p. 179]), the latter condensed with sodio-malonic ester in alcoholic solution by means of sodium ethoxide so as to form dimethylhydroresorcylic ester, and the ester decomposed by heating with barium hydroxide solution in order to obtain dimethylhydroresorcinol (Komppa, Ber. **32**, 1422: see also Vorländer, Ann. **294**, 314). The latter, on oxidation by sodium hypobromite, yields $\beta\beta$-dimethylglutaric acid (K. *loc. cit.* 1423). The dimethyl ester of this last acid and oxalic ester condense under the influence of sodium ethylate to form diketoapocamphoric ester (*Ibid.* 1424; **34**, 2472). By the action of sodium and methyl iodide the latter is converted into diketocamphoric ester, and this, on reduction in sodium carbonate solution by means of sodium amalgam, gives the corresponding dihydroxycamphoric acid, which, on heating with a strong solution of hydriodic acid in presence of red phosphorus, yields a racemic dehydrocamphoric acid. The latter combines with hydrogen bromide, when heated with an acetic acid solution of the hydracid, to form a saturated β-bromcamphoric acid. The bromo-acid on reduction with zinc dust and acetic acid gives a syrupy mixture of acids, from which, by the action of acetyl chloride, camphoric anhydride is obtained, and this, on solution in alkali and precipitation by acid, yields racemic camphoric acid (*Ibid.* **36**, 4332–4335).

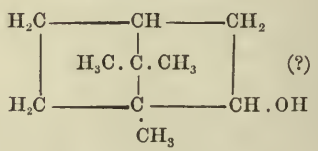
Camphoric anhydride on reduction in alcoholic solution with sodium amalgam is converted into 'campholide' $= C_8H_{14}\langle\begin{smallmatrix}CH_2\\CO\end{smallmatrix}\rangle O$ (Haller, Comp. Rend. **122**, 293), and this on heating with a solution of potassium cyanide is converted into 'cyancampholic acid' (= homocamphoric nitrile), from which homocamphoric acid can be obtained by hydrolysis. The lead or calcium salt of this acid on dry distillation yields camphor (*Ibid.* 446; Bull. Soc. [3] **15**, 324; Haller and Blanc, Comp. Rend. **130**, 376; Bredt and Rosenberg, Ann. **289**, 1).

Note:—$\beta\beta$-Dimethylglutaric acid has been obtained also by the condensation of dimethylacrylic ester (obtained from α-bromisovaleric ester) and sodio-malonic ester and decomposition and hydrolysis of the dimethylpropanetricarboxylic ester thus obtained (Auwers, Ber. 28, 1130; W. H. Perkin, junr., and Goodwin, Trans. Ch. Soc. 69, 1472).

[B.] *Borneol* [176] gives camphor on oxidation by nitric acid (Pelouze, Ann. **40**, 328; Montgolfier, Comp. Rend. **88**, 915; Ann. Chim. [5] **14**, 20. l-Borneol gives ordinary (d-) camphor (Montgolfier, Ann. Chim. [5] **14**, 29: compare Pope and Harvey, Trans. Ch. Soc. **79**, 76).

[C.] *Camphene* [177] gives camphor on contact oxidation by heated spongy platinum (Berthelot, Ann. **110**, 367), or by chromic acid mixture (Riban, Bull. Soc. [2] **24**, 19; Armstrong and Tilden, Trans. Ch. Soc. **35**, 756; Ber. **12**, 1756).

176. Borneol.



Natural Sources.

d-Borneol occurs in the pith cavities of the trunk of *Dryobalanops camphora* (= *aromatica*) from Borneo, Sumatra, Labuan and Jahore in the Straits Settlements (Martius, Ann. **27**, 63; Pelouze, Comp. Rend. **11**, 365; Ann. **40**, 326; Gerhardt, Ann. **45**, 38), in oil of spike from *Lavandula spica* (Bruylants, Journ. Pharm. [4] **30**, 139; Ch. Centr. 1879, 616; Bouchardat, Comp. Rend. **106**, 551; **117**, 53; 1094), in oil of rosemary from *Rosmarinus officinalis* (Bruylants, Journ. Pharm. [4] **29**, 508; Pharm. Journ. [3] **10**, 327; Jahresber. **1879**, 944; Weber, Ann. **238**, 89; Gildemeister and Stephan, Arch. Pharm. **235**, 585; Schimmel's Ber. Oct. 1897; Ch. Centr. 1898, **1**, 258), in Siam cardamom oil from

Amomum cardamomum (Schimmel's Ber. *loc. cit.*), and in lavender oil (*Ibid.* April, 1903; Ch. Centr. 1903, **1**, 1086; Charabot, Bull. Soc. [3] **17**, 380).

l-Borneol occurs in Chinese Ngai camphor from *Blumea balsamifera* (Plowman, Pharm. Journ. [3] **4**, 710; Flückiger, *Ibid.* 829; Hanbury, Jahresber. **1874**, 537; Schimmel's Ber. April, 1895), as ester of formic, acetic, butyric, and isovaleric acids in the oil of valerian (Gerhardt, Ann. **45**, 34; Bruylants, Ber. **11**, 452; Haller, Ann. Chim. [6] **27**, 396; Oliviero, Comp. Rend. **117**, 1096; Bull. Soc. [3] **11**, 150; **13**, 917), as ester of acetic and isovaleric acids in oil of kesso from *Valeriana officinalis* var. *angustifolia* (Bertram and Gildemeister, Arch. Pharm. **228**, 483), in citronella oil from *Andropogon nardus* (Schimmel's Ber. April, 1894), in oil of feverfew, *Matricaria* (*Pyrethrum*) *parthenium* (*Ibid.* Oct. 1894), and in oil of *Asarum canadense* (Power and Lees, Proc. Ch. Soc. **17**, 210).

l-Bornyl acetate is contained in the oils from many Coniferæ :—*Abies canadensis* (oil of hemlock), *A. pectinata*, *A. sibirica*, *Picea vulgaris*, *P. nigra* (or ?*alba*, spruce oil), *P. excelsa*, *Pinus pumilio*, *P. montana* (Bertram and Walbaum, Arch. Pharm. **231**, 290; Schimmel's Ber. Oct. 1897; Ch. Centr. 1898, **1**, 258; Hirschsohn, Pharm. Zeit. f. Russland, 1892, No. 38; Kremers, Pharm. Rund. **13**, 135; Hunkel, Pharm. Rev. **14**, 35).

Borneols or their esters (chiefly acetates) are found also in larch needle oil from *Larix decidua* (Schimmel & Co. *loc. cit.*), in Swedish oil from *Pinus sylvestris* (Bertram and Walbaum, *loc. cit.*), in Virginian snake-root oil from *Aristolochia serpentaria* (Spica, Gazz. **17**, 313), probably in the oil of *Aristolochia reticulata* (Peacock, Am. Journ. Pharm. **63**, 257; Ch. Centr. 1891, **2**, 379), in oil of golden rod from *Solidago* sp. (Schimmel's Ber. Oct. 1891; April, 1894; April, 1897), in oil of thyme from *Thymus vulgaris* (*Ibid.* Oct. 1894), and (d- and l- modifications) in oil of sage from *Salvia officinalis* (*Ibid.* Oct. 1895). Bornyl acetate is contained also in the oil of *Satureia thymbra* from Spain (*Ibid.* Oct. 1889).

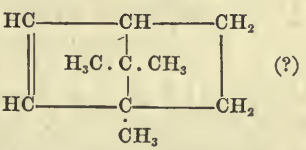
According to Jeanjean (Ann. **101**, 95) the fusel oil of brandy obtained from the spirit produced by the fermentation of the sugar from the madder root contains l-borneol (see Beilstein's 'Handbuch,' III, 471).

Synthetical Processes.

[**A.**] From *camphor* [**175**] by heating with alcoholic potash (Berthelot, Ann. Chim. [3] **56**, 78). Camphor by the action of sodium *per se* or by reduction with sodium in alcoholic or moist ethereal solution gives borneol, the optically isomeric camphors yielding to a preponderating extent the corresponding borneols (Baurigny, Zeit. [2] **2**, 408; **3**, 71; **4**, 208; 481; 687; Kachler, Ann. **197**, 99; Montgolfier, Ann. Chim. [5] **14**, 21; 38; Jackson and Menke, Am. Ch. Journ. **5**, 270; **6**, 406; Kachler and Spitzer, Monats. **5**, 50; Immendorff, Ber. **17**, 1038; Wallach, Ann. **230**, 225; Haller, Comp. Rend. **105**, 227; Ann. Chim. [6] **27**, 416; Brühl, Ber. **24**, 3384; Beckmann, Germ. Pat. 42458 of 1887; Ber. **21**, Ref. 321; Ann. **250**, 322; Ber. **22**, 912: for electrolytic reduction of camphor to borneol see Tafel and Schmitz, Zeit. Electroch. **8**, 288). By the action of sodium on camphor d- and isoborneol are formed (Bertram and Walbaum, Journ. pr. Ch. [2] **49**, 15; Beckmann, *Ibid.* **55**, 35).

[**B.**] From *camphene* [**177**] through camphor [**175**; **C**], and then as above under **A**.

177. Camphene.



Natural Sources.

l-Camphene is contained in citronella oil from *Andropogon nardus* (Schimmel's Ber. Oct. 1893; Bertram and Walbaum, Journ. pr. Ch. [2] **49**, 16), in kesso oil

from the Japanese *Valeriana officinalis* var. *angustifolia* (B. and W. *loc. cit.* 18), and in French oil of valerian (Oliviero, Comp. Rend. **117**, 1096; Bull. Soc. [3] **11**, 150; **13**, 917). d-Camphene is contained in oil of ginger (Schimmel's Ber. Oct. 1893; B. and W. *loc. cit.*), in oil of sweet orange (néroli oil from flowers) (Theulier, Bull. Soc. [3] **27**, 278: see also Hesse and Zeitschel, Journ. pr. Ch. [2] **66**, 481), in oil of spike from *Lavandula spica* (Bouchardat, Comp. Rend. **117**, 1094), and in American oil of turpentine (Schimmel's Ber. Oct. 1897: see also Armstrong and Tilden as below).

i-Camphene occurs in oil of rosemary (Gildemeister and Stephan, Arch. Pharm. **235**, 586; Schimmel's Ber. Oct. 1897).

A camphene is contained in Russian oil of turpentine, probably from *Abies* (*Pinus*) *sibirica* (Golubeff, Journ. Russ. Soc. **20**, 585; Ch. Centr. 1888, **2**, 1622), in French turpentine oil, and probably in other pinene-containing oils from Coniferæ (Armstrong and Tilden, Ber. **12**, 1753; Trans. Ch. Soc. **35**, 742; Power and Kleber, Pharm. Rund. **12**, 16; Bouchardat and Lafont, Comp. Rend. **113**, 551; **125**, 111).

Synthetical Processes.

[**A.**] From *borneol* [**176**] by heating with hydrogen potassium sulphate to 200° (Wallach, Ann. **230**, 239), or with dilute sulphuric acid to 60–100° (Konowaloff, Journ. Russ. Soc. **32**, 76). Or borneol can be converted into bornyl chloride by heating with hydrochloric acid (Berthelot, Ann. **112**, 366), or with phosphorus pentachloride (Wallach, *loc. cit.* 231; Kachler, Ber. **11**, 460; Ann. **197**, 93). The chloride gives camphene on heating with alcoholic potash (Riban, Ann. Chim. [5] **6**, 383), with water and magnesium oxide (Kachler, Ann. **197**, 96), or with aniline (Wallach, *loc. cit.* 233; Ber. **25**, 916). Water alone decomposes the chloride with the formation of camphene (Kachler and Spitzer, Ann. **200**, 342; Riban, *loc. cit.* 382).

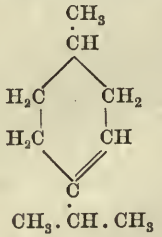
[**B.**] *Camphor* [**175**] on heating with ammonium formate gives formylbornylamine (Leuckart and Bach, Ber. **20**, 104; Wallach and Griepenkerl, Ann. **269**, 347), and this yields bornylamine on hydrolysis with hydrochloric acid. The amine or its formyl derivative gives camphene on heating to 200–210° with acetic anhydride (W. and G. *loc. cit.* 349). Or camphor by the action of phosphorus pentachloride at ordinary temperatures gives camphor chloride, $C_{10}H_{16}Cl_2$ (Spitzer, Ann. **196**, 262), and this on treatment with sodium in ethereal solution yields a camphene (Kachler, Ann. **197**, 127; K. and Spitzer, Ann. **200**, 341; Montgolfier, Ann. Chim. [5] **14**, 104).

Camphor by the action of sodium gives (with d-borneol) isoborneol (Bertram and Walbaum, Journ. pr. Ch. [2] **49**, 15), and this yields camphene on heating in benzene solution with zinc chloride or on boiling with dilute sulphuric acid (*Ibid.* 8). Isoborneol also gives camphene by heating to 220° with zinc dust (Semmler, Ber. **33**, 735).

Note:—Bornylamine is among the products formed by the reduction of camphoroxime with sodium in alcoholic solution (Leuckart and Bach, Ber. 20, 104: for electrolytic reduction of the oxime to bornylamine, see Böhringer and Söhne, Germ. Pat. 141346; Journ. Ch. Soc. 84, I, 551).

Camphor may also be converted into borneol [as under **176**, **A**], and the latter treated as above under **A**.

178. Menthene; Tetrahydro-p-Cymene; 1-Methyl-4-methoethyl-3-cyclohexene.



Natural Source.

According to Labbé menthene is contained in oil of thyme (Bull. Soc.

[3] 19, 1010: compare Gildemeister and Hoffmann, *op. cit.* p. 818). A menthene may occur in peppermint oil (Andres and Andréeff, Ber. 25, 609).

Synthetical Process.

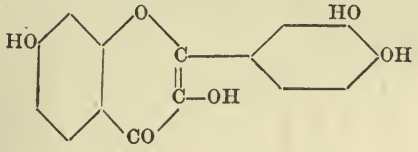
[A.] From *menthol* [41] by heating with sulphuric acid, phosphorus pentoxide, zinc chloride, anhydrous cupric sulphate, or acid potassium sulphate (Walter, Ann. 32, 288; Beckmann, Ann. 250, 358; Brühl, Ber. 25, 143; Sicker and Kremers, Am. Ch. Journ. 14, 291; Urban and Kremers, *Ibid.* 16, 397; Helbing, *Ibid.* 18, 762; Richtmann, *Ibid.* 763; Konowaloff, Journ. Russ. Soc. 32, 76).

Or menthol may be converted into menthyl chloride by heating with phosphorus pentachloride, and the menthyl chloride heated with aniline or quinoline (Wagner, Ber. 27, 1636; Tolloczko, Journ. Russ. Soc. 29, 48; Slawinski, *Ibid.* 118: see also Berkenheim, Ber. 25, 686; Kijner, Journ. Russ. Soc. 27, 473; Wallach, Ch. Centr. 1898, 1, 570; Masson and Reychler, Ber. 29, 1843; Tschugaeff, Ber. 32, 3332).

Note:—Menthene would precede cymene [6, p. 28] in the scheme of chemical classification. It is conveniently introduced here on account of its genetic relationship to the terpenes.

FLAVONE GROUP.

179. Fisetin; 3 : 3^1 : 4^1-Trihydroxyflavonol.



Natural Sources.

The occurrence of fisetin in the wood of *Quebracho colorado* and of *Rhus cotinus* is referred to under catechol [69, p. 139]. Fisetin and a glucoside thereof (not fustin) is also contained in the stem of the yellow cedar, *Rhus rhodanthema*, from N. S. Wales (A. G. Perkin, Trans. Ch. Soc. 71, 1194).

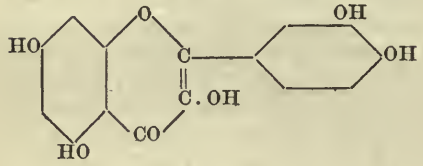
Synthetical Process.

[A.] From *resorcinol* [70], *vanillin* [121], *acetic acid* [Vol. II], *methyl* and *ethyl alcohols* [13; 14]. Resorcinol and acetic acid are converted into resacetophenone (see under pæonol [133; A, p. 231], and the latter into its ethyl ether by ethylation. Vanillin is methylated so as to form the methyl ether (veratric aldehyde), and the latter condensed with the resacetophenone ether by the action of alkali in alcoholic solution so as to form 2^1-hydroxy-4^1-ethoxy-3 : 4-dimethoxychalkone:—

$$C_2H_5 . O[4^1] . C_6H_3\langle{}^{[2^1]OH}_{[1^1]CO} . CH : [1]CH . C_6H_3(OCH_3)_2[3:4]$$

(Kostanecki and Różycki, Ber. 32, 2257). This unsaturated ketone on boiling with an alcoholic solution of dilute sulphuric acid is converted into 3-ethoxy-3^1 : 4^1-dimethoxyflavanone, which by interaction with amyl nitrite forms isonitroso-3-ethoxy-3^1 : 4^1-dimethoxyflavanone. The latter on heating with dilute sulphuric acid in acetic acid solution gives 3-ethoxy-3^1 : 4^1-dimethoxyflavonol, which on boiling with strong hydriodic acid is completely de-alkylated with the formation of fisetin (Kostanecki, Lampe, and Tambor, Ber. 37, 784).

180. Quercetin; 1 : 3 : 3^1 : 4^1-Tetrahydroxyflavonol.

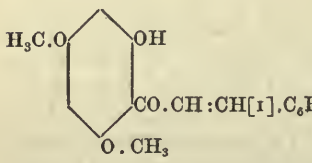


Natural Sources.

The sources of quercetin are given under catechol [**69**, pp. 138, 139]. To these must be added *Prunus spinosa*, *Viola odorata*, and *Trifolium repens*, white clover, in which the colouring-matter has been found (A. G. Perkin and Phipps, Trans. Ch. Soc. **85**, 56). Globulariacitrin, a glucoso-rhamnoside of quercetin, is contained in *Globularia alypum* (Tiemann, Arch. Pharm. **241**, 289).

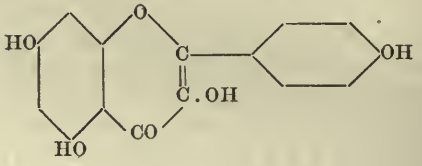
Synthetical Process.

[**A.**] From *phloroglucinol* [**86**], *vanillin* [**121**], *acetic acid* [Vol. II], and *methyl alcohol* [**13**]. Phloroglucinol dimethyl ether (see under hydrocotoïn [**134**; **A**, p. 231]) is condensed with acetyl chloride so as to form phloroacetophenone dimethyl ether (see under chrysin [**138**; **A**, p. 233]), and the latter by condensation with vanillin methyl ether (veratric aldehyde) converted into 2^1-hydroxy-4^1 : 6^1 : 3 : 4-tetramethoxychalkone :—



The latter on heating with alcoholic hydrochloric acid is converted into 1 : 3 : 3^1 : 4^1-tetramethoxyflavanone, from which the isonitroso-derivative is obtained by the action of amyl nitrite. On heating with dilute sulphuric acid in acetic acid the isonitroso-derivative forms 1 : 3 : 3^1 : 4^1-tetramethoxyflavonol, which is demethylated and converted into quercetin by heating with strong hydriodic acid (Kostanecki, Lampe, and Tambor, Ber. **37**, 1402).

181. Kampherol; 1 : 3 : 4^1-Trihydroxyflavonol.

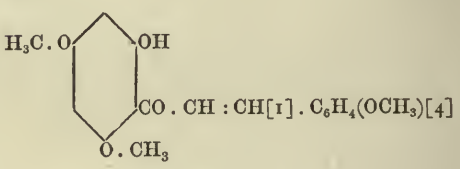


Natural Sources.

Natural sources of kampherol are given under phloroglucinol [**86**, p. 161, and this appendix, p. 287].

Synthetical Process.

[**A.**] From *phloroglucinol* [**86**], *anisic aldehyde* [**120**], *acetic acid* [Vol. II], and *methyl alcohol* [**13**]. Phloracetophenone dimethyl ether (see under chrysin [**138**; **A**, p. 233]) and anisic aldehyde condense in alcoholic solution in presence of sodium hydroxide to form 2^1-hydroxy-4^1 : 6^1 : 4-trimethoxychalkone :—



(Kostanecki and Tambor, Ber. **37**, 792). The latter, on boiling its alcoholic solution with dilute sulphuric acid, is converted into 1 : 3 : 4^1-trimethoxyflavanone, which by the action of nitrous acid (amyl nitrite) yields isonitroso-1 : 3 : 4^1-trimethoxyflavanone. On heating with dilute mineral acids the isonitroso-derivative gives 1 : 3 : 4^1-trimethoxyflavonol, and this, on demethylation by heating with strong hydriodic acid, yields kampherol (Kostanecki, Lampe, and Tambor, Ber. **37**, 2096).

Note :—Fisetin, quercetin, and kampherol belong to the same group as chrysin [**138**, p. 233], tectochrysin [**139**, p. 234], apigenin [**140**, p. 234], and luteolin [**141**, p. 234].

The following modes of occurrence and methods of production are supplementary to those recorded in the preceding pages:—

1. Methane (p. 21).

Methane is among the products of decomposition of egg-meat mixture by *Bacillus coli communis* (Rettger, Am. Journ. Physiol. **8**, 284). A ferment ('pseudosarcine') which produces methane has been obtained by Mazé from dead leaves. According to this author the ferment produces methane from the products formed by the butyric ferments (Comp. Rend. **137**, 887).

To be added to synthetical processes:—

[D, p. 22.] From *ethyl alcohol* [14], methane being among the products formed by passing the vapour over heated carbon, aluminium, or magnesium (Ehrenfeld, Journ. pr. Ch. [2] **67**, 49, &c.). With aluminium ethylene (see note, p. 23) is also produced. Methane is likewise formed by 'contact' decomposition of the vapour by finely divided heated copper, nickel, cobalt, and platinum (Sabatier and Senderens, Comp. Rend. **136**, 738).

Ethylene and methane are also formed by the catalytic action of heated alumina or fire-clay on alcohol vapour (Ipatieff, Ber. **36**, 1990; 2003).

[E, p. 24.] *Isopropyl alcohol* [16] gives methane among the products of decomposition by finely divided heated copper (210°) (Sabatier and Senderens, *loc. cit.* 983).

[J, p. 24.] *Acetone* [106] in aqueous solution yields methane (and acetic acid) by photochemical decomposition (Ciamician and Silber, Ber. **36**, 1575).

For the electrolytic preparation of iodoform from acetone see Howe Abbott, Journ. Physical Ch. 1903, pp. 84–91.

[S, p. 25.] *Malonic acid* [Vol. II] in glycerol or ethylene glycol gives methane among the products of decomposition on heating in a sealed tube (Œ. de Coninck and Raynaud, Comp. Rend. **135**, 1351).

[BB, p. 26.] *Malic acid* [Vol. II] gives methane among other products under the above conditions (*Ibid.*).

[CC, p. 26.] *Citric acid* [Vol. II] when heated in glycerol solution gives methane among other products (*Ibid.*).

[II, p. 26.] *Tartaric acid* [Vol. II] when heated in glycol solution with sulphuric acid gives methane among other products (*Ibid.*).

[JJ, p. 26.] *Camphor* [175] gives methane among the products of decomposition by heating with zinc chloride (Montgolfier, Ann. Chim. [5] **14**, 87). Or on heating with strong hydriodic acid at 200° methyl iodide is formed among other products (Markownikoff and Gorbenko, Ber. **30**, 1216), and this can be converted into methane by reduction, as under C, p. 22. Or on heating at 200° with iodine chloride, chlorinated camphor yields among other products carbon tetrachloride (Ruoff, Ber. **9**, 1048; 1483; 1499), and this can be converted into methane as under L, p. 25.

5. Hentriacontane (p. 28).

A hydrocarbon of the above composition (? normal) has been obtained from the East Indian kô-sam seeds from *Brucea sumatrana* (Power and Lees, Pharm. Journ. [4] **17**, 183).

6. Cymene (p. 28).

To be added to synthetical processes (p. 33):—

[N.] 'Terpinene is readily converted into cymene by the oxidising influence of sulphuric acid' (Heusler's 'Chemistry of the Terpenes,' Pond, p. 113).

[O.] From *camphor* [175] by heating with zinc chloride (?), phosphorus pentoxide, pentachloride or pentasulphide, or strong hydrochloric acid (Gerhardt, Ann. **48**, 234; Dumas and Delalande, Ann. **38**, 342; Pott, Ber. **2**, 121; Fittig, Köbrich, and Jilke, Ann. **145**, 129; Wright, Journ. Ch. Soc. **26**, 686; Beckett and Wright, *Ibid.* **29**, 1; Reuter, Ber. **16**, 694; Armstrong and Miller, Ber. **16**, 2259; Alexejeff, Journ. Russ. Soc. **12**, 187: according to Bredt, Rochussen, and Monheim, Ann. **314**, 369, carvenone is an intermediate product).

[P.] *Camphene* [177] when heated with phosphorus pentoxide gives an oily product, which may contain cymene (Heusler's 'Chemistry of the Terpenes,' Pond, p. 59).

[Q.] From *menthene* [178] by heating with anhydrous cupric sulphate at 250° (Brühl, Ber. **25**, 151).

7. Styrene (p. 33).

To be added to synthetical processes:—

[A, p. 33.] The formation of styrene from nascent acetylene and benzene in presence of aluminium chloride is confirmed by Parone (Journ. Ch. Soc. **86**, I, 26; from L'Orosi, **25**, 148).

9. Dipentene and Limonene (p. 36).

The presence of this hydrocarbon in néroli oil is confirmed by Hesse and Zeitschel (Journ. pr. Ch. [2] **66**, 481) and by Walbaum and Hüthig (*Ibid.* **67**, 315). The last-named authors (*loc. cit.*) confirm also the presence of dipentene in petit-grain oil from Paraguay. For further reference to the occurrence of l-limonene in verbena oil from *Verbena triphylla* see Theulier, Bull. Soc. [3] **27**, 1113.

13. Methyl Alcohol (p. 40).

The cohobation water of oil of savin from *Juniperus sabina* and the distillation water from the oil of W. Indian sandal-wood contain methyl alcohol (Schimmel's Ber. April, 1903; Ch. Centr. 1903, **1**, 1086). The presence of methyl salicylate and benzoate in ylang-ylang oil is confirmed (*Ibid.*), and the occurrence of methyl anthranilate in this same oil recorded (*Ibid.*). Methyl salicylate is a constituent of the oil of cassia flowers from *Acacia cavenia* and *A. farnesiana* (Walbaum, Journ. pr. Ch. [2] **68**, 235), and methyl anthranilate a constituent of the essential oil of tuberose blossoms. This last oil, when obtained by 'enfleurage' instead of by extraction with petroleum, contains also methyl salicylate (Hesse, Ber. **36**, 1459). Methyl anthranilate has been found in petit-grain oil from Paraguay (Walbaum and Hüthig, Journ. pr. Ch. [2] **67**, 315: for estimates of the quantities of methyl anthranilate and other constituents of average oil of néroli see further Hesse and Zeitschel, *Ibid.* **66**, 481).

To be added to synthetical processes:—

[D, p. 44.] Formic aldehyde gives methyl alcohol by catalytic reduction by hydrogen in presence of finely divided heated nickel at 90° (Sabatier and Senderens, Comp. Rend. **137**, 301).

[F, p. 44.] For the industrial production of methyl alcohol (and formic aldehyde) by the electrolysis of sodium acetate in presence of sodium chlorate see Moest's Germ. Pat. 138442; Journ. Ch. Soc. **84**, I, 546.

[L, p. 44.] *Camphor* [175] gives methyl iodide among other products when heated with strong hydriodic acid at 200° (Markownikoff and Gorbenko, Ber. **30**, 1216). From methyl iodide through methyl acetate followed by hydrolysis, or by any of the usual methods.

14. Ethyl Alcohol (p. 44).

Further researches on anaerobic, intramolecular alcoholic fermentation in sugar-beet have been published by Stoklasa, Jelínek, and Vítek (Beit. ch. Physiol. u. Path. **3**, 460; Zeit. Zucker-Ind. Böhm. **27**, 633), and in peas in potassium nitrate solution with dextrose or peptone by Nabokich (Ber. deutsch. bot. Gesell., **21**, 398; Ch. Centr. 1903, **2**, 1012). Further studies of the enzymes from the cells of the higher animals and plants which produce this fermentation have been undertaken by Stoklasa and Czerny (Ber. **36**, 4058). According to Cohnheim (Centr. Physiol. **17**, No. 17) and to Batelli (Comp. Rend. **137**, 1079) this alcoholic fermentation by supposed animal enzymes is due to micro-organisms.

With reference to selective fermentative action in connexion with stereochemical configuration (pp. 46–47), *Schizo-Saccharomyces octosporus* of Beyerinck and *Mucor alternans* ferment mal-

tose and methyl-d-glucoside, but not cane-sugar or α-methyl-d-fructoside. The enzymes extracted from cultivated *Aspergillus niger* resolve amygdalin and the β-d-glucosides, but not lactose or methyl-d-galactosides. Duclaux, Kayser, and Adametz's milk-sugar fermenting yeasts ferment milk-sugar and β-methyl-d-galactoside, and give an enzyme which acts on the two galactosides (Pottevin, Comp. Rend. **136**, 169).

With respect to 'zymase' (p. 48) the velocity of decomposition of dextrose and lævulose by the commercial product has been determined by Herzog, and found to agree with ordinary 'catalytic' actions (Zeit. physiol. Ch. **37**, 149). The velocity of the fermentative decomposition of dextrose by yeast has been determined by Aberson (Rec. Tr. Ch. **22**, 78). Further experiments on the fermentative properties of yeast-extract have been made by Meisenheimer (Zeit. physiol. Ch. **37**, 518).

The 'acclimatisation' of yeasts (p. 50) to solutions containing sodium fluoride and the fermentation of the must of Indian figs by such yeasts have been investigated by Ulpiani and Sarcoli (Atti Real. Accad. [5] **11**, II, 173). The species investigated were *S. pastorianus* II and *S. cerevisiæ*.

The mould, *Oïdium lactis* (p. 50), when grown upon media containing lævulose causes alcoholic fermentation of this sugar (Teichert, Milch-Zeit. **31**, 801; Journ. Ch. Soc. **84**, II, 229). The butyric ferment, *Clostridium pastorianum*, from the soil of St. Petersburg, forms alcohol (small quantity) among the products of fermentation of dextrose in presence of appropriate nitrogenous nourishment (Winogradsky, Centr. Bakter. II, **9**, 4354, 107–112). An organism isolated from milk, *Enterococcus*, decomposes sugars with the production of alcohol (traces) among other products (Tissier and Gasching, Ann. Inst. Past. **17**, 540). Alcohol has been found in milk which has undergone natural curdling (Kozai, Bied. Centr. **32**, 273). The bacteria which are capable of decomposing bone produce alcohol when sugar is added to the nutrient solution (Stoklasa, Duchâček, and Pitra, Beit. ch. Physiol. u. Path. **3**, 322). The bacteria capable of fermenting sugar belong to the type of *Bacillus coli communis* of Escherich, and produce alcohol from dextrose to the extent of 1·2 to 2·0 per cent. by weight (König, Spieckermann, and Olig, Abst. in Journ. Ch. Soc. **84**, II, 386). Alcohol is a product of glycolysis by the minced pancreas, liver, &c., or the juices expressed from these organs (Feinschmidt, Beit. ch. Physiol. u. Path. **4**, 511).

To be added to synthetical processes:—

[**D**, p. 54.] Alcohol is among the products of oxidation of ethane by ozone (Bone and Drugman, Proc. Ch. Soc. **20**, 127).

[**H**, p. 55.] *Acetic aldehyde* [**92**], when the vapour mixed with hydrogen is passed over finely divided nickel heated to 140°, gives an almost quantitative yield of alcohol (Sabatier and Senderens, Comp. Rend. **137**, 301).

[**S**, p. 56.] The amyl ester of acetic acid gives ethyl alcohol when reduced with sodium in amyl alcohol solution (Bouveault and Blanc, Comp. Rend. **137**, 60).

[**MM**, p. 58.] *Isopropyl alcohol* [**16**] gives ethane among other products by the catalytic action of finely divided, reduced copper at 210° (Sabatier and Senderens, Comp. Rend. **136**, 983). From ethane as under **D**, p. 54.

[**NN**, p. 58.] *Glycol* [**45**] gives ethyl iodide on heating with strong aqueous hydriodic acid. From ethyl iodide the alcohol can be obtained by any of the ordinary processes. Or from glycol through glycol chlorhydrin = chlorethyl alcohol (see under n-propyl alcohol [**15**; **A**, p. 59] and under isopropyl alcohol [**16**; **C**, p. 66]), the latter giving ethyl alcohol on reduction with sodium amalgam (Lourenço, Ann. **120**, 92).

Note:—Ethylene is also a direct generator of glycol chlorhydrin [**15**; **A**, p. 59, and **16**; **C**, p. 66].

[**OO**, p. 58.] *Camphor* [**175**] gives methyl iodide (see under methane [**1**; Appendix, **JJ**, p. 277]). From the latter through ethane, as under **D**, p. 54.

15. Normal Propyl Alcohol (p. 58).

Propyl alcohol is among the products of the butyric fermentation of dextrose by *Clostridium pastorianum* (Winogradsky, Centr. Bakter. II, **9**, 4354; 107–112).

To be added to synthetical processes:—

[**E**, p. 59.] Or allyl bromide in ethereal solution is acted upon by carbon dioxide in presence of magnesium with the formation of vinylacetic acid (Houben, Ber. **36**, 2897). From the latter through crotonic acid, as under **W**, p. 63, and **I**, p. 60, &c.

NOTE:—This synthesis of vinylacetic acid from glycerol *via* allyl bromide relates also to *formic aldehyde* [**91**; **GG**, p. 174], *acetic aldehyde* [**92**; **Z**, p. 180], and to *hexoic aldehyde* [**96**; **C**, p. 186].

[**N**, p. 61.] Propionic aldehyde is reduced to the alcohol by hydrogen under the contact influence of finely divided nickel at 102–145° (Sabatier and Senderens, Comp. Rend. **137**, 301).

16. Isopropyl Alcohol (p. 64).

To be added to synthetical processes:—

[**A**, p. 65.] Acetone vapour mixed with hydrogen and passed over finely divided nickel heated to 115–125° gives isopropyl alcohol (Sabatier and Senderens, *loc. cit.*).

[**B**, p. 65.] The vapour of n-propyl alcohol is decomposed at 560° by the 'contact' action of alumina into propylene and water almost quantitatively (Ipatieff, Ber. **36**, 1990).

[**O**, p. 67.] Acetyl carbinol (acetol) gives isopropyl alcohol among other products by direct reduction with sodium amalgam in alkaline solution (Kling, Comp. Rend. **135**, 970; Bull. Soc. [3] **29**, 92: see also under **A**, p. 65).

[**QQ**, p. 69.] From *camphor* [**175**], which gives isopropyl iodide among other products on heating with strong aqueous hydriodic acid at 200° (Markownikoff and Gorbenko, Ber. **30**, 1216). From the iodide as under **B**, p. 65.

17. Normal Butyl Alcohol (p. 69).

[**A**, p. 70.] From ethyl alcohol through ethylene oxide (see under acetic aldehyde [**92**; **A**, p. 175]). The latter interacts with magnesium ethyl bromide in ethereal solution at −15° to form a product which yields n-butyl alcohol on distillation in steam (Grignard, Comp. Rend. **136**, 1260).

[**L**, p. 71.] Methyl butyrate on reduction with sodium in alcoholic solution gives n-butyl alcohol (Bouveault and Blanc, Comp. Rend. **137**, 60).

18. Isobutyl Alcohol (p. 72).

For occurrence of butyl (? isobutyl) alcohol in Roman oil of chamomile see further Blaise, Bull. Soc. [3] **29**, 327. Isobutyl alcohol is among the products of butyric fermentation of dextrose by *Clostridium pastorianum* (Winogradsky, Centr. Bakter. II, **9**, 4354; 107–112).

To be added to synthetical processes:—

[**A**, p. 72.] Tertiary butyl alcohol also gives isobutylene by catalytic decomposition on passing the vapour over finely divided copper heated to 280–400° (Sabatier and Senderens, Comp. Rend. **136**, 983).

[**D**, p. 73.] Or from acetone through diacetonamine or mesityl oxide (see under acetic aldehyde [**92**; **S**, p. 179]). Diacetonamine by the action of nitrous acid is transformed into diacetone alcohol = dimethylacetonyl carbinol (Heintz, Ann. **178**, 342: see also Ann. **169**, 114). The latter is oxidised by bromine in presence of aqueous alkali to β-hydroxyisovaleric acid (Kohn, Monats. **24**, 765). From the latter through β-dimethylacrylic acid and isobutylene as under **C**, p. 73. Or mesityl oxide, on oxidation with bromine in presence of alkali, gives β-dimethylacrylic acid directly (Kohn, *loc. cit.*).

NOTE:—This synthesis affects also tertiary butyl alcohol [**19**; **D**, p. 75] and isobutyric aldehyde [**94**; **E**, p. 182].

[**E**, p. 73.] The vapour of isobutyric aldehyde mixed with hydrogen and passed over finely divided nickel at

135–160° gives isobutyl alcohol by catalytic reduction (Sabatier and Senderens, Comp. Rend. **137**, 301).

19. Tertiary Butyl Alcohol (p. 73).

[**B**, p. 74.] Isobutyl alcohol gives isobutylene as the only olefine by pyrogenic 'contact' decomposition of its vapour by heated alumina (Ipatieff, Ber. **36**, 2003). Isobutylene is absorbed at 0° by aqueous hydrobromic acid with the formation of tertiary butyl bromide, which can be converted into the alcohol by the usual processes (Ipatieff and Ogonowsky, *Ibid.* 1988; Journ. Russ. Soc. **35**, 452).

[**K**, p. 76.] From *methyl alcohol* [**13**] and *phosgene*, formed by the combination of carbon monoxide and chlorine. Magnesium methiodide and phosgene interact with the formation of trimethyl carbinol (Grignard, Comp. Rend. **136**, 815).

21. Methylpropyl Carbinol (p. 77).

To be added to synthetical processes :—

[**B**, p. 77.] Butyramide and magnesium methiodide interact to form a compound which is decomposed by water into methylpropyl ketone (Béis, Comp. Rend. **137**, 575).

[**E**, p. 78.] Propionic acid and *ethyl alcohol* [**14**] also yield diethyl ketone by the interaction of propionamide and magnesium ethobromide, and decomposition of the product with water (Béis, *loc. cit.*).

22. Isoamyl Alcohol (p. 79).

For occurrence of isoamyl alcohol in Roman oil of chamomile see further Blaise, Bull. Soc. [3] **29**, 327. An amyl alcohol (probably isoamyl) has been found in oil of lavender (Schimmel's Ber. April, 1903; Ch. Centr. 1903, **1**, 1086).

To be added to synthetical processes :—

[**A**, p. 80.] Isovaleric aldehyde vapour, when mixed with hydrogen and passed over reduced nickel at 135–165°, gives isoamyl alcohol by catalytic reduction (Sabatier and Senderens, Comp. Rend. **137**, 301).

[**C**, p. 80.] From *methyl* and *ethyl alcohols* [**13**; **14**] and *tartaric acid* [Vol. II]. The latter is converted into pyroracemic (pyruvic) acid (see under benzyl alcohol [**54**; **N**, p. 114]), and the ethyl ester of the latter allowed to interact with magnesium methiodide, when isoamyl α-hydroxyisobutyrate is formed (Grignard, Comp. Rend. **135**, 627). The alcohol could be obtained from its ester by hydrolysis.

Note :—Generators of pyroracemic acid other than tartaric acid are available for this synthesis.

24. Isohexyl Alcohol (p. 82).

To be added to synthetical processes :—

[**C**, p. 82.] From *ethyl* and *isobutyl alcohols* [**14**; **18**] and *acetoacetic ester* [Vol. II]. Ethyl isobutyl-acetoacetate on reduction in alcoholic solution with sodium gives isohexyl alcohol (Bouveault and Blanc, Comp. Rend. **137**, 328).

25. Active Hexyl Alcohol (p. 83).

Further confirmation of the presence of this alcohol in Roman oil of chamomile is given by Blaise, Bull. Soc. [3] **29**, 327.

27. Isoheptyl Alcohol (p. 83).

To be added to synthetical processes :—

[**A**, p. 83.] Or from ethyl alcohol through ethylene oxide [**92**; **A**, p. 175] and isoamyl magnesium bromide. The latter interacts with ethylene oxide in ethereal solution to form a compound which gives isoheptyl alcohol on steam distillation (Grignard, Comp. Rend. **136**, 1260).

28. Normal Primary Octyl Alcohol (p. 84).

To be added to synthetical processes :—

[C, p. 84.] From *n-octoic acid* [Vol. II], the methyl ester of which gives n-octyl alcohol on reduction with sodium in alcoholic solution (Bouveault and Blanc, Comp. Rend. **136**, 1676).

29. Secondary Nonyl Alcohol = Methyl-n-heptyl Carbinol (p. 85).

For further details concerning the production of this alcohol by the reduction of the ketone see Thoms and Mannich, Ber. **36**, 2544.

30. Secondary Hendecatyl Alcohol = Methyl-n-nonyl Carbinol (p. 85).

See further Thoms and Mannich as above for the production of this alcohol from the ketone.

35. Dimethylheptenol (p. 86).

[B, p. 86.] Barbier's synthesis of this alcohol from methylheptenone and magnesium methiodide has been repeated by Harries and Weil (Ber. **37**, 845).

36. Geraniol (p. 87).

Further observations on the occurrence of geraniol and geranyl acetate in néroli oil are given by Hesse and Zeitschel (Journ. pr. Ch. [2] **66**, 481 : compare Walbaum and Hüthig, *Ibid.* **67**, 315), in lavender oil by Schimmel & Co. (Sch. Ber. April, 1903 ; Ch. Centr. 1903, **1**, 1086). Geranyl caproate is also present in this last oil (*Ibid.*). The presence of geraniol and geranyl acetate in petit-grain oil from Paraguay is confirmed by Walbaum and Hüthig (*loc. cit.*). The influence of season, temperature, &c., upon the composition of petit-grain oil has been studied by Jeancard and Satie (Bull. Soc. [3] **29**, 1088).

37. Linaloöl (p. 88).

The quantity of linalyl acetate in néroli has been estimated by Hesse and Zeitschel (Journ. pr. Ch. [2] **66**, 481). The presence of l-linaloöl and its ester in this oil and in petit-grain oil from Paraguay is recorded also by Walbaum and Hüthig (*Ibid.* **67**, 315). Linaloöl has been found in the oil from the bark of *Cinnamomum pedatinervium* from Fiji (Goulding, Trans. Ch. Soc. **83**, 1099).

38. Citronellol (p. 89).

d-Citronellol is the alcohol corresponding to d-citronellal (p. 192), and its formula is accordingly :—

$$CH_2 : C(CH_3)[CH_2]_3 . CH(CH_3) . CH_2 . CH_2 . OH$$

2 : 6-Dimethyl-1-octenol-8.

For occurrence in Réunion geranium oil see further Tiemann and Schmidt, Ber. **30**, 36.

The formula given on p. 89 is that of the l-alcohol contained in the plant oils there referred to, and is the 'rhodinol' of Barbier and Bouveault. Since l-citronellol and d-citronellol are now proved to be *structurally* isomeric the former name is inappropriate.

Note :—The synthetical process A on p. 89 gives d-citronellol and not rhodinol. d-Rhodinol may be contained in pelargonium oil (Monnet and Barbier, Comp. Rend. 117, 1092 ; Barbier and Bouveault, *Ibid.* 122, 530 ; 673 ; Bouveault, Bull. Soc. [3] 23, 458 ; 465).

39. Terpineol = 1-Methyl-4-methoethylol-4[1]-cyclohexene-1 (p. 90).

d-Terpineol is contained in néroli oil and in the oil mixed with the aqueous distillate from orange flowers (Hesse and Zeitschel, Journ. pr. Ch. [2] **66**, 497 : for occurrence in néroli oil and in petit-grain oil from Paraguay see also Walbaum and Hüthig, *Ibid.* **67**, 315). l-Terpineol is present in distilled oil of limes (Burgess and Page, Trans. Ch. Soc. **85**, 414).

To be added to synthetical processes :—

[D, p. 91.] From *methyl* and *ethyl alcohols* [13; 14], *glycerol* [48], *potassium cyanide* [172], and *acetic acid* [Vol. II]. Ethyl chloracetate is converted into ethyl cyanacetate by interaction with potassium cyanide and glycerol into β-iodopropionic acid and ester (see under resorcinol [70; F, p. 114] and, for preparation of β-iodopropionic ester, also W. H. Perkin, junr., Trans. Ch. Soc. 85, 422, note). Cyanacetic and β-iodopropionic esters condense under the influence of sodium ethoxide to form ethyl γ-cyanopentane-αγε-tricarboxylate: the latter on hydrolysis by hydrochloric acid yields pentane-αγε-tricarboxylic acid (*Ibid.* 422). The tricarboxylic acid when digested with acetic anhydride gives δ-ketohexahydrobenzoic acid, the ester of which interacts with magnesium methiodide to form among other products *cis*-δ-hydroxyhexahydro-p-toluic acid (W. H. P., junr., Proc. Ch. Soc. 20, 86: see also Stephan and Helle, Ber. 35, 2153). The latter acid (or its lactone formed by the action of heat) combines with hydrogen bromide to form δ-bromhexahydro-p-toluic acid, and this on debromination by the action of pyridine or sodium carbonate is converted into Δ^3-tetrahydro-p-toluic acid, the ester of which interacts in ethereal solution with magnesium methiodide to form a product which yields inactive terpineol on decomposition by hydrochloric acid (W. H. P., junr., *loc. cit.*).

Note :—Succinic acid is also a generator of β-iodopropionic acid (see under resorcinol [70; F, p. 145]). Cyanacetic acid is also obtainable from oxalacetic ester (see under n-propyl alcohol [15; Z, p. 63]).

40. Cineole (p. 91).

Cineole (eucalyptole) is always present in peppermint oil from *Mentha piperita* (Charabot and Hébert, Ann. Agronom. 28, 595). The presence of cineole in lavender oil has been confirmed (Schimmel's Ber. April, 1903; Ch. Centr. 1903, 1, 1086). Cineole is a constituent of the oil of Californian laurel from *Umbellularia californica* (Power and Lees, Proc. Ch. Soc. 20, 88).

41. Menthol (p. 93).

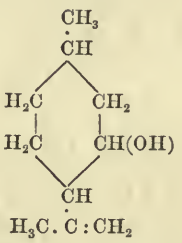
For variation in composition of peppermint oil from *Mentha piperita* according to climate, cultivation, &c., see Charabot and Hébert, Ann. Agronom. 28, 595. For quantities of menthol in Italian peppermint oils see Zay, Staz. sper. agrar. 35, 816; Ch. Centr. 1903, 1, 331.

To be added to synthetical processes :—

[B, p. 93.] For reduction of menthone to menthol see further Beckmann's Germ. Pat. 42458 of 1887; Ber. 21, Ref. 321.

42. Isopulegol (p. 93).

The relationship of this compound to d-citronellal [105] and the modification of the formula of the latter (see this appendix under citronellol [38, above]) makes the formula of isopulegol :—



For transformation of d-citronellal into isopulegol by the action of dilute sulphuric acid see Barbier and Leser, Comp. Rend. 124, 1309.

44. Methylacetyl Carbinol (p. 94).

To be added to synthetical processes :—

[D, p. 94, note.] Magnesium ethiodide or bromide and *acetamide* interact to form a compound which on decomposition by water yields methyl ethyl ketone (Béis, Comp. Rend. 137, 575).

48. Glycerol (p. 96).

Glycerol is formed during the anaerobic (intramolecular) respiration of the sugar beet (Stoklasa, Jelínek, and Vítek, Zeit. Zucker-Ind. Böhm. **27**, 633).

According to Nicloux, glycerol (traces) is normally present in the blood of dogs and rabbits (Comp. Rend. **136**, 764; 1576: compare Mouneyrat, Comp. Rend. Soc. Biol. **55**, 1207; Nicloux, *Ibid.* 1229).

51. Mannitol (p. 104).

The ferment of sour wine forms mannitol in presence of lævulose. Reducing bacteria which liberate hydrogen and the amylo-bacteria cultivated in invert sugar solution in presence of chalk are incapable of producing mannitol from lævulose (Mazé and Perrier, Ann. Inst. Past. **17**, 597).

54. Benzyl Alcohol (p. 107).

Benzyl alcohol and ester are present in the oil obtained from tuberose blossoms by distillation or by enfleurage (Hesse, Ber. **36**, 1459). Benzyl alcohol (with its acetic and benzoic esters) is contained in ylang-ylang oil (Schimmel's Ber. April, 1903; Ch. Centr. 1903, **1**, 1086).

To be added to synthetical processes:—

[**A**, p. 108.] Benzene can be converted into toluene by the interaction of phenyl magnesium bromide and dimethyl sulphate in ethereal solution (Werner and Zilkens, Ber. **36**, 2116; Houben, *Ibid.* 3083; Werner, *Ibid.* 3618).

[**R**, p. 115.] Phthalic acid can be obtained from the naphthols, nitronaphthalene, the naphthylamines, nitronaphthols, naphthalene sulphonic acids, &c., by oxidising with metallic oxides in presence of heated alkaline hydroxides (Basler, Ch. Fab. Germ. Pats. 138790; 139956; 140999; Journ. Ch. Soc. **84**, I, 487; 561).

[**DD**, p. 116.] Sodium ethyl succinate on electrolysis gives, among other products, a small quantity of ethyl acrylate (Bouveault, Bull. Soc. [3] **29**, 1043). From acrylic acid as under **I**, p. 111, &c.

[**KK**, p. 116.] *Camphor* [**175**] gives toluene among the products of its decomposition by heating with zinc chloride (Fittig, Köbrich, and Jilke, Ann. **145**, 129; Reuter, Ber. **16**, 694), or with zinc dust (Schrötter, Ber. **13**, 1621).

55. Saligenin (p. 116).

The quantity of salicin in buds, leaves, and bark of *Salix purpurea* at various periods of growth has been determined by Weevers (Proc. k. Akad. Wetensch. Amsterdam, **5**, 295).

57. Phenylethyl Alcohol (p. 118).

For occurrence of this alcohol in néroli oil see further Walbaum and Hüthig, Journ. pr. Ch. [2] **67**, 315: also Schimmel's Ber. April, 1903; Ch. Centr. 1903, **1**, 1086.

To be added to synthetical processes:—

[**A**, p. 118.] Phenylacetic ethyl ester is reduced to phenylethyl alcohol by sodium in alcoholic solution (Bouveault and Blanc, Comp. Rend. **137**, 60).

Note:—The alcohol obtained by Grignard and Tissier (Comp. Rend. **134**, 107) by the condensation of trioxymethylene and magnesium benzyl chloride is not, as at first supposed, benzyl carbinol, but the isomeric o-toluyl carbinol (Tiffeneau and Delange, Comp. Rend. **137**, 573).

58. Methylphenyl Carbinol (p. 118).

The alcohol has been found in the steam-distilled oil of orange blossoms (Hesse and Zeitschel, Journ. pr. Ch. [2] **66**, 481).

59. Phenylpropyl Alcohol (p. 119).

To be added to synthetical processes:—

[**B**, p. 119.] From *cinnamic acid* [Vol. II], the ethyl ester of which gives the above alcohol on reduction

with sodium in alcoholic solution (Bouveault and Blanc, Comp. Rend. **137**, 328).

60. Phenol (p. 119).

Phenol is among the products of the decomposition of fodder by micro-organisms (König, Spieckermann, and Olig, Journ. Ch. Soc. **84**, II, 447).

To be added to synthetical processes :—

[**A**, p. 120.] Haloid derivatives of benzene, e. g. brombenzene, interact with magnesium in ethereal solution to form a phenyl-magnesium halide, which is oxidised by air with the formation of a product which yields phenol (18 per cent.) on treatment with aqueous alkali (Bodroux, Bull. Soc. [3] **31**, 33).

[**U**, p. 124, note.] For preparation of glutaconic ester from acetonedicarboxylic acid *via* β-hydroxyglutaric acid see further Blaise, Bull. Soc. [3] **29**, 1012.

61. Orthocresol (p. 124).

To be added to synthetical processes :—

[**A**, p. 124.] Also from toluene through o-bromtoluene, o-bromtoluyl magnesium bromide, and oxidation, &c., of latter as under phenol (**60**; **A**, above; Bodroux, *loc. cit.*).

[**J**, p. 127.] Dihydrocarveol by oxidation is converted into trihydroxyhexahydrocymene, which by further oxidation with sulphuric and chromic acids gives 1-methyl-4-ethylonecyclohexanol-2, and this by the action of sodium hypobromite yields 1-methylcyclohexanol-2-carboxylic-4-acid. By the action of bromine at 190° the latter is converted into 2-hydroxy-p-toluic acid (Tiemann and Semmler, Ber. **28**, 2144 : see also Einhorn and Willstätter, Ann. **280**, 88), which gives o-cresol as under **A**, p. 125.

[**L**, p. 128.] From *camphor* [**175**] through cymene and then as under **C**, p. 127. According to Reuter (Ber. **16**, 694), o-cresol is among the products obtained by heating camphor with zinc chloride. Pseudocumene is also among the products of decomposition of camphor by this last process (*Ibid.*) and possibly among the products obtained by heating camphor with zinc dust (Schrötter, Ber. **13**, 1621). From pseudocumene through m-xylene, &c., as under **B**, p. 126.

62. Metacresol (p. 128).

To be added to synthetical processes :—

[**A**, p. 129.] p-Xylene can be obtained also from toluene or benzene by the interaction of p-toluyl magnesium bromide and dimethyl sulphate (Werner and Zilkens, Ber. **36**, 2116), or of p-bromphenyl magnesium bromide and dimethyl sulphate in ethereal solution (Houben, *Ibid.* 3083).

[**C**, p. 129.] Or the ethyl ester of m-hydroxyuvitic (= α-coccinic) acid is decomposed on heating with the formation of 5-hydroxy-o-toluic acid (Claisen, Ann. **297**, 46). From the latter as under **A**, p. 128.

Note :—m-Hydroxyuvitic ester has been obtained also from ethoxymethylene-acetoacetic ester (from acetoacetic and orthoformic ethyl esters condensed by means of acetic anhydride, Claisen, Ber. **26**, 2731) and acetonedicarboxylic ester (see under orcinol [**75**; **C**, p. 154]). The two esters condense in presence of sodium ethylate to form methylhydroxytrimesic triethyl ester, the sodium derivative of which is converted into the diethyl ester on boiling with water. The diethyl ester on distillation at 220–230° under 60 mm. pressure gives m-hydroxyuvitic acid (Errera, Ber. **32**, 2785 ; for production of the ethyl ester of m-hydroxyuvitic acid from methenylbisacetoacetic ester see further Claisen, Ann. **297**, 43).

[**K**, p. 130.] From *camphor* [**175**], p-xylene being among the products formed by heating this compound with zinc dust (Schrötter, Ber. **13**, 1621). From p-xylene as under **A**, p. 129.

63. Paracresol (p. 130).

To be added to synthetical processes :—

[**A**, p. 131.] Or from toluene through p-bromtoluene, p-bromtoluyl magnesium bromide, and oxidation, &c., of the latter as under phenol (**60**; **A**, above in this appendix; Bodroux, Bull. Soc. [3] **31**, 33).

[G, p. 133.] From *phenylacetic acid* [Vol. II] through the 2:4-dinitro-acid and 2:4-dinitrotoluene (see under o-cresol [61; H, p. 127]). From the latter as under A, p. 131.

64. Phlorol (p. 133).

To be added to synthetical processes:—

[A, p. 133.] Ethylbenzene can be obtained from *toluene* by the interaction of benzyl magnesium chloride and dimethyl sulphate in ethereal solution (Houben, Ber. **36**, 3083). Also by the action of nascent *acetylene* on benzene in presence of aluminium chloride (Parone, Journ. Ch. Soc. **86**, I, 26).

66. Carvacrol (p. 135).

To be added to synthetical processes:—

[C, p. 136.] *Camphor* [175] gives carvacrol when heated with iodine (Kekulé and Fleischer, Ber. **6**, 1088: see also Claus, Journ. pr. Ch. **25**, 264; Schweizer, *Ibid.* **26**, 118; Ann. **40**, 329; Armstrong and Miller, Ber. **16**, 2259). Carvacrol is among the products formed by heating camphor or bromcamphor with zinc chloride (Armstrong and Miller, *loc. cit.* 2255; R. Schiff, Ber. **13**, 1408).

69. Catechol (p. 137).

The catechol (protocatechuic acid) complex is apparently contained in the colouring-matter of the Japanese 'fukugi' (A. G. Perkin and Phipps, Trans. Ch. Soc. **85**, 60). The catechol complex may be contained in epinephrine = adrenalin = suprarenin, the active principle of the suprarenal glands (Jowett, Proc. Ch. Soc. **20**, 18). The cerebrospinal fluid from a case of hydrocephalus examined by Coriat did not contain catechol (Am. Journ. Physiol. **10**, 111: compare Halliburton as quoted, p. 140).

To be added to synthetical processes:—

[A, p. 140.] Phenol-p-sulphonic acid on chlorination at 50° gives 2-chlorphenol-p-sulphonic acid. The latter, on heating the sodium salt with acid or water at 180–200°, yields o-chlorphenol, which can be converted into catechol as on p. 140 (Hazard-Flamand, Germ. Pat. 141751; Journ. Ch. Soc. **84**, I, 622).

70. Resorcinol (p. 142).

The resorcinol complex is apparently contained in ononin, a glucoside obtained from the root of rest-harrow, *Ononis spinosa* (v. Hemmelmayr, Monats. **24**, 132).

71. Quinol (p. 146).

Quinol and arbutin are contained in the leaves and quinol in the flowers of cranberry (Kanger, Arch. exp. Path. **50**, 46; Ch. Centr. 1903, **2**, 893).

75. Orcinol (p. 152).

Protocetraric acid, which is contained in the lichens *Ramalina ceruchis*, *Dendrographa leucophæa*, *Cetraria islandica* and vars. *vulgaris*, *platyna*, *crispa*, *subtubulosa*, &c., *C. complicata* = *C. laureri* = *Platysma complicatum*, *Sticta palmonaria*, *Cladonia rangiferina* var. *vulgaris*, *C. silvatica*, *C. fimbriata* var. *chordalis*, *Parmelia saxatilis* vars. *sulcata*, *panniformis*, and *retiruga* (Hesse, Journ. pr. Ch. [2] **57**, 255; 272; 295; 441; **58**, 467; 469; **62**, 321; 430; **68**, 1; Zopf, Ann. **324**, 39), gives rise to cetraric acid by hydrolysis (*Ibid.* [2] **57**, 300): the latter, and therefore its generator, contains the orcinol complex (Simon, Arch. Pharm. **240**, 521). Cetraric acid itself may exist ready formed in the lichens *Pertusaria amara*, *Cladonia rangiferina*, *C. silvatica*, and *Citraria fahluensis* (Hesse, Journ. pr. Ch. [2] **58**, 502; **62**, 477; Zopf, Ann. **300**, 323; 328; 352: compare Hesse, *loc. cit.* **62**, 477), and also in *Cetraria islandica* (Simon, *loc. cit.*).

77. β-Orcinol (p. 156).

To be added to synthetical processes:—

[B, p. 156.] From *camphor* [175] through p-xylene as under m-cresol

[62, in this appendix, p. 285]. From p-xylene as under **A**, p. 156.

79. Isoeugenol (p. 157).

For occurrence of isoeugenol in ylang-ylang oil see further Schimmel's Ber. April, 1903; Ch. Centr. 1903, **1**, 1086.

81. Methyleugenol = Eugenol Methyl Ether (p. 157).

This ether has also been found in ylang-ylang oil (Schimmel & Co. as above) and probably in the volatile oil of the bark of *Cinnamomum pedatinervium* from Fiji (Goulding, Trans. Ch. Soc. **83**, 1097). Has been found also in the essential oil of Californian laurel from *Umbellularia californica* (Power and Lees, Proc. Ch. Soc. **20**, 88).

84. Pyrogallol (p. 159).

The pyrogallol (gallic acid) complex is contained in glucogallin and tetrarin, two glucotannoids from Chinese rhubarb (Gilson, Comp. Rend. **136**, 385).

86. Phloroglucinol (p. 160).

The phloroglucinol complex appears to be contained in catechin (Clauser, Ber. **36**, 101) and in the Japanese dyestuff, 'fukugi' (A. G. Perkin and Phipps, Trans. Ch. Soc. **85**, 60). Kampherol, which contains the phloroglucinol complex (p. 161, *ante*), has been obtained from the flowers of the blackthorn, *Prunus spinosa* (*Ibid.* 57).

87. Antiarol (p. 163).

To be added to synthetical processes:—

[**A**, p. 163.] Pyrogallol can be converted into its trimethyl ether by agitating with dimethyl sulphate in presence of alkali (Ullmann, Ann. **327**, 104).

90. α-Hydrojuglone (p. 165).

Syntheses of Naphthalene.

[**A**, p. 166.] Naphthalene is among the products of decomposition of the vapour of ethyl alcohol at 500° (Berthelot, 'Traité de Chimie Organique,' 1872, p. 164).

91. Formic Aldehyde (p. 169).

To be added to synthetical processes:—

[**C**, p. 169.] Methyl alcohol gives formic aldehyde on oxidation by ozone (Harries, Ber. **36**, 1933). The vapour of methyl alcohol mixed with air and passed over a platinum spiral gives at 200° chiefly methylal; at a dark red heat formic aldehyde is also produced (Trillat, Bull. Soc. [3] **29**, 35: for technical process depending on the oxidation of the alcohol by air in a heated coppered tube see also this author's Germ. Pat. 55176 of 1889; Ber. **24**, Ref. 434).

[**D**, p. 170.] Methylene iodide from ethyl alcohol *via* iodoform gives methylene bromide by the action of bromine (Butleroff, Ann. **111**, 251). The bromide, on heating with water or with lead oxide and water at 150°, gives in the latter case a quantitative yield of formic aldehyde (Klöss, Monats. **24**, 783).

The conversion of trioxymethylene into the monomolecular aldehyde can be effected by the action of a methyl alcoholic solution of hydrogen chloride on the polymeride in presence of condensing agents so as to form chlormethyl methyl ether, $ClCH_2 . O . CH_3$. The latter is decomposed by water with the formation of the monomolecular aldehyde (Wedekind, Germ. Pat. 135310 of 1901; Ch. Centr. 1902, **2**, 1164; Pharm. Zeit. **47**, 836; Ch. Centr. 1902, **2**, 1301).

[**H**, p. 171.] For electrolytic preparation of formic aldehyde from sodium acetate in presence of sodium chlorate see also Moest's Germ. Pat. 138442 of 1902; Journ. Ch. Soc. **84**, I, 546).

92. Acetic Aldehyde (p. 174).

The bacteria which cause the decomposition of vegetable foods, and which belong to the type of *Bacillus coli communis*, produce aldehyde among

other compounds in a solution of dextrose (König, Spieckermann, and Olig, Journ. Ch. Soc. **84**, II, 386). The presence of acetic aldehyde in oil of peppermint has been confirmed by Charabot and Hébert (Ann. Agronom. **28**, 595).

To be added to synthetical processes:—

[**A**, p. 175.] Ethylene oxide is completely converted into acetic aldehyde by the 'contact' action of alumina on the vapour at 200° (Ipatieff and Leontowitsch, Ber. **36**, 2016).

[**B**, p. 175.] Acetic aldehyde is among the products of oxidation of ethane by ozone (Bone and Drugman, Proc. Ch. Soc. **20**, 127).

[**C**, p. 175.] For further study of the oxidation of alcohol to aldehyde from the electrochemical point of view see paper by Slaboszewicz, Zeit. physik. Ch. **42**, 343. The production of aldehyde from alcohol vapour by pyrogenic decomposition at 500° is referred to by Berthelot, 'Traité de Ch. Org.' 1872, p. 164. For further researches on the pyrogenic 'contact' conversion of alcohol into aldehyde, &c., by heated metals and metallic oxides see paper by Ipatieff, Ber. **36**, 1990.

94. Butyric Aldehyde (p. 181).

To be added to synthetical processes:—

[**D**, p. 182.] For production of isobutyric aldehyde from isobutylene oxide by the 'contact' action of alumina on the vapour at 200° see paper by Ipatieff and Leontowitsch, Ber. **36**, 2016.

95. Valeric Aldehyde (p. 183).

A valeric aldehyde occurs in peppermint oil from *Mentha piperita* (Charabot and Hébert, Ann. Agronom. **28**, 595). A valeric aldehyde is possibly present in lavender oil (Schimmel's Ber. April, 1903; Ch. Centr. 1903, **1**, 1086).

96. Hexoic Aldehyde (p. 185).

Methylpropylacetaldehyde.

To be added to synthetical processes:—

[**A**, p. 185.] Propylene oxide, when the vapour is passed through a tube containing aluminium oxide heated to 200°, is resolved chiefly into propionic aldehyde (Ipatieff and Leontowitsch, Ber. **36**, 2016).

100. Decoic Aldehyde (p. 189).

The occurrence of this aldehyde in néroli oil is recorded by Walbaum and Hüthig (Journ. pr. Ch. [2] **67**, 315: see also Hesse and Zeitschel, *Ibid.* **66**, 481). The aldehyde has been found in the oil of cassia flowers from *Acacia cavenia* (Walbaum, *Ibid.* **68**, 235).

101. Acroleïn (p. 190).

To be added to synthetical processes:—

[**A**, p. 190.] Glycerol gives acroleïn when heated with succinic acid, with d-tartaric acid, or with malic acid (Œ. de Coninck and Raynaud, Comp. Rend. **135**, 1351).

102. Crotonic Aldehyde (p. 190).

Solanin, a gluco-alkaloid found in the berries of *Solanum nigrum*, *S. dulcamara*, *S. verbascifolium*, in stalks and leaves of *S. lycopersicum*, and in shoots of the potato, apparently contains the crotonic aldehyde complex (Hilger and Merkens, Ber. **36**, 3204).

To be added to synthetical processes:—

[**J**, p. 190.] From *glycol* [45], crotonic aldehyde being among the products of decomposition of this compound by zinc chloride at 250° (Bauer, 'Répertoire de Chimie Pure,' **2** [1860], 244).

104. Citral (p. 191).

For occurrence of citral in verbena oil from *Verbena triphylla* see paper by Theulier, Bull. Soc. [3] **27**, 1113.

Note:—Since the rhodinal of Bouveault (see under citronellal [105, p. 192]) is the aldehyde derived from l-citronellol = rhodinol [38, p. 89; **A**, note, and this appendix, p. 282] and is not identical with citral, the synonyms rhodinal and licareal given for the latter (p. 191) must be deleted. Rhodinal has not yet been shown to be a natural product.

105. Citronellal (p. 192).

The formula assigned to this compound on p. 192 has been confirmed (Barbier and Leser, Comp. Rend. **124**, 1308; Harries and Röder, Ber. **32**, 3363: see also the note on p. 192). It is therefore 2:6-dimethyl-1-octenal-8, and is the aldehyde of d-citronellol [**38**, p. 89, and this appendix]. For occurrence in oil of lemon and of lemon-grass see further Tiemann, Ber. **32**, 812; 834: compare also Stiehl, Journ. pr. Ch. [2] **58**, 62.

To be added to synthetical processes:—

[**B**, p. 192.] From *d-citronellol* [**38**] by oxidation with chromic acid mixture (Tiemann and Schmidt, Ber. **30**, 34).

106. Acetone (p. 192).

Acetone is said to be present in normal horse urine (Kiesel, Pflüger's Arch. **97**, 480). Acetone occurs in the expired air and in the urine of man only in grave cases of diabetes (Le Goff, Comp. Rend. **137**, 216). Acetone has been found in the fluid from a pancreatic cyst (Alay and Rispal, Journ. Pharm. [6] **17**, 319).

To be added to synthetical processes:—

[**B**, p. 193.] Isopropyl alcohol is readily converted into acetone by passing the vapour over reduced copper heated to 250–430°. At 300° platinum sponge acts in a similar way. Reduced nickel is less effective (Sabatier and Senderens, Comp. Rend. **136**, 983).

A small quantity of acetone is formed when the vapour of propylene oxide is passed over aluminium oxide heated to 200° (Ipatieff and Leontowitsch, Ber. **36**, 2016).

[**K**, p. 196.] A solution of sodium isobutyrate gives acetone when electrolysed in presence of sodium chlorate (Moest, Germ. Pat. 138442 of 1902; Journ. Ch. Soc. **84**, I, 546).

[**V**, p. 199.] Methylheptenone gives acetone among other products on oxidation by ozone (Harries, Ber. **36**, 1933).

113. Diacetyl (p. 203).

To be added to synthetical processes:—

[**B**, p. 203.] Oxalic ester and magnesium methiodide interact in ethereal solution to form a small quantity of diacetyl (Gattermann and Maffezzoli, Ber. **36**, 4152).

114. Benzoic Aldehyde (p. 205).

To be added to synthetical processes:—

[**A**, p. 205.] Toluene, on passing the vapour over heated lead oxide, gives stilbene = symmetrical diphenylethylene (Behr and Van Dorp, Ber. **6**, 754; Lorenz, Ber. **7**, 1096; **8**, 1455), or benzal chloride gives stilbene on treatment with sodium or zinc dust in appropriate solvents (Limpricht, Ann. **139**, 318; Lippmann and Hawliczek, Jahresber. **1877**, 405). Stilbene gives benzoic aldehyde among other products on oxidation with chromic acid mixture. By photochemical oxidation stilbene yields benzoic aldehyde as an intermediate product (Ciamician and Silber, Ber. **36**, 4266).

Benzene and *formic acid* [Vol. II] give benzoic aldehyde by the interaction of phenyl magnesium bromide (from brombenzene and magnesium) and formic ester in ethereal solution (Gattermann and Maffezzoli, Ber. **36**, 4152).

[**B**, p. 208.] By the action of nitrous gas on styrene in ethereal solution a 'pseudonitrosite' is formed. This gives benzoic aldehyde among the products of decomposition by hot aqueous alkali or by sodium ethoxide solution (Wieland, Ber. **36**, 2558).

[**C**, p. 209.] Benzamide and magnesium methiodide interact to form a compound which is decomposed by water with the formation of acetophenone (Béis, Comp. Rend. **137**, 575).

Note:—This synthesis affects all products of which acetophenone is a generator, e.g. methylphenyl carbinol [**58**; **C**, p. 118.]

[**D**, p. 209.] For production of benzoic aldehyde by the electrolysis of a solu-

tion of sodium phenylacetate in presence of sodium chlorate see Moest's Germ. Pat. 138442 of 1902; Journ. Ch. Soc. **84**, I, 546.

[**E**, p. 209.] Cinnamic acid yields benzoic aldehyde (with glyoxylic acid) when oxidised by ozone (Harries, Ber. **36**, 1933).

The phenyl-$\alpha\beta$-dibrompropionic acid or ester obtained by the combination of cinnamic acid or ester with bromine (see p. 209), on treatment with hot alcoholic potash, gives two isomeric α-bromcinnamic acids or esters (Glaser, Ann. **143**, 325; Sudborough and Thompson, Trans. Ch. Soc. **83**, 666). Both these, which are stereo-isomerides, yield benzoic aldehyde on oxidation by potassium permanganate (Erlenmeyer, Ber. **23**, 2130).

[**L**, p. 211.] Benzyl alcohol gives benzoic aldehyde and hydrogen when the vapour is passed over reduced copper heated to 300° (Sabatier and Senderens, Comp. Rend. **136**, 983).

[**N**, p. 211.] From *formic* and *cinnamic aldehydes* [**91**; **123**], a mixture of these aldehydes giving benzoic aldehyde when allowed to stand in contact with lime or baryta and water at 30–50° for 1–2 days (Van Marle and Tollens, Ber. **36**, 1347).

119. Parahydroxybenzoic Aldehyde (p. 215).

To be added to synthetical processes:—

[**A**, p. 215.] The condensation of phenol with hydrogen cyanide by means of hydrogen chloride may take place without the use of aluminium or zinc chloride (Farb. vorm. F. Bayer & Co., Germ. Pat. 106508 of 1898; Ch. Centr. 1900, **1**, 742).

[**B** and **E**, p. 216.] p-Nitrobenzoic aldehyde is best reduced to the amino-aldehyde by acid sodium sulphite (Cohn and Springer, Monats. **24**, 87).

[**G**, p. 219.] *Parahydroxybenzoic acid* [Vol. II] when heated with chloroform in presence of alkali gives parahydroxybenzoic aldehyde (Reimer and Tiemann, Ber. **9**, 1268).

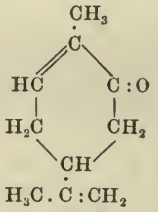
120. Anisic Aldehyde (p. 218).

To be added to synthetical processes:—

[**B**, p. 218.] Or from anisole and *formic ester* [Vol. II] through p-bromanisole and p-methoxyphenyl magnesium bromide, the latter interacting with formic ester in ethereal solution to form anisic aldehyde (Gattermann and Maffezzoli, Ber. **36**, 4153).

127. Carvone (p. 226).

The formula given in the text is erroneous. The relationship of this compound to limonene (see under **9**; **E**, p. 38) indicates for carvone the formula:—



For literature relating to constitution see Wagner, Ber. **27**, 1653; 2270; Wallach, Ber. **28**, 1773; Tiemann and Semmler, *Ibid.* 1778.

128. Pulegone (p. 226).

The ethereal oil, 'marjolaine,' of *Calamintha nepeta* contains pulegone (Genvresse and Chablay, Comp. Rend. **136**, 387). The botanical source is erroneously given as *Origanum majorana* on p. 226.

129. Menthone (p. 227).

The variation in the composition of peppermint oil from *Mentha piperita* containing menthone, according to conditions of climate, mode of cultivation, &c., has been studied by Charabot and Hébert (Ann. Agronom. **28**, 595).

To be added to synthetical processes:—

[**A**, p. 227.] For details of method of oxidising menthol to menthone by potassium dichromate and sulphuric acid see further Flatau and Labbé, Bull. Soc. [3] **19**, 788.

144. Metahydroxyanthraquinone (p. 236).

Syntheses of Anthracene.

Nascent acetylene acts on benzene in presence of aluminium chloride with the formation of anthracene among other products (Parone, Journ. Ch. Soc. **86**, I, 26; from L'Orosi, **25**, 148).

To be added to synthetical processes:—

[**C**, p. 238.] Anthraquinone is oxidised by ammonium persulphate in sulphuric acid solution with the formation of m-hydroxyanthraquinone (Wacker, Journ. pr. Ch. [2] **54**, 89).

145. Alizarin (p. 238).

To be added to synthetical processes:—

[**A**, p. 238.] For synthesis of alizarin from catechol and phthalic anhydride see further Liebermann and Hohenemser, Ber. **35**, 1779).

[**B**, p. 239.] Anthraquinonesulphonic acid on extreme reduction by hydriodic acid and phosphorus or by sodium amalgam or ammonia and zinc dust gives 2-anthracenesulphonic acid (Liebermann, Ann. **212**, 48; 57; Bischof and Liebermann, Ber. **13**, 47; **15**, 852: according to Heffter, Ber. **28**, 2262, this sulphonic acid is also formed by the direct sulphonation of anthracene by dilute sulphuric acid). By alkaline fusion this sulphonic acid yields 2-anthrol (Liebermann, Ann. **212**, 49). By the action of sodium nitrite and zinc chloride in alcoholic solution the latter forms a nitroso-derivative, which reduces to an amino-derivative. The latter is oxidised by chromic and sulphuric acids to 1 : 2-anthraquinone, and this is reduced by zinc dust and acetic acid to 1 : 2-anthraquinol. The anthraquinol diacetate is oxidised by chromic acid in acetic acid solution to alizarin diacetate, and this yields alizarin on hydrolysis (Lagodzinski, Ber. **27**, 1438; **28**, 116; 1422; 1427; 1533; **36**, 4020).

Anthraquinone is directly oxidised to alizarin by ammonium persulphate in sulphuric acid solution (Wacker, Journ. pr. Ch. [2] **54**, 90).

148. Anthragallol (p. 240).

To be added to synthetical processes:—

[**D**, p. 240.] From *m-hydroxyanthraquinone* [**144**] through the 1 : 3-dinitro-derivative by nitration (Simon, Ber. **14**, 464). The latter, on reduction in strongly alkaline solution, or by heating the corresponding 1 : 3-diamino-derivative with aqueous hydrochloric acid under pressure, or by the diazo-method from the diamino-compound, yields anthragallol (*Ibid.* Germ. Pat. 119755 of 1898; Ch. Centr. 1901, **1**, 979).

149. Purpurin (p. 240).

To be added to synthetical processes:—

[**A**, p. 241.] Or quinizarin on bromination yields a 2-bromo-derivative (Liebermann and Rüber, Ber. **33**, 1658; Farb. vorm. F. Bayer & Co., Germ. Pat. 114199 of 1899; Ch. Centr. 1900, **2**, 884). The latter, or the corresponding chlorquinizarin, gives purpurin on alkaline fusion (B. & Co., *loc. cit.*). Quinizarin also gives purpurin on heating with sulphuric and nitrous acids in presence of boric acid (*Ibid.* as below under **F**).

[**C**, p. 241.] Alizarin gives purpurin also on oxidation by ammonium persulphate in sulphuric acid solution (Wacker, Journ. pr. Ch. [2] **54**, 90).

[**F**, p. 241.] From *m-hydroxyanthraquinone* [**144**], which, on treatment with nitrous acid in the presence of strong sulphuric and boric acids, yields quinizarin (Farb. vorm. F. Bayer & Co., Germ. Pat. 81245 of 1893; Ber. **28**, Ref. 703; 86630 of 1895; Ber. **29**, Ref. 470). From quinizarin as under **A**, p. 241, and above in this appendix.

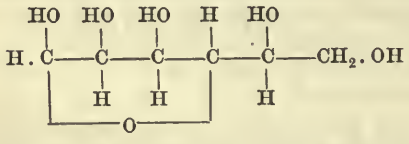
Note:—Anthraquinone gives first quinizarin and then purpurin on heating with sulphuric acid in presence of boric acid (B. & Co. Germ. Pat. 81960 of 1893; Ber. 28, Ref. 806).

151. Dihydroxyacetone (p. 242).

An oxidising *Bacterium* obtained from wine vinegar produces dihydroxyacetone from glycerol (Sazerac, Comp. Rend. **137**, 90).

154. Dextrose (p. 244).

In place of the constitutional formula given in the text a 'lactone' (alkylene oxide) formula was proposed by Tollens in 1883 (Ber. **16**, 923) :—



Further evidence in support of this formula has recently been advanced, so the literature is now given :—Sorokin, Journ. pr. Ch. [2] **37**, 312; Erwig and Koenigs, Ber. **22**, 2207; **23**, 672; Skraup, Monats. **10**, 401; Wohl, Ber. **23**, 2098; E. F. Armstrong, Trans. Ch. Soc. **83**, 1305; Lowry, *Ibid.* 1314.

Dextrose is present in small quantity in all the organs and tissues of the dog and horse in the normal state (Cadéac and Maignon, Comp. Rend. **136**, 1682). Human cerebrospinal fluid drawn by lumbar puncture contains dextrose (Rossi, Zeit. physiol. Ch. **39**, 183: see also Donath, *Ibid.* 526). The globulins of blood on decomposition by hydrobromic acid yield dextrose among other carbohydrates, and may therefore contain the dextrose complex (Langstein, Ch. Centr. 1903, **1**, 239). Glycollic aldehyde administered to rabbits appears as dextrose in the urine (Paul Mayer, Zeit. physiol. Ch. **38**, 135). Dextrose is present in human cephalorachid liquid (Grimbert and Coulaud, Comp. Rend. **136**, 391).

155. Lævulose (p. 247).

Further researches on the relationship between the soluble ferments and the polysaccharides which they hydrolyse (gentianose, &c.) have been published by Bourquelot (Comp. Rend. **136**, 762).

Stachyose, a sugar obtained from the tubercles of *Stachys tuberifera*, contains the galactose, dextrose, and lævulose complexes (v. Planta and Schulze, Ber. **23**, 1692; **24**, 2705; Landw. Versuchs. Sta. **35**, 473). According to Tanret this tetrose is identical with the manneotetrose (p. 248) of manna (Comp. Rend. **136**, 1569).

Lævulose is among the carbohydrates resulting from the decomposition of the globulins from horse blood serum by hydrobromic acid (Langstein, Monats. **24**, 445).

156. Mannose (p. 248).

Salep mucilage (p. 248) has been shown by analysis to be a tetrasaccharide of d-mannose, and it is converted quantitatively into the latter sugar on hydrolysis (Hilger, Ber. **36**, 3199). A manno-galactan has been obtained from *Melilotus leucantha* (Hérissey, Comp. Rend. Soc. Biol. **54**, 1174).

161. Methyl Mercaptan (p. 252).

Egg-meat mixture is rapidly decomposed by *Bacillus coli communis* with the formation of mercaptan (? methyl) among other products (Rettger, Am. Journ. Physiol. **8**, 284).

165. Secondary Butyl Isothiocyanate (p. 254).

To be added to synthetical processes :—

[**A**, p. 254.] The vapour of n-butyl alcohol passed over alumina heated to 500–520° gives 25–30 per cent. n-butylene (Ipatieff, Ber. **36**, 1999).

169. Benzyl Isothiocyanate (p. 257).

To be added to synthetical processes :—

[**A**, p. 258.] Benzamide in pyridine solution is converted into benzonitrile by the action of carbonyl chloride (Einhorn and Mettler, Ber. **35**, 3647).

[**B**, p. 258.] For electrolytic reduction of benzaldoxime to benzylamine see Germ. Pat. 141346, Böhringer and Söhne; Journ. Ch. Soc. **84**, I, 550.

[**E**, p. 259.] By the action of nitrous gas on styrene in ethereal solution a 'pseudonitrosite' is formed, which on boiling with water is transformed into β-styrene nitrosite = α-nitroacetophenone-oxime. The latter, on boiling with strong hydrochloric acid, yields (with benzoic acid) benzonitrile (Wieland, Ber. **36**, 2558 : see also Sommer, Ber. **29**, 356).

170. Phenylethyl Isothiocyanate (p. 260).

To be added to synthetical processes :—

[**A**, p. 260.] Or benzyl magnesium bromide (from benzyl bromide and magnesium) interacts in ethereal solution with *formic ester* [Vol. II] to form phenylacetic = α-toluic aldehyde (Gattermann and Maffezzoli, Ber. **36**, 4153).

172. Hydrogen Cyanide (p. 262).

The presence of hydrogen cyanide in sorghum has been confirmed and the quantity estimated by Slade (Journ. Am. Ch. Soc. **25**, 55). Experiments on the formation and determinations of the quantity of hydrogen cyanide in sorghum and other fodder-plants have been undertaken by the Queensland Department of Agriculture at the Brisbane Botanic Garden, and are described in the paper referred to on p. 263 (Brünnich, Trans. Ch. Soc. **83**, 788). A cyanogenetic glucoside, gynocardin, has been obtained from the seeds of *Gynocardia odorata* (Power and Gornall, Proc. Ch. Soc. **20**, 137).

To be added to synthetical processes :—

[**A**, p. 263.] Hydrogen cyanide is formed by passing electric sparks through a mixture of hydrogen, nitrogen, and carbon monoxide (Gruszkiewicz, Zeit. Elektroch. **9**, 83). Further experiments on the production of cyanides from nitrogen in presence of strongly heated carbon and alkaline carbonates, hydroxides, iron, &c., have been carried out by Täuber (Ch. Ind. **26**, 26; Ch. Centr. 1903, **1**, 434).

[**HH**, p. 268.] From *benzoic* and *acetic acids* [Vol. II] through acetophenone and its nitroso- (isonitroso-) derivative (see under benzoic aldehyde [**114**; **G**, p. 210]). The sodium compound of isonitrosoacetophenone on heating, or by the action of strong acid or excess of aqueous alkali, is resolved into benzoic acid and hydrogen cyanide (Claisen and Manasse, Ber. **20**, 2194; Sluiter, Proc. Akad. Wetensch. Amsterdam, Jan. 30, 1904).

INDEX

The numbers refer to pages only. The chief reference to natural products is printed in thick type.

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ERRATA ET CORRIGENDA.

Page 23, right column, line 23 from top, *for* 'Tischtschenko' *read* 'Tistschenko.' The same error occurs on p. 55, right column, line 9 from top; on p. 60, left column, line 12 from bottom; and on p. 71, left column, line 21 from top.

30, right column, line 4 from top, *for* 'α-xylic' *read* 'α-xylidic.'

36, right column, line 6 from top, *for* '*fericia*' *read* '*sericea*.'

37, left column, line 7 from top, *for* '*Xanthoxylum*' *read* '*Xanthoxylon*.' Also on p. 42, left column, line 22 from bottom.

62, right column, line 30 from top, *for* 'nitro-propane' *read* 'nitropropane.'

89, for revision of the formula of 'citronellol' see Appendix, p. 282.

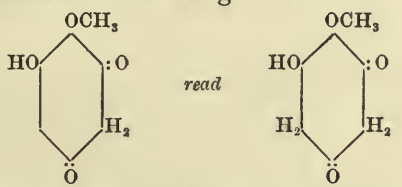
93, for revision of the formula of 'isopulegol' see Appendix, p. 283.

97, left column, line 21 from bottom, *for* '*Eurotiopis*' *read* '*Eurotiopsis*.'

139, left column, line 24 from bottom, *for* '*Querbracho*' *read* '*Quebracho*.'

148, right column, line 14 from top, *for* '**B**' *read* '**C**.'

164, *for* the formula of 'iretol' as given :—



164, right column, line 7 from bottom, *for* '*arfolium*' *read* '*arifolium*.'

174, left column, line 14 from bottom, *for* '*circellinoïdes*' *read* '*circinelloïdes*.'

190, left column, line 1 from top, *for* '8·5' *read* '5·7.'

205, right column, line 12 from top, *for* '*Attingia*' *read* '*Altingia*.'

226, for revision of the formula of 'carvone' see Appendix, p. 290.

„ right column, line 17 from bottom, *for* '*origanifolium*' *read* '*origanifolius*.'

228, left column, line 15 from top, *for* 'o-nitro-p-toluidine' *read* '3-nitro-p-toluidine.'

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