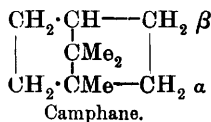


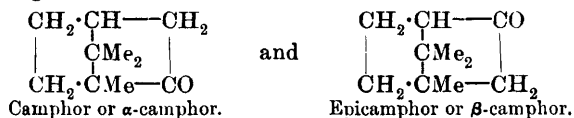
2182 BREDT AND PERKIN: L-EPICAMPHOR (L- β -CAMPHOR).CCXXXI.—l-*Epicamphor* (l- β -*Camphor*).

By JULIUS BREDT and WILLIAM HENRY PERKIN, jun.

THE hydrocarbon from which camphor and its many derivatives may be said to be directly derived is camphane (Aschan, *Ber.*,



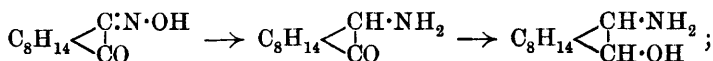
1900, **33**, 1009), and it is clear that this hydrocarbon must yield two different keto-derivatives by the substitution, on the one hand, of the α -, and on the other of the β -CH₂ group by CO, namely, the following:



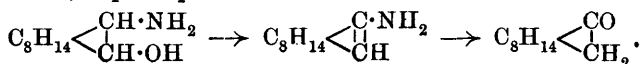
It is well known that Brett (*Ber.*, 1893, **26**, 3047; *Annalen*, 1896, **292**, 33) originally suggested that the first of these formulæ most probably represents the constitution of camphor, and the correctness of this view has been abundantly proved by the great mass of experimental evidence which has accumulated, especially during the last few years.

The other possible isomeride—*epicamphor*—must be a substance the importance of which, at all events from the chemical point of view, can hardly be less than that of camphor itself, and indeed the study of the reactions and decompositions of epicamphor might be expected to afford clues to the constitution and relationship of some of the more complex derivatives of camphor which can hardly be obtained, or at least not so readily, from the study of camphor itself.

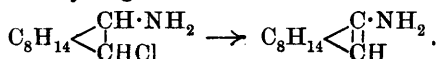
It is indeed obvious that the study of epicamphor, and especially the careful comparison of the properties of its derivatives with those of the corresponding derivatives of camphor, is a problem so attractive that it is not surprising to find evidence that repeated efforts have been made from time to time by different investigators to devise some process for the preparation of epicamphor, but, until recently, without success. In 1900, Duden and Macintyre (*Annalen*, **313**, 59) attempted to solve the problem by starting with *isonitrosocamphor*, which they first reduced to aminocamphor and then to aminoborneol:



they proposed then to remove water from the latter substance in order to obtain *l*-aminobornylene, from which, by the action of nitrous acid, *l*-epicamphor should result:



It was, however, not found possible to remove water directly from aminoborneol, and this base was therefore treated with phosphorus pentachloride, when it yielded α -chloro- β -aminocamphane, a substance which might be expected to yield aminobornylene by the elimination of hydrogen chloride:

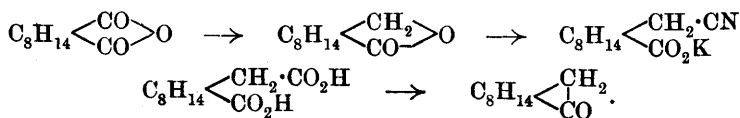


Elimination of hydrogen chloride did actually take place when the chloroamino-compound was distilled with aqueous sodium hydroxide, but the base (camphenamine) which was produced is not aminobornylene since, in place of epicamphor, it yields a substance having the properties of an unsaturated tertiary alcohol

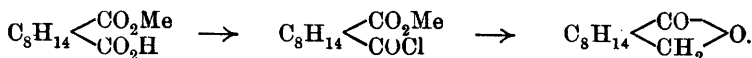
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(isocamphor) when it is treated with nitrous acid. It is therefore clear that intramolecular change must have taken place, probably during the elimination of hydrogen chloride from chloroamino-camphane.

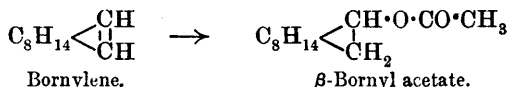
At a somewhat later date (*Compt. rend.*, 1905, **141**, 697) Haller and Blanc attempted to obtain epicamphor by a process similar to that which they had employed with success in the case of camphor itself. When camphoric anhydride is reduced by sodium amalgam it yields α -campholide, and this reacts with potassium cyanide to form an additive product, which, on hydrolysis, is converted into homocamphoric acid, and camphor is obtained by the distillation of the calcium or lead salt of this acid:



Haller and Blanc now prepared β -campholide from methyl hydrogen camphorate by conversion into the acid chloride and subsequent reduction with sodium and alcohol:



This substance should yield epicamphor by a process similar to that by which camphor had been obtained, but, unfortunately, all attempts to bring about combination between β -campholide and potassium cyanide were unsuccessful. An investigation which is of special importance in connexion with the present communication was published by Wagner in 1903 (*Chem. Zeit.*, **27**, 271; compare *Ber.*, 1903, **36**, 4602), since he there describes the preparation and derivatives of a substance which he claims to be epicamphor (β -camphor). Wagner subjected bornylene to the action of acetic acid and sulphuric acid, and thus converted it, by the well known Bertram and Walbaum process (*J. pr. Chem.*, 1894, [ii], **49**, 1), into a substance which he considered was the acetyl derivative of β -borneol:



This substance distilled at 229—230°/755 mm., and gave, on hydrolysis, the corresponding borneol (m. p. 203—204°), and, by oxidising this with permanganate, a ketone was obtained which distilled at 207—208°, melted at 160—161°, and this Wagner assumed to be β -camphor. He also prepared the oxime (m. p. 119—119.5°) and the semicarbazone (m. p. 201—202°).

The investigation of *l*-epicamphor, described in the present communication, shows, however, that the properties of this substance are in reality quite different from those of the substance obtained by Wagner.

l-Epicamphor melts at 183.5–184°, distils at 212°, yields an oxime melting at 103–104° and a semicarbazone melting at 236–238°, and *l*-epiborneol melts at 182°.

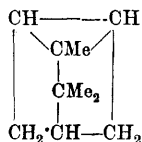
On the other hand, camphor melts at 179°, distils at 207°, yields an oxime melting at 119° and a semicarbazone melting at 246–248°, and borneol melts at 203°.

The researches of Brett (*Annalen*, 1909, **366**, 52) have shown conclusively that the hydrocarbon employed by Wagner in his experiments could not have been pure bornylene, but must have been a mixture of bornylene and camphene or cyclene.*

There can therefore be little doubt that the ketone obtained by Wagner consisted largely of impure camphor, and this view is borne out by some of the physical properties which he ascribed to his product and its derivatives. In order to obtain further evidence on this point, Brett and Hilbing (*J. pr. Chem.*, 1911, [ii], **84**, 783) investigated the addition of acetic acid to pure bornylene, and obtained a large yield (86 per cent.) of an ester distilling at 103–104°/14 mm., but this was not a single substance, since it yielded on hydrolysis a mixture of borneols melting at 175–178°, which could not be separated by fractional crystallisation, and the only substance that could be obtained by the oxidation of this mixture was camphor.

Before proceeding to a description of the methods by which *l*-epicamphor may now be obtained, some of the processes which were tried without success may be briefly mentioned. In the first place, *d*-bornylene-3-carboxylic acid was reduced to camphan-3-carboxylic acid (p. 2198); the amide of this was prepared, and submitted to the Hofmann reaction with the object of obtaining β -bornylamine, from which, by the action of nitrous acid, β -borneol

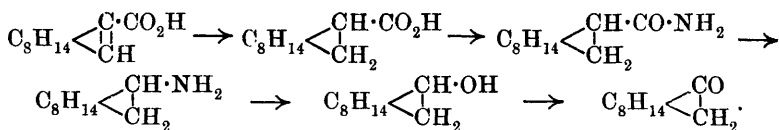
* Tschugaev (*Annalen*, 1912, **388**, 280) considers that the by-product obtained during the preparation of bornylene by the decomposition of methyl bornyl xanthate, $C_{10}H_{17}O \cdot CS_2Me$, consists of cyclene,



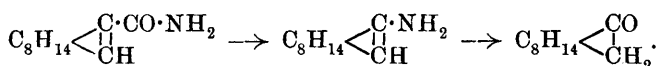
It is remarkable that this hydrocarbon, which is so stable to permanganate that it may be purified by oxidising the mixture with bornylene with permanganate until the latter hydrocarbon is destroyed (compare Henderson and Caw, *T.*, 1912, **101**, 1416), should be oxidised by hydrogen peroxide more readily than bornylene.

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(epiborneol) should result, and be converted, by oxidation, into epicamphor:

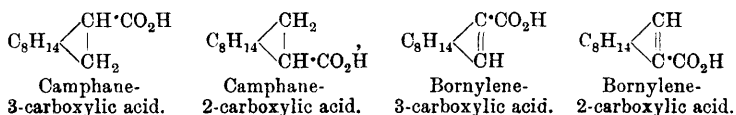


Experiment showed that a basic substance is actually obtained in this way, and this reacted with nitrous acid, but the product proved to be a mixture of borneols, and attempts to separate these have, so far, been unsuccessful. *d*-Bornylene-3-carboxylic acid itself was next converted into the amide in the hope that, by the careful application of the Hofmann reaction, this might yield the β -amino-bornylene which Duden and Macintyre (*loc. cit.*) had endeavoured to prepare, since this substance would doubtless react with nitrous acid to yield epicamphor:

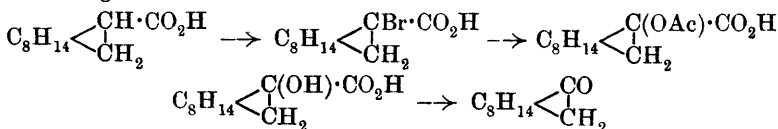


These various interactions resulted in the formation of a small quantity of a neutral substance, which was quite homogeneous, melted at 135°, and was evidently a ketone, since it reacted readily with phenylhydrazine. Examination showed, however, that it contained halogen, and it is probable that this substance was bromoepicamphor (p. 2210), which melts at the same temperature. Many other processes, which seemed likely to lead to the formation of epicamphor, were also investigated, but it is unnecessary to discuss these here. The first published account of the preparation of *l*-epicamphor is contained in a notice by F. R. Lankshear and W. H. Perkin, jun. (P., 1911, **27**, 167), in which it is shown that this substance may be obtained from *d*-camphane-3-carboxylic acid by the following process. The chloride of this acid is treated with bromine, the product poured into alcohol, and the bromo-ester thus obtained digested with potassium acetate in acetic acid solution. After hydrolysis with alcoholic potassium hydroxide, the crude α -hydroxycamphane-3-carboxylic acid is oxidised by lead peroxide,

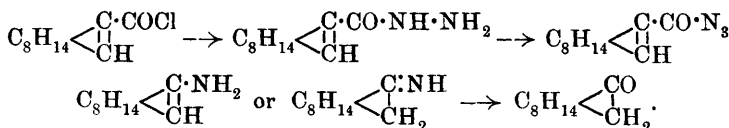
* In order that the letters α - and β - may be reserved in the usual manner for indicating the position of substituents in relation to the carboxyl group, the following scheme of nomenclature for the camphane- and bornylene- carboxylic acids has been adopted:



permanganate, or chromic acid, when *l*-epicamphor is obtained according to the scheme:



The first specimens of *l*-epicamphor, obtained in this way, were too small to allow of purification by means of the semicarbazone or by recrystallisation, and the melting point given (about 165°) was that of the crude product. Subsequently, considerable quantities (30 grams) were prepared by this process, and the purified substance then melted at 178—182°, had $\alpha_D -57.9$, and yielded an oxime melting at 103° and a semicarbazone melting at 236°. While these researches were in progress, Brecht and his co-workers had also succeeded in preparing *l*-epicamphor by a different method, and a preliminary account of this investigation appeared in the same year (*Chem. Zeit.*, 1911, **35**, 765). The process which these investigators employed was the conversion of *d*-bornylene-3-carboxylic acid, through the acid chloride, into the hydrazide, which, when subjected to the Curtius method, yielded the azide, and from this, by boiling with hydrochloric acid, *l*-epicamphor was obtained:



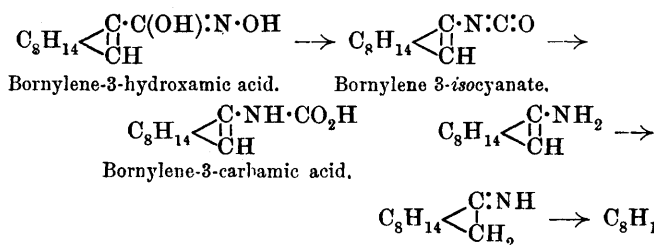
Since epicamphor had been obtained simultaneously in the laboratories at Aachen and Manchester, it was thought that the best plan would be to join forces; this was done, and the present publication is the result of that arrangement. Of the two processes just indicated for the preparation of *l*-epicamphor, the azide method is much to be preferred, because it not only gives much better yields, but also a purer product. It has this serious drawback, however, that there is always danger of explosion during the formation and extraction of the azide, and the process can therefore only be carried out safely with comparatively small quantities of material. For these reasons a large number of experiments were made with the object of devising a more satisfactory process for the preparation of epicamphor than either of those mentioned above, and, after many failures, this was ultimately accomplished with the aid of *d*-bornylene-3-hydroxamic acid.

This acid is produced almost quantitatively when methyl

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d-bornylene-3-carboxylate is treated with hydroxylamine in the presence of sodium methoxide (compare Lossen, *Annalen*, 1875, 175, 313; 178, 213; Thiele and Pickard, *Annalen*, 1899, 309, 189); it is a crystalline substance, and is remarkable for the ease with which it is converted into *l*-epicamphor under a variety of conditions. When a small quantity of the acid is heated alone, it decomposes just above its melting point (136°), with almost explosive violence and development of much heat; ammonia, and steam are liberated, and epicamphor is formed. The principal product of the decomposition is, however, a pale yellow, transparent resin, which may be distilled, and this, in contact with hydrochloric acid and subsequent distillation in steam, gives a large yield of epicamphor.

The explanation of this curious decomposition is probably the following: Bornylene-3-hydroxamic acid on heating loses water, the product undergoes molecular rearrangement, and the yellow, volatile resin is bornylene 3-*isocyanate*. The water produced during this process decomposes some of the *isocyanate*, with formation of epicamphor and ammonia, and the remainder is decomposed in the same direction by the subsequent treatment with hydrochloric acid and distillation in steam:



The sodium salt of *d*-bornylenehydroxamic acid also decomposes with considerable violence at as low a temperature as 105°, and the product, on treatment with hydrochloric acid, yields *l*-epicamphor, and, again, the aqueous solution of the sodium salt gradually clouds when it is boiled, owing to the separation of epicamphor. These pyrogenetic decompositions, owing to their violence, are not suitable as methods of preparation of epicamphor, but the discovery that the acetyl and benzoyl derivatives of *d*-bornylenehydroxamic acid, which decompose in a similar manner, do so more quietly, led ultimately to the working out of a valuable method for the preparation of epicamphor, which consists in bringing about the intramolecular change mentioned above, with the aid of toluene-*p*-sulphonyl chloride and several hundred grams of *l*-epicamphor have been made in this way (compare p. 2206).

This method of preparation gives a good yield of *l*-epicamphor,

and its great advantage over the azide process (p. 2187) lies in the fact that it proceeds without the risk of explosion, and may therefore be carried out with comparatively large quantities of material.

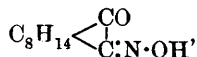
All the methods for obtaining *l*-epicamphor which are at present available have *d*-bornylene-3-carboxylic acid for their starting point, and not only is the preparation of this acid a long and tedious process, but its subsequent conversion into epicamphor involves a complicated series of reactions, and thus, with ordinary laboratory apparatus, several months are required in order to prepare two or three hundred grams of epicamphor.

It is therefore to be hoped that the further experiments on which we are at present engaged will lead to the discovery of a simpler method for the preparation of this important substance.

Comparison of the Properties of l-Epicamphor with those of d-Camphor.

l-Epicamphor has an odour very similar to, but yet distinct from, that of camphor, it melts at 182°, distils at 213°, and is lævorotatory, the value for α_D in benzene being -58.21° ; epicamphoroxime melts at 103–104°, and has $\alpha_D +100.5^\circ$; epicamphorsemicarbazone melts at 237–238°; on oxidation, epicamphor yields *d*-camphoric acid.

d-Camphor melts at 177–178°, distils at 207°, and has $\alpha_D +39.1^\circ$ in benzene; the oxime melts at 119°, and has $\alpha_D -56.0^\circ$, and the semicarbazone melts at 247–248°.* When *l*-epicamphor is treated, in ethereal solution, with *iso*amyl nitrite and sodamide, it yields the two stereoisomeric *isonitroso-l-epicamphors*,



the α -modification melts at 163–170° and has $\alpha_D -201.9^\circ$, and the β -modification melts at 138–140°, and has $\alpha_D -183.5^\circ$, and of these the latter is the unstable form, since it is converted into the former by melting or boiling with water. These two *isonitroso-l-epicamphors* have also recently been prepared by Forster and Spinner by another process (T., 1912, 101, 1348), and correspond with the two *isonitrosocamphors*, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} \cdot \text{N} \cdot \text{OH} \\ \diagup \\ \text{CO} \end{array}$, which melt at 152–153° and 114°, and have respectively $\alpha_D +196.6^\circ$ and

* The semicarbazone of camphor was first prepared by Tiemann (*Ber.*, 1895, 28, 2191), who stated that it melts at 236–238°, and this is usually given as the actual melting point. Rimini (*Gazzetta*, 1900, 30, 603) pointed out, however, that the true melting or decomposing point is 245°, and we have prepared this substance in different ways and also find that it melts and decomposes at 245° or 247–248° (corr.)

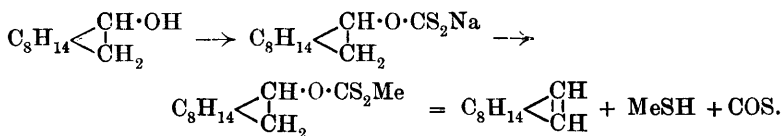
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+172.9°, and in this case also the higher melting isomeride is the stable form, since it is readily formed from the isomeride of lower melting point by the action of heat. The α - and β -modifications of *isonitroso-l-epicamphor* both yield camphorquinone on treatment with formaldehyde and hydrochloric acid, and are converted into the imide of *d*-camphoric acid by heating with sulphuric acid, and these are reactions which are also shown by the *isonitroso-camphors*.

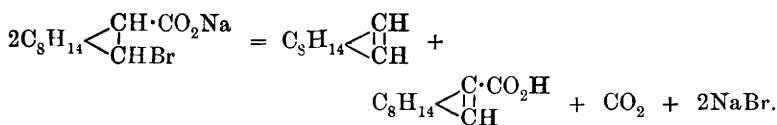
Reduction with zinc dust and sodium hydroxide converts both α - and β -*isonitroso-l-epicamphor* into the same *amino-l-epicamphor*, $C_8H_{14} \begin{smallmatrix} \text{CO} \\ \diagdown \\ \text{CH} \cdot \text{NH}_2 \end{smallmatrix}$, which melts at 168—170°, has, in benzene, $\alpha_D + 15^\circ$, and is a substance which crystallises well, and is comparatively stable, whereas aminocamphor, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NH}_2 \\ \diagdown \\ \text{CO} \end{smallmatrix}$, melts at 226—228°, and is a waxy substance, which readily undergoes change (compare Duden and Pritzkow, *Annalen*, 1899, **307**, 209).

l-Epicamphor is readily reduced when sodium is dissolved in its boiling alcoholic solution, with the formation of *l-epiborneol*, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{OH} \\ \diagdown \\ \text{CH}_2 \end{smallmatrix}$, a crystalline substance, which melts at 181—182.5°, and yields a phenylurethane melting at 82°. It is remarkable that epiborneol has no rotation, but it is not really an inactive substance, as is shown by the fact that, when it is converted by loss of water into the hydrocarbon, the substance which results is *l*-bornylene, with the rotation $\alpha_D - 18.45^\circ$.

For the purpose of the elimination of water, *l*-epiborneol was converted, by the action of sodium and then of carbon disulphide, into *l*-epibornyl xanthate, and then, by treatment with methyl iodide, into methyl *l*-epibornyl xanthate, which, on distillation, is decomposed with elimination of methyl mercaptan and carbonyl sulphide, and formation of *l*-bornylene (method of Tschugaev):



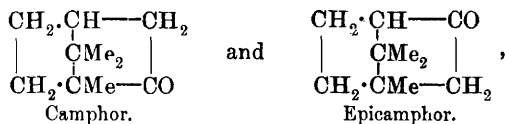
The *l*-bornylene, produced in this way, melted at 114°, and had, in solution in toluene, $\alpha_D - 18.45^\circ$; it yielded *d*-camphoric acid on oxidation, and was evidently identical with the *l*-bornylene which Bredt (*Annalen*, 1909, **366**, 46) had previously obtained by the decomposition of sodium β -bromodihydrobornylenecarboxylate by boiling with water:



During the experiments on the reduction of *l*-epicamphor with sodium and alconol we have endeavoured to determine whether, besides *l*-epiborneol, a second isomeride (*epiisoborneol*) is produced, and, although the melting points of different specimens varied slightly and seemed to indicate that such a substance might be present, if this is the case, it must be present in small quantity, and we have not been able to isolate it. Bertram and Wahlbaum (*J. pr. Chem.*, 1894, [ii], **49**, 12; compare Wallach, *Annalen*, 1885, **230**, 225) have shown that the product of the reduction of *d*-camphor with sodium and alcohol contains, besides *d*-borneol, sometimes as much as 20 per cent. of *l*-isoborneol.

d-Borneol melts at 208°, has $\alpha_D + 38.39^\circ$, and, like *l*-epiborneol, yields *l*-bornylene where it is converted into the methyl xanthate, and this is distilled. *l*-isoBorneol, obtained from *d*-camphor by reduction, melts at 212°, and has $\alpha_D - 33^\circ$.

If the formulæ of camphor and epicamphor are compared it is

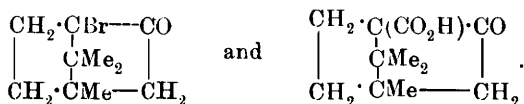


at once evident that, apart from the relative positions of the carbonyl and methylene groups, the most striking difference is that one of the linkings of the carbonyl group is attached to the tertiary >CMe group in the case of camphor, whereas, in epicamphor, it is attached to the secondary >CH group, and it was therefore to be expected that the carbonyl group of epicamphor might show greater reactivity than that in camphor. It is well known that camphor does not combine with hydrogen cyanide, but we were surprised to find that, in spite of the presence of the $\text{>CH}\cdot\text{CO}\cdot\text{CH}_2$ -group in epicamphor, this substance is also not capable of yielding an additive product with hydrogen cyanide, at all events, under the favourable conditions described on p. 2210. This is the more remarkable since Lapworth and Chapman (*T.*, 1901, **79**, 378) have shown that the >CO group in camphorquinone combines quite readily with hydrogen cyanide; again, Manasse (*Ber.*, 1897, **30**, 662) has shown that camphorquinone may be reduced by zinc dust and acetic acid, whereas epicamphor is unchanged under the same conditions, and these results seem to indicate that any difference

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in the relative reactivity of the carbonyl groups in camphor and epicamphor is, at the most, only a slight one.

Another consideration connected with the difference in the constitutional formulæ of camphor and epicamphor is the possibility that the presence of the $>\text{CH}$ group adjacent to the carbonyl group in epicamphor and its absence in camphor might well lead to a difference in the constitution of the substitution derivatives, and that, for example, whilst bromocamphor and camphorcarboxylic acid contain the groupings $-\text{CHBr}\cdot\text{CO}-$ and $-\text{CH}(\text{CO}_2\text{H})\cdot\text{CO}-$, the corresponding derivatives of epicamphor might have the following constitutions:



The sodium salt of *l*-epicamphorcarboxylic acid is produced when a boiling ethereal solution of *l*-epicamphor is treated with carbon dioxide in the presence of sodium, but it is more readily obtained and in much better yield when the solution of epicamphor in benzene is boiled with sodamide and a stream of carbon dioxide passed (p. 2214). The free acid melts at $120-122^\circ$, and is very similar in properties to *d*-camphorcarboxylic acid (m. p. $125-126^\circ$), since both acids are decomposed somewhat above their melting points into carbon dioxide and epicamphor or camphor respectively. Epicamphorcarboxylic acid gives a green coloration when ferric chloride is added to its alcoholic solution (camphorcarboxylic acid gives a blue in similar circumstances), and it therefore is clear that it must contain the grouping $>\text{CH}\cdot\text{CO}_2\text{H}$, and

its formula must be $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CO} \\ | \\ \text{CH} \end{smallmatrix} \cdot \text{CO}_2\text{H}$, and not that suggested above as a possible alternative. When this acid is treated with bromine at the ordinary temperature it yields bromo-*l*-epicamphorcarboxylic acid (m. p. 145°) and, as this acid gives no coloration with ferric chloride, its constitution must be that represented by

the formula $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CO} \\ | \\ \text{CBrl} \end{smallmatrix} \cdot \text{CO}_2\text{H}$.

Now this acid is decomposed when it is heated a few degrees above its melting point with elimination of carbon dioxide and formation of a bromo-*l*-epicamphor, which melts at 136° , has $\alpha_D - 86.6^\circ$ (bromocamphor melts at 76° and has $\alpha_D + 140^\circ$), and

the constitution of this substance must evidently be $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CO} \\ | \\ \text{CH} \end{smallmatrix} \cdot \text{Br}$, a view which is confirmed by the fact that it yields *d*-camphoric acid when it is oxidised by dilute nitric acid. This same bromo-

epicamphor, however, is also obtained by the direct bromination of epicamphor (p. 2210), and it follows, therefore, that hydrogen of the $>\text{CH}_2$ group, and not of the $>\text{CH}$ group, is substituted during the conversion of epicamphor into epicamphorcarboxylic acid and bromoepicamphor.

The l-Epiborneolcarboxylic Acids, l-Bornylene-2-carboxylic Acid, l-Camphane-2-carboxylic Acid, and the Conversion of l-Epicamphor into d-Camphor.

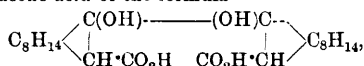
Roser, in 1885 (*Ber.*, **18**, 3114), first called attention to the fact that camphorcarboxylic acid, although it is a β -ketonic acid, cannot be reduced by sodium amalgam, and showed that reduction does not even take place under the conditions which so readily convert camphor into borneol, namely, when the acid or its ester is treated with sodium and alcohol. These observations were confirmed by Bredt (*Annalen*, 1906, **348**, 200; 1909, **366**, 1), who discovered, however, that camphorcarboxylic acid may be reduced electrolytically, using potassium amalgam as the cathode, and that it then yields two acids, namely, *cis*-borneolcarboxylic acid (m. p. 101–102°) and *cis-trans*-borneolcarboxylic acid (m. p. 171°),

whereas four isomeric acids of the formula C_8H_{14} $\begin{matrix} \text{CH}\cdot\text{CO}_2\text{H} \\ | \\ \text{CH}\cdot\text{OH} \end{matrix}$ are theoretically possible.

Owing to the difference in constitution between epicamphorcarboxylic acid and camphorcarboxylic acid (compare p. 2192), it seemed possible that the former might exhibit less resistance to reducing agents than the latter, and experiment showed that epicamphorcarboxylic acid is actually reduced when the solution of its sodium salt is boiled with sodium amalgam, but the process is very slow and incomplete.

When, however, *l*-epicamphorcarboxylic acid was reduced electrolytically under the same conditions as camphorcarboxylic acid, it was more readily reduced than the latter, and yielded a product from which, by fractional crystallisation from light petroleum, four *l*-epiborneolcarboxylic acids, C_8H_{14} $\begin{matrix} \text{CH}\cdot\text{OH} \\ | \\ \text{CH}\cdot\text{CO}_2\text{H} \end{matrix}$, were separated, namely, A (m. p. 125°, $\alpha_D + 2.36^\circ$), B (m. p. 143–145°, $\alpha_D - 4.8^\circ$), C (m. p. 173°, $\alpha_D + 15.18^\circ$), and D (m. p. 237°, $\alpha_D + 77.9^\circ$).* When a mixture of these acids is dehydrated with

* The results of analysis indicate that this isomeride of high melting point (D) may possibly be a pinacone acid of the formula

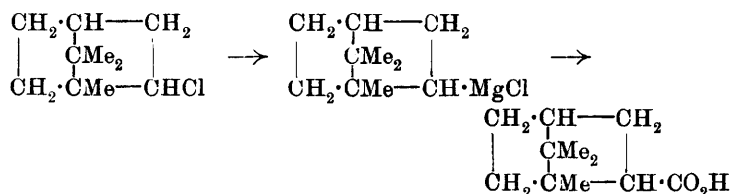


but this seems improbable in view of the fact that it dissolves almost as readily in

acetyl chloride and the product distilled, *l*-bornylene-2-carboxylic acid, $C_8H_{14} \begin{smallmatrix} \text{CH} \\ | \\ \text{C} \cdot \text{CO}_2\text{H} \end{smallmatrix}$, is obtained, which melts at 115° , has $\alpha_D - 95.7^\circ$, and is very similar to *d*-bornylene-3-carboxylic acid, $C_8H_{14} \begin{smallmatrix} \text{C} \cdot \text{CO}_2\text{H} \\ | \\ \text{CH} \end{smallmatrix}$, (m. p. 112° , $\alpha_D + 149.5^\circ$), in its properties.

l-Camphane-2-carboxylic acid, $C_8H_{14} \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH} \cdot \text{CO}_2\text{H} \end{smallmatrix}$, is obtained in quantitative yield when *l*-bornylene-2-carboxylic acid is reduced by hydrogen in the presence of palladium and gum arabic (compare p. 2219); it melts at $78-80^\circ$, has $\alpha_D - 37.8^\circ$, and closely resembles *d*-camphane-3-carboxylic acid, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H} \\ | \\ \text{CH}_2 \end{smallmatrix}$, which melts at $90-91^\circ$, and is produced by the reduction of *d*-bornylene-3-carboxylic acid under the same conditions (p. 2198).

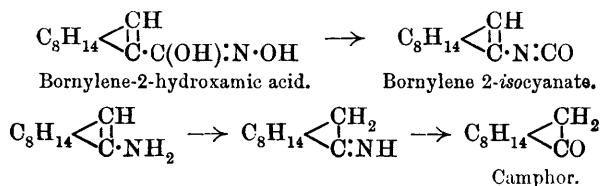
Epicamphane-2-carboxylic acid had already been prepared by Houben and Kesselkaul (*Ber.*, 1902, **35**, 3696) from pinene hydrochloride by conversion into the magnesium derivative and subsequent decomposition by carbon dioxide and water:



and these investigators state that the free acid crystallises and distils at $156^\circ/12$ mm. Zelinsky (*Ber.*, 1902, **35**, 4417; compare *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 646) prepared the same acid (called by him "camphanecarboxylic acid") from borneol by converting it into bornyl iodide, and then acting on this with magnesium and carbon dioxide, and he states that it melts at $69-71^\circ$. At a later date, Houben (*Ber.*, 1905, **38**, 3799) again prepared the acid (hydropinenecarboxylic acid) from pinene hydrochloride, and describes it as a crystalline substance, melting at $72-74^\circ$ and distilling at $153^\circ/13$ mm.

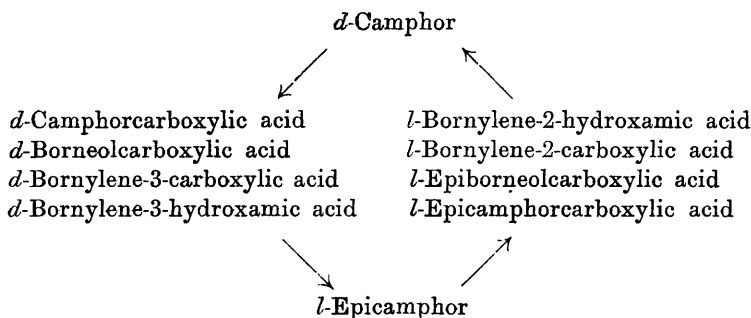
Methyl *l*-bornylene-2-carboxylate reacts readily with hydroxylamine in the presence of sodium methoxide, with the formation of *l*-bornylene-2-hydroxamic acid, a syrup which, on heating, decomposes vigorously, and yields steam, ammonia, some camphor, and a pale yellow, resinous substance. The latter, which doubtless consists of bornylene 2-isocyanate, gives a large yield of *d*-camphor so vents as the other isomerides, and that an acid of this kind has not been observed among the products of the reduction of camphorcarboxylic acid.

when it is mixed with hydrochloric acid and distilled in steam, and the whole process, which may be represented thus:



is exactly similar to the formation of *l*-epicamphor from *d*-bornylene-3-hydroxamic acid under the same conditions. Lastly, the above intramolecular change was brought about by treating the sodium salt of *l*-bornylene-2-hydroxamic acid with toluene-*p*-sulphonyl chloride (compare p. 2221), and, after decomposing with hydrochloric acid, the product was distilled in steam, when a comparatively large yield of *d*-camphor was obtained. The *d*-camphor resulting from these two experiments melted at 176°, had, in ethyl acetate solution, $\alpha_D + 47.7^\circ$, and yielded an oxime melting at 119°, whereas ordinary *d*-camphor melts at 178°, has $\alpha_D + 48.0^\circ$, and camphoroxime melts at 119°.

The conversion of *l*-bornylene-2-carboxylic acid into *d*-camphor completes the interesting cycle, *d*-camphor \rightleftharpoons *l*-epicamphor, and the whole scheme may be clearly represented thus:



Comparison of some Physiological Properties of d-Camphor and l-Epicamphor.

The following experiments, which deal with the comparative action of camphor and epicamphor on the beat of the heart in a frog, following the administration of chloral, were carried out by Professor van der Velden and Dr. P. Leyden in the laboratories of the Mediz. Klinik der Akademie für prakt. Mediz. in Düsseldorf.

The administration of a drop of a 5 per cent. oil solution of

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camphor doubled the beat of the heart from thirteen to twenty-six, and the heart curve tracing was unusually regular; the same experiment with epicamphor showed no appreciable action. When a 10 per cent. oil solution of camphor was employed, it was found that three drops increased the beat from seven to twenty-two, and that the beat then became very constant, and the curve tracing was again remarkably regular. The same quantity of epicamphor increased the beat slowly from six to twelve, and then a gradual decrease was observed and the beat became very irregular.

The administration of three drops of a 20 per cent. oil solution of camphor increased the beat from six to eighteen; then a decrease to eleven occurred, and the well-known poisonous action of camphor became evident.

In a similar experiment with epicamphor the beat was increased from six to twenty-seven, but rapidly decreased to thirteen in five minutes. A subsequent administration had no further effect, and the curve, which at first was very regular, became weaker.

These results show that favourable action of epicamphor on the beat of the heart does not become apparent until the solution administered is about four times stronger than that which produces the same effect in the case of camphor. A further series of experiments has, moreover, clearly shown that, even at this concentration, epicamphor has not the same favourable action as camphor because the effect soon disappears, whereas in the case of camphor (provided that it is absolutely pure) the action induced persists for a much longer time. The action of camphor is toxic at the concentration necessary for favourable action in the case of epicamphor.

We are at present engaged in a further investigation of the properties and derivatives of epicamphor, and hope shortly to publish an account of the results of these experiments.

EXPERIMENTAL.*

d-Bornylene-3-carboxylic Acid and its Derivatives.

The preparation of bornylene-3-carboxylic acid from camphor-carboxylic acid by electrolytic reduction to the isomeric borneol-

* Wilhelm Hilbing and Joseph Regout assisted Prof. Brecht in Aachen, the former in the preparation of epicamphor by the bornylenecarboxylic acid azide method and in converting it into the oxime, semicarbazone, and into epicamphorcarboxylic acid by the sodium, carbon dioxide, process, and also in preparing several derivatives of bornylenecarboxylic acid, such as the ester, acid chloride and amide; the latter prepared most of the epiborneol employed in this research, and converted it into bornylene by the Tschugaev xanthate method.

Mr. F. R. Lankshear assisted Prof. Perkin by preparing much of the bornylene-

carboxylic acids and subsequent elimination of water, has already been described by Bredt and his co-workers (*Annalen*, 1906, **348**, 200; 1909, **366**, 1).

The acid employed in the present research was purified by distillation either alone or in a current of steam or by recrystallisation from acetone, from which it separates in large, colourless crystals; it melts at 112—113°, distils at 156—157°/13 mm., and yields an anhydride, which melts at 96—97° and distils at 236°/21 mm.

The *barium* salt, $(C_{10}H_{15}\cdot CO_2)_2Ba, 4H_2O$, was prepared by dissolving the acid in pure barium hydroxide, and, after removing the excess of the latter by carbon dioxide and concentrating the filtrate, the salt separated in needles. For analysis it was recrystallised from water, and then exposed to the air for several days:

0.2738, on drying at 120°, lost 0.0360 H_2O and gave 0.1112 $BaSO_4$. $H_2O = 13.2$; $Ba = 24.2$.

$(C_{11}H_{15}O_2)_2Ba, 4H_2O$ requires $H_2O = 12.7$ and $Ba = 24.2$ per cent.

The *acid chloride*, $C_{10}H_{15}\cdot COCl$, may be prepared by adding the acid (20 grams) to phosphorus pentachloride covered with light petroleum (100 c.c., b. p. 35—60°), and after the vigorous decomposition has subsided, the whole heated on the steam-bath for two hours, the light petroleum distilled off, and the residue fractionated under diminished pressure.

This chloride may be prepared even more conveniently by warming equal weights of the acid and thionyl chloride; as soon as the reaction is complete, the product is distilled, when an almost quantitative yield of the pure chloride is obtained.

Bornylene-3-carboxyl chloride distils at 120—121°/19 mm., and is a comparatively stable substance, which fumes only slightly in the air:

0.2600 gave 0.1811 $AgCl$. $Cl = 17.3$.

$C_{11}H_{15}OCl$ requires $Cl = 17.8$ per cent.

The *acid amide*, $C_{10}H_{15}\cdot CO\cdot NH_2$.—This substance may be prepared from the anhydride by heating with concentrated aqueous ammonia at 100°, when a clear solution is obtained, from which the amide crystallises on cooling. A specimen was also prepared by gradually adding the acid chloride to concentrated aqueous ammonia, the whole being well cooled and stirred during the

3-carboxylic acid used in Manchester for the preparation of epicamphor and by photographing the absorption spectra of epicamphor and its derivatives. Valuable assistance was also rendered by Messrs. Reginald Furness and Harold Goodwin, not only in the preparation of bornylenecarboxylic acid, but also in working out the details of the formation of epicamphor by the bornylenehydroxamic acid process, of the preparation of epicamphorcarboxylic acid by the sodamide—carbon dioxide method, and of the conversion of epicamphor into camphor.

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operation. The amide is best crystallised from dilute ammonia, from which it at first frequently separates as a milky precipitate, but on rubbing or the addition of a crystal, crystallisation at once sets in. It melts at 119—122°, and yields a crystalline hydrochloride when its solution in light petroleum is saturated with hydrogen chloride, but this is unstable, and decomposes on keeping:

0.2367 gave 16 c.c. N_2 at 18° and 752 mm. $N=8.0$.

$C_{11}H_{17}ON$ requires $N=7.8$ per cent.

The *methyl* ester, $C_{10}H_{15} \cdot CO_2Me$.—The esters of bornylene-3-carboxylic acid must not be prepared by the action of the acid chloride on the alcohols or by saturating the alcoholic solutions of the acid with hydrogen chloride, because the esters obtained in both cases, although they distil constantly, invariably contain chlorine. The large quantities of the methyl ester used in this research were prepared as follows: The pure acid (10 grams), dissolved in methyl alcohol (50 grams) and sulphuric acid (5 grams), was left for twenty-four hours, and then heated on the steam-bath for two hours. After diluting with water, the ester was extracted with ether, washed with water and dilute sodium carbonate, dried, and distilled.

Under these conditions, esterification is practically complete, and the methyl ester distils at 158°/100 mm.:

0.1112 gave 0.3021 CO_2 and 0.0941 H_2O . $C=73.9$; $H=9.4$.

$C_{12}H_{18}O_2$ requires $C=74.2$; $H=9.4$ per cent.

1.6464, made up to 20 c.c. in ethyl acetate, gave $n_D + 100.5^\circ$.

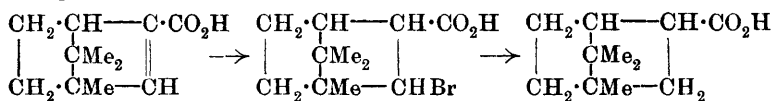
The *ethyl* ester, prepared in a similar manner, distils at 115°/12 mm. or 168°/100 mm.:

0.1211 gave 0.3330 CO_2 and 0.1079 H_2O . $C=74.9$; $H=9.9$.

$C_{13}H_{20}O_2$ requires $C=75.0$; $H=9.6$ per cent.

d-Camphane-3-carboxylic Acid.

Camphane-3-carboxylic acid was first prepared by Bredt (*Annalen*, 1909, **366**, 60) from *d*-bornylene-3-carboxylic acid by conversion into β -bromohydrobornylene-3-carboxylic acid (β -bromocamphane-3-carboxylic acid) and subsequent reduction by potassium amalgam:



A more direct and convenient process is the reduction of bornylenecarboxylic acid by hydrogen in the presence of palladium and gum arabic under the conditions recommended by Skita (*Ber.*, 1909, **42**, 1630).

Pure bornylene-3-carboxylic acid (10 grams) dissolved in methyl alcohol was mixed with 5 c.c. of a 20 per cent. gum arabic solution and 0.5 gram of palladium chloride; 150 c.c. of hot water was then added, and the whole placed in a long, narrow cylinder, and hydrogen passed for several hours. The product was rendered alkaline by sodium carbonate, the methyl alcohol and most of the water distilled off, the solution filtered, acidified, and the crude camphanecarboxylic acid, which separated as a crystalline mass, collected and distilled in steam. The acid, which was not quite stable to permanganate, was dissolved in sodium carbonate, mixed with powdered ice, and left in contact with excess of permanganate for half an hour; the permanganate was then destroyed by sulphur dioxide, and the filtrate from the manganese precipitate concentrated and acidified. Finally, the camphane-3-carboxylic acid was recrystallised from dilute acetic acid, from which it separated as a voluminous mass of thin plates, and melted at 90—92°:

0.1072 gave 0.2847 CO_2 and 0.0951 H_2O . $\text{C}=72.4$; $\text{H}=9.9$.

$\text{C}_{11}\text{H}_{18}\text{O}_2$ requires $\text{C}=72.5$; $\text{H}=9.9$ per cent.

Conversion of d-Camphane-3-carboxylic Acid into l-Epicamphor.

This process, which is discussed on p. 2186, may be carried out under the following conditions: *d*-Camphane-3-carboxylic acid (18 grams) is mixed with phosphorus pentachloride (22 grams) in a flask fitted with a ground-in air-tube, heated on the steam-bath until decomposition is complete, and, after cooling, bromine (18 grams) is added, and the whole transferred to a pressure-tube and gradually heated in a water-bath for several hours. The product, which is almost free from bromine, is poured into alcohol, and, after remaining for twenty-four hours, water is added and the bromo-ester extracted with ether.

The ethereal solution is thoroughly washed with water, carefully dried, evaporated, and the residue mixed in a reflux apparatus with glacial acetic acid (50 c.c.) and anhydrous potassium acetate (20 grams) and heated in the oil-bath to boiling for forty-five minutes, when potassium bromide separates in quantity and there is some darkening.

The product is diluted with water, extracted with ether, the ethereal solution washed well, evaporated, and left during twenty-four hours with a solution of potassium hydroxide (25 grams) in methyl alcohol.

After heating for three hours on the steam-bath, the methyl alcohol is removed by evaporation, the residue then acidified and extracted with ether, when, on evaporation, crude α -hydroxy-

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camphane-3-carboxylic acid remains as a pale brown syrup, and *l*-epicamphor was obtained from this in three different ways:

I. *By Oxidation with Permanganate*.—The syrupy acid (5 grams) was dissolved in a slight excess of dilute potassium hydroxide, gradually mixed with permanganate (1.5 grams), and the whole heated on the steam-bath until oxidation was complete. After acidifying with sulphuric acid, the same quantity of permanganate was again added, and the whole distilled in a current of steam, when a semi-solid mass passed over, which consisted of a mixture of epicamphor and bornylene-3-carboxylic acid. The distillate was made alkaline with dilute potassium hydroxide, extracted with ether, the ethereal solution dried, and the ether removed by careful distillation with a column, when a buttery mass resulted (0.7 gram), which in contact with porous porcelain became quite dry and melted at 165° (compare Lankshear and Perkin, P., 1911, 27, 166), and, on treatment with hydroxylamine hydrochloride and sodium acetate, yielded *l*-epicamphoroxime melting at 102° (p. 2208).

Subsequently, a larger quantity of *l*-epicamphor (30 grams) was prepared by this process, and purified by conversion into the semicarbazone (p. 2209); it then melted at 178—182°, and yielded the following results on analysis:

0.1071 gave 0.3089 CO₂ and 0.1034 H₂O. C=78.7; H=10.7.

C₁₀H₁₆O requires C=79.0; H=10.5 per cent.

II. *By Oxidation with Chromic Acid*.—In this experiment crude hydroxycamphanecarboxylic acid (3 grams), dissolved in a little water, was gradually mixed with an aqueous solution of chromic acid (1 gram), care being taken that the temperature did not rise above 35°.

When the product was heated in a steam distillation apparatus, carbon dioxide was eliminated, and an oil passed over which had the pungent odour of epicamphor, and on cooling became a butter-like mass.

This was collected and left in contact with porous porcelain until dry; it then melted at about 165—167°, and was proved to consist of epicamphor by conversion into the oxime (m. p. 102°) and the semicarbazone (m. p. 235—237°).

III. *By Oxidation with Lead Peroxide*.—In this experiment the crude hydroxycamphanecarboxylic acid (7 grams) was mixed with water (5 c.c.) and acetic acid (100 c.c.); precipitated lead peroxide (20 grams) was then added, and, after boiling for ten minutes in a reflux apparatus, during which carbon dioxide was evolved, the whole was distilled in steam, when epicamphor distilled as a buttery mass, and a further small quantity was obtained by adding more

lead peroxide and continuing the distillation. The distillate was extracted with ether, the ethereal solution shaken with sodium carbonate, which removed a considerable quantity of bornylene-3-carboxylic acid, dried, and evaporated, when crude epicamphor (2 grams) was obtained, which, in contact with porous porcelain, became quite hard, and was identified as before by conversion into the oxime (m. p. 103°) and semicarbazone (m. p. $235-237^{\circ}$).

Preparation of l-Epicamphor from d-Bornylene-3-carboxylic Acid by the Azide Method of Curtius.

It is remarkable that the bornylene-3-carboxylic hydrazide, $C_{10}H_{15} \cdot CO \cdot NH \cdot NH_2$, necessary for this process is a substance which is very difficult to obtain except under certain very definite conditions.

In the first experiments, bornylenecarboxylic ester was treated with hydrazine hydrate in the usual manner (Curtius, *J. pr. Chem.*, 1894, [ii], 50, 275) in or without the presence of alcohol, in the cold and at the boiling temperature, but in no case was the normal hydrazide obtained, and the only crystalline product which could be isolated was always the dibornylene-3-carboxylic hydrazide, $C_{10}H_{15} \cdot CO \cdot NH \cdot NH \cdot CO \cdot C_{10}H_{15}$, a description of which is given below. The action of the acid chloride on hydrazine hydrate was next investigated in the hope that the equation:

$C_{10}H_{15} \cdot COCl + 2N_2H_4 \cdot H_2O = C_{10}H_{15} \cdot CO \cdot NH \cdot NH_2 + N_2H_4 \cdot HCl + H_2O$ might be realised, but, except when the unusual conditions described below were employed, the result was always a negative one.

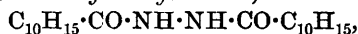
Thus, for example, when bornylenecarboxyl chloride was rubbed in a mortar with excess of hydrazine hydrate, a rather vigorous reaction set in with considerable development of heat, and this was checked by keeping the containing vessel in a freezing mixture. After an hour the product was mixed with water, the solid collected, washed with water and dilute sodium carbonate, and then crystallised from benzene or dilute alcohol, from which it separated as a glistening mass of needles, which became soft at 218° and melted at about 224° :

0.1326 gave 0.3623 CO_2 and 0.1083 H_2O . C=74.5; H=9.0.

0.1428 „ 10.4 c.c. N_2 at 17° and 745 mm. N=8.2.

$C_{22}H_{32}O_2N_2$ requires C=74.2; H=9.0; N=7.8 per cent.

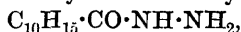
Di-d-bornylene-3-carboxylic hydrazide,



is almost insoluble in water, but readily so in alcohol, and is a remarkably stable substance, since it is only very slowly decomposed when digested with alcoholic potassium hydroxide or hydrochloric acid.

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Ultimately, normal *d*-bornylene-3-carboxylic hydrazide,



was obtained, in almost quantitative yield, by adding an alcoholic solution of hydrazine hydrate to an ethereal solution of the acid chloride under the following conditions: The pure acid chloride (20 grams), dissolved in dry ether (150 grams) and cooled to 0° , is gradually added from a jacketed funnel containing a freezing mixture to a solution of hydrazine hydrate (15 grams) in alcohol, which must be cooled below 0° . The liquid soon becomes milky, and needle-shaped crystals of hydrazine hydrochloride form on the sides of the vessel. After several hours, the clear solution is decanted from this salt and evaporated under diminished pressure, when a syrupy residue is obtained, which readily crystallises, and this mass is left for some days over concentrated sulphuric acid to remove the remainder of the alcohol. The white mass (19.5 grams) is almost pure, and may be recrystallised from benzene or a mixture of benzene and light petroleum, from which it separates in needles:

0.1944 gave 25.9 c.c. N_2 at 16.5° and 738 mm. $\text{N}=14.9$.

$\text{C}_{11}\text{H}_{18}\text{ON}_2$ requires $\text{N}=14.4$ per cent.

d-Bornylene-3-carboxylic hydrazide melts at $109\text{--}110^\circ$, and is readily soluble in alcohol, but sparingly so in ether or cold water; it dissolves readily in dilute hydrochloric acid, and is reprecipitated on the addition of sodium carbonate. The *hydrochloride*, which was required for the preparation of the azide, was obtained by dissolving the hydrazide (20 grams) in alcohol (25 grams) and adding a solution of alcoholic hydrogen chloride saturated at 0° (60 grams), when the hydrochloride separated at once. After remaining for two hours in ice-water, the crystalline precipitate was collected, washed with a little alcoholic hydrogen chloride, and left over solid potassium hydroxide in a vacuum desiccator for two days:

0.2210 gave 0.1380 AgCl . $\text{Cl}=15.4$.

$\text{C}_{11}\text{H}_{18}\text{ON}_2\cdot\text{HCl}$ requires $\text{Cl}=15.38$ per cent.

This hydrochloride melts and decomposes at 202° , and may be recrystallised either from water or alcohol, or best from a mixture of both. In a series of experiments the yields of the hydrazide and its hydrochloride from bornylenecarboxylic acid were the following:

One hundred grams of bornylenecarboxylic acid gave 103 grams of acid chloride (94 per cent.); this yielded 95 grams of hydrazide (94 per cent.), and from this, 103 grams of hydrochloride (92 per cent.) were obtained, or, the yield of hydrazide hydrochloride from 100 grams of bornylenecarboxylic acid is 80.6 per cent. of that theoretically possible.

Conversion of d-Bornylene-3-carboxylic Hydrazide into l-Epicamphor.

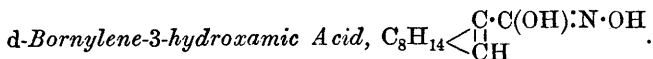
This experiment, which, owing to the well-known explosive nature of the azides, must be very carefully made and with small quantities of material, has been repeatedly carried out without accident under the following conditions: The hydrochloride of the hydrazide (10 grams) dissolved in water (200 c.c.) is covered with a layer of ether (100 c.c.), and the whole cooled in ice and salt. Sodium nitrite (3.1 grams) dissolved in a little water is then gradually added drop by drop, the temperature being maintained at 0° during the whole operation.

The addition of the nitrite produces a milkiness in the aqueous solution, but, by shaking, the oily azide passes into the ether, and at the end of the operation a few drops of dilute hydrochloric acid are added in order to ensure that nitrous acid is present in slight excess. The ethereal solution is separated, the aqueous layer extracted once with ether, and the combined extracts washed with ice-water, dried rapidly over calcium chloride, and mixed with alcohol (100 c.c.).

The ether is now removed on the steam-bath, and the alcoholic solution boiled in a reflux apparatus for two hours, and, after the alcohol has been distilled off under diminished pressure, a yellow syrup remains, which doubtless consists of the corresponding urethane.

This is dissolved in concentrated hydrochloric acid, and, after a few minutes, the solution is mixed with ice-water, when epicamphor separates in white flocks, and is best purified by distillation in steam, during which operation the bulk of the epicamphor, together with some bornylenecarboxylic acid, crystallises in the condenser. The whole is dissolved in ether, the bornylenecarboxylic acid carefully removed by repeated shaking with sodium carbonate, the ethereal solution dried, the ether slowly distilled off,* and the crude epicamphor left exposed to air with constant stirring until the residual ether has evaporated, and then placed in contact with porous porcelain, or the epicamphor may be directly distilled.

The yield of this nearly pure *l*-epicamphor is 5.5 grams.



After a long series of comparative experiments the best conditions for the preparation of this acid—a process which is also the

* Epicamphor is appreciably volatile with ether, and therefore the ether distilled from solutions of this substance was always carefully kept and used for subsequent extractions.

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first step in the preparation of epicamphor (p. 2206)—appear to be the following.* Hydroxylamine hydrochloride (15 grams) is dissolved in hot methyl alcohol (100 c.c.), and, after cooling, mixed with a solution of sodium (4.6 grams) in methyl alcohol (60 c.c.). Methyl bornylene-3-carboxylate (39.2 grams) is then added, together with a solution of sodium (5 grams) in methyl alcohol (60 c.c.). After remaining over night in a cool place, during which crystals of the sodium salt of bornylene-3-hydroxamic acid (see below) frequently separate, the whole is heated in a thermostat at 50° for two days. The product (A) is rendered just acid by the addition of acetic acid, and mixed with excess of a concentrated solution of copper acetate, when a pale green, voluminous precipitate separates, which is collected, washed with water, drained on porous porcelain, and then dried at 60°. The powdered salt is covered with ether, saturated with hydrogen sulphide, at first in the cold and then at the boiling point; the filtrate and ether washings of the copper sulphide are evaporated, and the syrupy residue left over sulphuric acid in a vacuum desiccator until it crystallises, which it quickly does if it is rubbed from time to time. The nearly solid mass is left in contact with porous porcelain until free from oily impurity, and the colourless residue recrystallised from benzene, from which it separates as a voluminous mass of colourless, microscopic, hexagonal plates:

0.1243 gave 0.3077 CO₂ and 0.0954 H₂O. C=67.5; H=8.5.

0.1334 gave 8.5 c.c. N₂ at 16° and 761 mm. N=7.4.

C₁₁H₁₇O₂N requires C=67.7; H=8.7; N=7.2 per cent.

d-Bornylene-3-hydroxamic acid melts at 136°, and is readily soluble in alcohol, ether, or hot benzene, sparingly so in cold benzene, light petroleum, or cold water, but it dissolves readily in hot water. The aqueous solution gives, on the addition of ferric chloride, an intense claret coloration. The sodium salt, obtained as described above, crystallises from methyl alcohol, in which it is comparatively sparingly soluble in the cold, in glistening prisms, which become opaque on exposure to the air, and the air-dry substance loses approximately 14.6 per cent. over phosphoric oxide under diminished pressure. When the salt is heated in the water-oven, it gradually decomposes, and swells up into threads, and, if heated in a capillary tube, the salt decomposes suddenly at about 105° and gives a white sublimate, which melts to a syrup at about 110°. If the experiment is carried out in a test-tube with about 0.1 gram of the salt, and the product of the decomposition is

* This process is modelled on the preparation of phenylpropionylhydroxamic acid (hydrocinnamylhydroxamic acid), recommended by Thiele and Pickard (*Annalen*, 1899, 309, 197).

moistened with hydrochloric acid, diluted with water, and boiled, epicamphor distils with the steam, and crystallises on the cold part of the tube. Boiling with water also slowly decomposes the sodium salt, with the formation of epicamphor. When sulphuric acid is added to the dry salt an almost explosive decomposition occurs, and a white sublimate is formed. The sodium salt is very readily soluble in water, and yields, on the addition of hydrochloric acid, an immediate crystalline precipitate of the pure hydroxamic acid.

The Acetyl Derivative.—Bornylenehydroxamic acid dissolves gradually in twice its weight of pure acetic anhydride in the cold, and, after remaining for twenty-four hours, the product, on decomposition with water, yields a crystalline mass, which separates from benzene in hard prisms.

A still more convenient method of preparing this acetyl derivative is to moisten the sodium salt with acetic anhydride, and, after a few hours, to add water and purify the product by crystallisation from benzene:

0.1457 gave 0.3493 CO₂ and 0.1038 H₂O. C=65.4; H=7.9.

0.1569 „ 8.3 c.c. N₂ at 15° and 758 mm. N=6.1.

C₁₃H₁₉O₃N requires C=65.8; H=8.0; N=5.9 per cent.

Acetylbornylene-3-hydroxamic acid melts at 115–116°, and is readily soluble in alcohol, ether, chloroform, or hot benzene, but it is comparatively sparingly soluble in cold benzene. It is very sparingly soluble in cold light petroleum, but separates well from the boiling solvent (b. p. 70–80°) in microscopic prisms. When the acetyl derivative is heated, it begins to decompose, with evolution of gas, at about 140°; decomposition is rapid at 150° and at higher temperatures an oil distils which, when boiled with hydrochloric acid, yields epicamphor. When the solution of the sodium salt of bornylenehydroxamic acid was shaken with a slight excess of benzoyl chloride and a little sodium hydroxide, a thick gum was produced, which, after extraction with ether and thoroughly washing, crystallised. The substance separated from a mixture of benzene and light petroleum in colourless crusts, melted at about 123°, and was doubtless the *benzoyl* derivative of the hydroxamic acid:

0.1962 gave 8.4 c.c. N₂ at 18.6° and 761 mm. N=4.9.

C₁₈H₂₁O₃N requires N=4.7 per cent.

On dry distillation this benzoyl derivative gives a pungent smelling oil, which when boiled with dilute hydrochloric acid develops the odour of epicamphor.

The Formation and Preparation of l-Epicamphor from d-Bornylene-3-hydroxamic Acid.

I. *Formation of l-Epicamphor by the Action of Heat on d-Bornylene-3-hydroxamic Acid.*—In studying this curious decomposition bornylenehydroxamic acid (5 grams) was gradually heated in a sulphuric acid bath until it just commenced to melt, when vigorous decomposition set in, a pale yellow resin was formed, and at the same time ammonia was eliminated, and a strong odour of epicamphor also became apparent. The product was shaken with hydrochloric acid, and, after remaining for fifteen minutes, water was added, when a brown syrup separated, which soon became semi-solid. The whole was now distilled in steam, which carried over epicamphor and left only a small, brown, resinous residue; the distillate was extracted with ether, the ethereal solution shaken with sodium carbonate,* dried, and evaporated, when 3 grams of crude epicamphor remained, and, after contact with porous porcelain and without further purification, had α_D -48.1° . For the purpose of complete identification, the substance was converted into the oxime (m. p. 103°) and semicarbazone (m. p. $236-238^\circ$).

II. *Preparation of l-Epicamphor from d-Bornylene-3-hydroxamic Acid by the Agency of Toluene-p-sulphonyl Chloride.*—This process, which has been employed for the preparation of more than 400 grams of epicamphor, is, in its first stage, carried out much in the way already described in the case of the preparation of bornylene-3-hydroxamic acid (p. 2204), except that epicamphor appears to be produced in larger yield when a considerable excess of hydroxylamine and sodium methoxide is used. Hydroxylamine hydrochloride (21 grams), dissolved in methyl alcohol (150 c.c.), is mixed with methyl bornylene-3-carboxylate (40 grams), sodium (14 grams), dissolved in methyl alcohol (180 c.c.), is then gradually added, the temperature being kept below 20° during this operation. After remaining for twenty-four hours, the product is heated in a thermostat at 50° for two days, cooled, mixed with powdered ice, and then toluene-p-sulphonyl chloride (65 grams) added, and the whole vigorously shaken in a bottle on the machine for twelve hours continuously.

It is most important that the decomposition of the sodium salt of the hydroxamic acid by the sulphonyl chloride should be as complete as possible, and the shaking must therefore be very thorough, and as some heat is developed during the first two hours, care is taken to cool the bottle and release the pressure from time to time.

* On acidifying the sodium carbonate extract, 0.8 gram of crude bornylene-3-carboxylic acid separated and melted at $106-107^\circ$.

The product is mixed with water, and extracted twice with ether*; the ethereal solution is washed and evaporated, and the residue mixed with two volumes of hydrochloric acid and well shaken during half an hour; water is then added, and the whole distilled in steam, when crude epicamphor mixed with bornylene-carboxylic acid passes over as a semi-solid mass, which frequently blocks the condenser. Ether is distilled down the condenser, the distillate extracted with ether, and the ethereal solution evaporated; the residue is warmed with methyl-alcoholic potassium hydroxide (10 grams KOH) for an hour, water is then added, and the epicamphor, which separates as a solid, extracted with ether. The ethereal solution is washed very thoroughly, dried and evaporated, when a syrup remains, which, when stirred in a current of air, soon becomes nearly solid. After contact with porous porcelain, the epicamphor, which remains as a colourless solid, is sufficiently pure for all ordinary purposes. The porous porcelain from several such operations is extracted with ether in a Soxhlet apparatus, the extract evaporated and distilled under 100 mm. pressure, and, in this way, a considerable additional quantity of pure epicamphor is obtained.

The alkaline aqueous solution is evaporated until free from ether and methyl alcohol, acidified, and the nearly pure bornylene-3-carboxylic acid which separates is collected, washed, dried on porous porcelain, and employed in a subsequent operation.

The yields obtained in this preparation vary in a manner which it is difficult to explain, but, if the operation is successful, the result should be about as follows:

Epicamphor, obtained directly	14	grams.
„ recovered from plates by distillation ...	5	„
Recovered bornylenecarboxylic acid	6.9	„

The yield of epicamphor, allowing for the recovered bornylene-carboxylic acid, is therefore nearly 76 per cent. of that theoretically possible. It may be further purified by conversion into the semi-carbazone (p. 2209) and subsequent regeneration by means of hydrochloric acid:

0.2145 gave 0.6151 CO_2 and 0.2062 H_2O . $\text{C}=78.2$; $\text{H}=10.7$.

0.1975 „ 0.5693 CO_2 „ 0.1876 H_2O . $\text{C}=78.6$; $\text{H}=10.6$.

$\text{C}_{10}\text{H}_{16}\text{O}$ requires $\text{C}=79.0$; $\text{H}=10.5$ per cent.

During the purification of the crude epicamphor by distillation in steam, as described above, the liquid remaining in the steam distillation flask generally deposits colourless crystals on keeping, sometimes in considerable quantity.

These were collected and recrystallised from dilute hydrochloric

* See footnote, p. 2203.

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acid, from which the substance separated in glistening plates melting at 135—137°. On investigation this substance was recognised as toluene-*p*-sulphonamide, $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ (Found, C=48.9; H=5.3; N=8.2. $\text{C}_7\text{H}_9\text{O}_2\text{S}$ requires C=49.1; H=5.3; N=8.2 per cent.), and it is remarkable that this amide should be sufficiently stable to survive the long-continued distillation with dilute hydrochloric acid.

The Properties and Derivatives of l-Epicamphor.

l-Epicamphor melts at about 182° and distils at 213° (camphor melts at 177—178° and distils at 207°), and has a penetrating odour closely resembling and yet distinct from that of *d*-camphor. It is sparingly soluble in water, but readily so in alcohol or ether, and when placed on water it rotates like camphor. It is very readily volatile in steam. *l*-Epicamphor is lævorotatory, the value at 19° in benzene solution at a concentration of 13.1205 being $\alpha_D -58.21^\circ$, whereas camphor, under similar conditions, has $\alpha_D +39.1^\circ$. On reduction, *l*-epicamphor is converted into *l*-epiborneol (p. 2222), but it is comparatively stable to oxidising agents, and is scarcely attacked by cold dilute permanganate or when boiled with dilute nitric acid (D 1.25), but more concentrated acid gradually attacks it, with formation of *d*-camphoric acid. In carrying out this oxidation, epicamphor (1 gram) was heated with nitric acid (13 c.c. of D 1.3) in a sealed tube for three hours at 100°, and then for a further three hours at 115°, when, on keeping, a crystalline substance separated, and a further quantity was obtained by evaporating the acid liquid and rubbing the semi-solid residue with chloroform. The substance was recrystallised from water, and shown to be camphoric acid by the fact that it melted at 186°, yielded an anhydride melting at 222—224°, and that mixtures of these substances with ordinary camphoric acid and its anhydride exhibited no alteration in their melting points. As was to be expected, the camphoric acid obtained by the oxidation of epicamphor showed exactly the same dextrorotation as a specimen prepared from ordinary camphor.

l-Epicamphoroxime, $\text{C}_8\text{H}_{14}\text{C}(\text{N}\cdot\text{OH})\text{CH}_2$, may be obtained by adding

sodium ethoxide and hydroxylamine hydrochloride to the alcoholic solution of *l*-epicamphor, but it is more conveniently prepared, and in almost quantitative yield, by the following process. Epicamphor (5 grams), hydroxylamine hydrochloride (4 grams), and excess of sodium acetate are digested with alcohol for an hour. On adding water, the milky liquid soon crystallises, and, after collecting, washing with water, and drying on porous porcelain, the oxime

melts at 98—100°, and is almost pure. It separates from dilute methyl alcohol at first as a milky precipitate, but this on stirring at once crystallises in glistening needles:

0.1398 gave 0.3710 CO₂ and 0.1315 H₂O. C=72.3; H=10.4.

0.2238 „ 16.8 c.c. N₂ at 22° and 760 mm. N=8.6.

0.1397 „ 10.8 c.c. N₂ „ 25° „ 758 mm. N=8.5.

C₁₀H₁₇ON requires C=71.8; H=10.2; N=8.4 per cent.

Epicamphoroxime melts at 103—104°, is very readily soluble in the usual organic solvents, and has the odour of mice so characteristic of camphoroxime. It is dextrorotatory, the solution of 0.6293 gram, made up to 10 c.c. in benzene, having $\alpha_D +100.5^\circ$. Camphoroxime is levorotatory, the solution of 0.5196 gram, made up to 10 c.c. in benzene, having $\alpha_D -56.0^\circ$.

l-Epicamphorsemicarbazone, C₈H₁₄ $\begin{smallmatrix} \text{C:N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$.—In order

to prepare this derivative, *l*-epicamphor (7.7 grams), dissolved in alcohol, was mixed with a solution of semicarbazide hydrochloride (6.5 grams) and crystallised sodium acetate (8 grams) in water (20 grams), and boiled for one and a-half hours on the steam-bath, and then left over-night, during which the bulk of the semicarbazone (8.3 grams) had crystallised, and a further quantity (1.4 grams) was precipitated from the alcoholic solution by the addition of water. The substance was purified by recrystallisation from alcohol, from which it separated in microscopic, flat needles, which are quite different in appearance from the short prisms of camphorsemicarbazone:

0.1483 gave 0.3444 CO₂ and 0.1239 H₂O. C=63.3; H=9.3.

0.1039 „ 19 c.c. N₂ at 22° and 760 mm. N=20.7.

C₁₁H₁₉ON₃ requires C=63.2; H=9.1; N=20.1 per cent.

When rapidly heated, epicamphorsemicarbazone melts and decomposes at 237—238° (camphorsemicarbazone melts and decomposes at 247—248°); it is very sparingly soluble in water, but dissolves readily in hot methyl or ethyl alcohol. It dissolves in concentrated hydrochloric acid, and, if the solution is at once diluted with water, part separates unchanged, but when the whole is distilled in steam, the unchanged substance dissolves, decomposition rapidly takes place, and pure epicamphor distils over.

Bromo-l-epicamphor, C₈H₁₄ $\begin{smallmatrix} \text{CO} \\ | \\ \text{CHBr} \end{smallmatrix}$.—In order to prepare this

substance, epicamphor (3 grams) was mixed in a tube with bromine (3.5 grams) and heated in the steam-bath for two hours. The crystalline product which separated was collected, dissolved in ether, in which it is not very readily soluble, the ethereal solution washed with dilute sodium hydroxide, dried and evaporated, and the pale

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brown, crystalline mass left in contact with porous porcelain until quite dry. The substance was then dissolved in light petroleum (b. p. 50—60°), and the solution concentrated, when, on cooling, groups of needles crystallised, but when the solution was allowed to concentrate spontaneously the substance separated in glistening, elongated prisms. The mother liquors were carefully examined, and yielded a further quantity of the same substance, but there was no evidence of the presence of any isomeride:

0.1488 gave 0.1198 AgBr. Br=34.2.

$C_{10}H_{15}OBr$ requires Br=34.6 per cent.

Bromo-l-epicamphor melts at 133—134° (bromocamphor at 76°), and dissolves readily in chloroform or benzene, but less so in alcohol; it is rather sparingly soluble in cold light petroleum, and much more readily so on warming:

0.7242, dissolved in ethyl acetate and made up to 20 c.c., had $\alpha_D - 86.6^\circ$, whereas the rotation of bromocamphor in 10 per cent. alcoholic solution is $\alpha_D + 140^\circ$.

Behaviour of l-Epicamphor in Contact with Hydrocyanic Acid.

For reasons stated in the introduction (p. 2191), the behaviour of epicamphor in contact with hydrocyanic acid was investigated under various conditions, but in no case could any signs of combination be observed; thus, in one experiment, finely-divided epicamphor (2 grams) was shaken in a stoppered bottle with pure potassium cyanide (5 grams) dissolved in a little water, and made nearly acid by the addition of acetic acid. The epicamphor liquefied, and, after twenty-four hours, the whole was extracted with ether, the ethereal solution dried and evaporated, when a solid residue of epicamphor was left, and almost the whole was recovered in this way, so that, if any combination had taken place, it must have been to a very slight extent.

The isoNitroso-l-epicamphors and Amino-l-epicamphor.

The two (α - and β -) *isonitroso-l-epicamphors* are obtained together by the action of sodamide and *isoamyl nitrite* on the ethereal solution of epicamphor under the following conditions (P., 1912, 28, 57).

Epicamphor (10 grams), dissolved in anhydrous ether (100 c.c.), is mixed with finely-powdered sodamide (4 grams), and, after two hours, freshly distilled *isoamyl nitrite* (9 c.c.) is gradually added, the temperature being kept at 0° during the addition. After remaining for twenty-four hours at the ordinary temperature, the orange-red solution is mixed with ice-water, the ethereal layer

separated, and the aqueous solution once more extracted with ether; it is then freed from ether by passing a stream of air, and acidified with acetic acid, when an oil separates in quantity, and gradually solidifies. The solid (8.5 grams) was collected, left in contact with porous porcelain over sulphuric acid in a vacuum desiccator, and then dissolved in hot light petroleum (b. p. 80–85°) with the addition of a little benzene, when, on keeping, groups of long needles separated first, and these were rapidly collected and purified by repeated recrystallisation from the same solvent:

0.1363 gave 0.3320 CO₂ and 0.1022 H₂O. C=66.4; H=8.3.

0.1156 „ 8.0 c.c. N₂ at 19° and 750 mm. N=7.8.

C₁₀H₁₅O₂N requires C=66.2; H=8.3; N=7.7 per cent.

α -isoNitroso-l-epicamphor melts at 168–170°, and dissolves readily in warm alcohol, benzene, or chloroform, and it differs from the β -modification (see below) by being much more sparingly soluble in light petroleum. It dissolves readily in dilute sodium hydroxide with a pale yellow colour, and when the solution is acidified with acetic acid it may remain clear for some time, and then gradually deposits crystals of the pure α -modification. A solution containing 0.799 in benzene, made up to 20 c.c., gave $\alpha_D - 201.9^\circ$. Forster and Spinner, who obtained *α -isonitrosoepicamphor* by another process (T., 1912, 101, 1350), found the melting point to be 170° and the rotation, in chloroform, $\alpha_D - 200.1^\circ$. They also prepared the benzoyl derivative (m. p. 122.5°, $\alpha_D - 128.7^\circ$), the *O*-methyl ether (m. p. 100°, $\alpha_D - 201.5^\circ$), and the phenylurethane (m. p. 106°, $\alpha_D - 110.2^\circ$).

α -isoNitroso-l-epicamphor dissolves readily in a 40 per cent. formaldehyde solution, and if, after heating on the steam-bath for an hour, hydrochloric acid is added and the solution boiled, it at once turns yellow and deposits crystals of camphorquinone. Concentrated sulphuric acid dissolves *α -isonitrosoepicamphor*, and the solution, heated on the steam-bath for two or three minutes and then diluted with water, yields a white, crystalline precipitate, which, after recrystallisation, melts at 244–245°, and consists of the imide of *d*-camphoric acid.

β -isoNitroso-l-epicamphor.—The light petroleum mother liquors from the crystallisation of the α -derivative yielded, on slow evaporation, a small crop of crystals, which consisted of a mixture of the α - and β -isomerides, and then pale yellow prisms of the almost pure β -derivative. These were collected and further purified by fractional crystallisation from light petroleum:

0.1453 gave 0.3526 CO₂ and 0.1091 H₂O. C=66.2; H=8.4.

0.1722 „ 12.1 c.c. N₂ at 18° and 752 mm. N=8.0.

C₁₀H₁₅O₂N requires C=66.2; H=8.3; N=7.7 per cent.

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β -isoNitroso-l-epicamphor melts at 138—140°, and dissolves readily in alcohol, benzene, chloroform, or light petroleum, and is also moderately soluble in boiling water. Rotation: 1.0138 dissolved in benzene and made up to 20 c.c., gave $\alpha_D -183.5^\circ$. Forster and Spinner (T., 1912, 101, 1349) also found that this substance melts at 140°, and they give the rotation for the solution in chloroform as -179.4° , rising to -191.4° in seven days. β -isoNitroso-l-epicamphor is converted into the α -isomeride by heating above its melting point or when its solution in water is boiled. It yields camphorquinone on treatment with formaldehyde and then with hydrochloric acid, and the imide of camphoric acid when it is heated with concentrated sulphuric acid (Claisen and Manasse, *Annalen*, 1893, 274, 73). The benzoyl derivative (m. p. 80°, $\alpha_D -130.0^\circ$), the O-methyl ether (m. p. 77°, $\alpha_D -173.6^\circ$), and the phenylurethane (m. p. 118°, $\alpha_D -124.3^\circ$) have been prepared by Forster and Spinner (*loc. cit.*, pp. 1349—1350).

Amino-l-epicamphor, $C_8H_{14} \begin{smallmatrix} \diagup CO \\ CH \cdot NH_2 \end{smallmatrix}$, is produced by the reduc-

tion either of α - or β -isonitrosoepicamphor by means of zinc dust and aqueous alkali. The isonitrosoepicamphor (10 grams) is dissolved in sodium hydroxide (40 c.c. of 30 per cent.), and then zinc dust (12 grams) added in small quantities at a time, when the deep yellow colour of the solution almost completely disappears. The oily precipitate is extracted with ether, the ethereal solution dried over potassium carbonate, evaporated, and the thick syrup, which has a penetrating and most unpleasant odour, is stirred until it has completely crystallised. The mass is left in contact with porous porcelain, and then recrystallised by dissolving it in boiling light petroleum (b. p. 45—50°), and then cooling in a freezing mixture, and, since it becomes viscid and decomposes on heating, it was dried in a current of air free from carbon dioxide:

0.1425 gave 0.3749 CO_2 and 0.1281 H_2O . C=71.7; H=10.0.

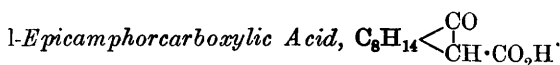
0.1917 „ 13.9 c.c. N_2 at 18° and 761 mm. N=8.3.

$C_{10}H_{17}ON$ requires C=71.8; H=10.2; N=8.4 per cent.

Amino-l-epicamphor melts at 168—170°, and is readily soluble in alcohol, ether, benzene, or light petroleum, and also in water; the solution of 0.5902 in benzene, made up to 10 c.c., gave $\alpha_D +15.0^\circ$.

Forster and Spinner (*loc. cit.*, p. 1355) found that aminoepicamphor melted at 168—169°, and, in alcoholic solution, had $\alpha_D +11.9^\circ$. We have not noticed that aminoepicamphor changes so rapidly as these authors seem to suggest, and specimens which have been sealed up for a year seem hardly to have altered in appearance. The discrepancy in the rotations ($\alpha_D +30.15^\circ$ instead

of $+15.07^\circ$; compare P., 1912, **28**, 57) which Forster and Spinner seem to think may have been due to partial change of the substance into epidihydrodicamphenepyzazine, was in reality due to a mistake in our calculation, the volume of the benzene solution having been taken as 20 c.c. instead of 10 c.c. We can confirm the statement of Forster and Spinner that the α - and β -isonitroso-*l*-epicamphors both yield the same amino-*l*-epicamphor on reduction, and, therefore, in most of our experiments, the isomeric isonitroso-derivatives were not first separated, but the mixture was directly used for the reduction.



The first specimens of this acid were prepared by a method similar to that recommended for the preparation of camphorcarboxylic acid (Brühl, *Ber.*, 1891, **24**, 3384; compare Bredt, *Annalen*, 1909, **366**, 11), namely, by acting on sodium *l*-epicamphor with carbon dioxide. Thin sodium ribbon (2.2 grams) was covered with a solution of epicamphor (10 grams) in absolute ether (120 c.c.) in a double-necked flask, fitted with a very efficient condenser and a tube for the delivery of carbon dioxide, and heated on the steam-bath whilst a rapid stream of carbon dioxide was passed. The reaction commences at once, and, if care is taken not to let it slacken, the sodium will, at the end of two to three hours, have been almost completely used up; the mass is then allowed to remain over-night, and the heating and passage of carbon dioxide continued for another hour. The product is decomposed by ice, the aqueous solution separated, extracted with ether, and carefully concentrated on the steam-bath, when, on fractionally precipitating with dilute hydrochloric acid, a resinous substance first separates, and, after removing this by filtration, almost pure epicamphorcarboxylic acid separates on the further addition of the hydrochloric acid, but the yield is not more than 2 grams. The ethereal solution, on evaporation, deposited 5.1 grams of a solid, and from this, on distillation in steam, 2 grams of a substance was obtained, which melted at $177\text{--}179^\circ$, and consisted of *l*-epiborneol (p. 2222) mixed with a little epicamphor. The portion not volatile in steam contains a substance which crystallises from light petroleum in slender needles, melts at $256\text{--}257^\circ$, and is probably the pinacone of *l*-epicamphor, since it yielded the following results on analysis:

0.1657 gave 0.4743 CO_2 and 0.1683 H_2O . C=78.1; H=11.3.

$(\text{C}_{10}\text{H}_{17}\text{O})_2$ requires C=78.4; H=11.2 per cent.

Other crystalline substances of lower melting point were also present, the nature of which could not be determined.

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Since the yield of epicamphorcarboxylic acid obtained by the above process was seldom more than 20 per cent. of that theoretically possible, and this loss of valuable epicamphor was serious, a long series of experiments was made first with the object of improving the method of preparation of camphorcarboxylic acid, and of then applying the process to epicamphor and with excellent results, since it is now possible to prepare epicamphorcarboxylic acid in a yield of at least 90 per cent. of that theoretically possible. This process consists in treating epicamphor with sodamide and carbon dioxide, but in benzene solution, since the reaction does not proceed with a satisfactory yield when ether is employed as the solvent.* Epicamphor (20 grams), dissolved in benzene (150 c.c.), is mixed with finely-powdered sodamide (14 grams) and heated to boiling in a two-necked flask connected with a condenser, and a rapid stream of carbon dioxide is passed through a tube which must be fitted with a wide end in order to avoid stoppage by the thick, gelatinous mass which rapidly forms. After about an hour the product is mixed with ice and water, the benzene solution separated, and the aqueous layer filtered and acidified with hydrochloric acid, when epicamphorcarboxylic acid separates in an almost pure condition, and a small quantity of less pure acid is obtained by extraction with ether. The benzene solution containing the unchanged epicamphor, and the amount of which may be approximately calculated from the weight of epicamphorcarboxylic acid resulting from the first operation, is thoroughly dried, half the benzene is removed by careful fractionation with a Young column, and the remaining solution again treated with sodamide and carbon dioxide, and this process is repeated until no more epicamphor remains in the benzene, and in this way an almost quantitative yield of epicamphorcarboxylic acid has been obtained on several occasions. The acid may be purified by contact with porous porcelain and recrystallisation from a mixture of benzene and light petroleum, from which it separates in colourless needles, but the best method is to dissolve the acid in a slight excess of sodium carbonate in a beaker fitted with a mechanical stirrer, and then to add very dilute hydrochloric acid until the small quantity of sticky impurity has been removed; after filtering, the acid obtained as a colourless precipitate on the addition of excess of hydrochloric acid is pure:

0.1937 gave 0.4473 CO_2 and 0.1444 H_2O . C=67.4; H=8.3.

0.1741 „ 0.4295 CO_2 „ 0.1295 H_2O . C=67.3; H=8.3.

$\text{C}_{11}\text{H}_{16}\text{O}_3$ requires C=67.3; H=8.2 per cent.

l-Epicamphorcarboxylic acid is rather sparingly soluble in cold

* This process may be employed with equal success in the preparation of camphorcarboxylic acid.

water, but dissolves easily in alcohol, ether, or benzene, less readily in light petroleum. Owing to the fact that this acid, like camphorcarboxylic acid, is readily decomposed on heating with elimination of carbon dioxide, the melting point is difficult to determine. The behaviour of both acids was observed on the same thermometer, when epicamphorcarboxylic acid melted at 120—122°, camphorcarboxylic acid at 125—126°. In both cases decomposition took place on slowly raising the temperature, until the contents of the wide capillary tubes solidified to very pure epicamphor and camphor, which then melted sharply at 184—184.5° and 178—179° respectively.

Rotation of l-Epicamphor Carboxylic Acid: 0.7775, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D - 18.5^\circ$; the rotation of *d*-camphorcarboxylic acid determined for the sake of comparison gave: 1.1615, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D + 57.4^\circ$.

Oxidation to Camphoric Acid.—In order to determine the position of the carboxyl group in *l*-epicamphorcarboxylic acid (compare p. 2192) a small quantity of this acid was dissolved in sodium carbonate and oxidised by permanganate.

Camphorcarboxylic acid, under these conditions, yields camphorquinone as well as camphoric acid, and epicamphorcarboxylic acid might be expected to exhibit the same behaviour, but the formation of camphorquinone could not be observed. When the oxidation was complete, the alkaline filtrate from the manganese precipitate was evaporated to a small bulk and acidified, when camphoric acid separated and was identified by the melting point (186°) and the melting point of the anhydride (222°).

α -Bromo-l-epicamphorcarboxylic Acid, $C_8H_{14} \begin{array}{c} \diagup CO \\ | \\ CHBr \cdot CO_2H \end{array}$ —

This substance is readily prepared by heating epicamphorcarboxylic acid (0.5 gram), dissolved in glacial acetic acid (5 c.c.) with bromine (0.6 gram) in a sealed tube in the water-bath. The change is a gradual one, but is complete in about four hours; the product is then mixed with two volumes of water, and allowed to remain for twenty-four hours. The bromo-acid which will have been deposited is collected, dissolved in dilute sodium carbonate, the solution filtered and acidified, when a voluminous mass of microcrystalline stars separate, which are collected, washed with water, and dried over phosphoric oxide:

0.1802 gave 0.1233 AgBr. Br = 29.1.

$C_{11}H_{15}O_3Br$ requires Br = 29.1 per cent.

α -Bromo-l-epicamphorcarboxylic acid melts, if rapidly heated, at about 145° with evolution of carbon dioxide, but it decomposes

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at a considerably lower temperature if the determination is slowly carried out (α -bromocamphorcarboxylic acid melts at 112—113°). It is very sparingly soluble in water, more readily so in alcohol, and the alcoholic solution gives no coloration on the addition of ferric chloride.

When this bromo-acid is heated at 150° until the elimination of carbon dioxide is complete, a crystalline substance remains, which separates from light petroleum in plates, melts at 132—134°, and is identical with the bromo-*l*-epicamphor obtained by the direct bromination of epicamphor (p. 2210), since a mixture of the two substances melted at the same temperature as the components.



It is well known that camphorcarboxylic acid cannot be reduced by sodium amalgam under the usual conditions, and, assuming this fact to be due to the proximity of the tertiary carbon atom to the CO-group, it seemed possible that epicamphorcarboxylic acid, in which the CO-group is not attached to a tertiary carbon atom, might behave quite normally, and be readily reduced on treatment with sodium amalgam. *l*-Epicamphorcarboxylic acid (5 grams) was therefore dissolved in dilute sodium carbonate and shaken on the machine with a large excess of sodium amalgam for several hours; the alkaline solution was then decanted from the mercury, acidified, and distilled in steam, when a quantity of epicamphor passed over, showing that a good deal of the epicamphorcarboxylic acid had remained unchanged. When the residue from the steam distillation was extracted with ether, the ethereal solution left, on evaporation, only a small quantity (0.6 gram) of a gum which possibly contained epiborneolcarboxylic acids, but it is evident that epicamphorcarboxylic acid, like camphorcarboxylic acid, cannot be effectively reduced under these conditions. The acid is, however, readily reduced by means of potassium amalgam produced electrolytically in an apparatus similar to that recommended by Bredt (*J. pr. Chem.*, 1911, [ii], **84**, 792) for the reduction of camphorcarboxylic acid. The aqueous layer from this reduction of about 60 grams of epicamphorcarboxylic acid was nearly neutralised with hydrochloric acid, filtered, and then acidified, when a chalky precipitate separated, which was collected and left in contact with porous porcelain until quite dry. This represented practically the whole of the product, since ether extracted only about 2 grams from the filtrate. The chalky mass was carefully extracted with several quantities of boiling light petroleum (b. p. 80—100°) until an acid remained which melted at 168—172°. This was then twice crystallised from

boiling toluene, from which it separated as a voluminous mass of thin plates, and, when dry, had a beautiful, satiny appearance. The pure acid, which weighed 2.5 grams, melted at 173°, and is called (C)-l-*epiborneolcarboxylic acid*; the analysis and rotation of the acid are given below. The mother liquors from this acid were freed from solvent by distillation from the steam-bath under reduced pressure, the mass was dissolved in sodium carbonate, the acid again precipitated, dried, and extracted with boiling light petroleum (b. p. 60–70°) until the residue melted at 140–145°, and this, which we propose to name (B)-l-*epiborneolcarboxylic acid*, weighed 24.5 grams, and was the principal product of the reduction.

The light petroleum mother liquors were exposed to the air and allowed to concentrate spontaneously, when they next deposited 5.8 grams of curious, warty nodules melting at 120–122°, and these were collected and again crystallised by solution in light petroleum and spontaneous concentration, when the melting point rose to 125°, and was not altered by further crystallisation. This acid is called (A)-l-*epiborneolcarboxylic acid*. The combined light petroleum mother liquors were now allowed to concentrate very slowly in the ice-chest, and yielded 1.5 grams of an acid which softened at 230° and melted at 237°, and it is curious that this acid, although apparently the least soluble of all the isomerides, should separate after the others. This acid, for which the name (D)-l-*epiborneolcarboxylic acid* is proposed, was recrystallised from light petroleum, from which it separated in warty groups melting at 237° with decomposition and slight previous softening. The final mother liquors were evaporated, and yielded a mixture of the epiborneolcarboxylic acids, which were not separated by fractional crystallisation, but used directly for the preparation of bornylene-2-carboxylic acid (p. 2218).

Analyses and rotations of the epiborneolcarboxylic acids:

(A)-l-*Epiborneolcarboxylic Acid*, m. p. 125°.

0.1110 gave 0.2700 CO₂ and 0.0910 H₂O. C=66.4; H=9.1.

C₁₁H₁₈O₃ requires C=66.7; H=9.1 per cent.

0.9299, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D + 2.36^\circ$.

(B)-l-*Epiborneolcarboxylic Acid*, m. p. 145°.

0.1224 gave 0.2985 CO₂ and 0.1004 H₂O. C=66.4; H=9.1.

1.1046, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D - 4.8^\circ$.

(C)-l-*Epiborneolcarboxylic Acid*, m. p. 173°.

0.1175 gave 0.2865 CO₂ and 0.0952 H₂O. C=66.5; H=9.0.

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0.2174, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D + 15.18^\circ$.

(D)-1-*Epiborneolcarboxylic acid* melts at 237° with evolution of gas, but without darkening, and the melted mass did not crystallise on cooling. It is almost insoluble in hot water, but dissolves readily in alcohol, boiling light petroleum (b. p. $90-100^\circ$), or in boiling toluene:

0.1452 gave 0.3555 CO_2 and 0.1134 H_2O . $\text{C}=66.8$; $\text{H}=8.7$.

0.1306 „ 0.3201 CO_2 „ 0.1028 H_2O . $\text{C}=66.7$; $\text{H}=8.7$.

0.1386, dissolved in ethyl acetate and made up to 20 c.c., had $\alpha_D + 77.9^\circ$.

$\text{C}_{11}\text{H}_{18}\text{O}_3$ requires $\text{C}=66.7$; $\text{H}=9.1$ per cent.

$\text{C}_{22}\text{H}_{34}\text{O}_6$ requires $\text{C}=67.0$; $\text{H}=8.6$ per cent. (compare p. 2193).

All the epiborneolcarboxylic acids are stable to permanganate, that is to say, their solutions in a slight excess of sodium carbonate mixed with ice do not decolorise permanganate on keeping for about a minute, and the most readily oxidisable of the isomerides appears to be the (A)-acid.

1-Bornylene-2-carboxylic Acid, C_8H_{14} $\begin{array}{c} \text{CH} \\ | \\ \text{C} \cdot \text{CO}_2\text{H} \end{array}$, and 1-Camphane-

2-carboxylic Acid, C_8H_{14} $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH} \cdot \text{CO}_2\text{H} \end{array}$.

In preparing *l*-bornylene-2-carboxylic acid, the crude mixture of *l*-epiborneolcarboxylic acids (p. 2216, 30 grams) was mixed with acetyl chloride (150 c.c.) and heated to boiling in a reflux apparatus for fifteen hours; the excess of acetyl chloride was then distilled off, and the syrupy mass distilled under diminished pressure (15 mm.), when almost the whole passed over, and only a small, crystalline residue remained.

The syrupy distillate and the residue were dissolved in methyl alcohol (200 c.c.) and sulphuric acid (15 c.c.), and, after remaining over-night, the whole was heated in a reflux apparatus for one hour; water was then added, and the oily methyl ester extracted with ether.

The ethereal solution was well washed with sodium carbonate, dried, evaporated, and the oil twice distilled under diminished pressure, when almost the whole quantity passed over at $155^\circ/100$ mm.:

0.1668 gave 0.4533 CO_2 and 0.1410 H_2O . $\text{C}=74.1$; $\text{H}=9.4$.

$\text{C}_{12}\text{H}_{18}\text{O}_2$ requires $\text{C}=74.2$; $\text{H}=9.3$ per cent.

0.6596, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D - 95.7^\circ$, but this value must not be taken as the true rotation of this methyl ester.

The *methyl l-bornylene-2-carboxylate* thus obtained (25 grams) was hydrolysed by boiling for an hour with methyl-alcoholic potassium hydroxide (KOH=20 grams); water was added, the solution nearly neutralised with hydrochloric acid, and the methyl alcohol removed by evaporation. When the filtered solution was acidified, a syrup separated, which soon crystallised, and, after remaining in contact with porous porcelain until dry, the acid was further purified by recrystallisation from dilute acetone or formic acid, or it may be distilled in steam, with which, however, it passes over somewhat slowly:

0.1386 gave 0.3715 CO₂ and 0.1107 H₂O. C=73.1; H=8.9.

0.1471 „ 0.3922 CO₂ „ 0.1166 H₂O. C=72.7; H=8.9.

C₁₁H₁₆O₂ requires C=73.3; H=8.9 per cent.

0.5161, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D - 98.82^\circ$.*

l-Bornylene-2-carboxylic acid melts at 115°, and is readily soluble in alcohol, benzene, light petroleum, ether, or acetic acid, but very sparingly so in water, and crystallises from dilute acetic acid in irregular plates.

The solution of the sodium salt decolorises permanganate, although not instantaneously.

Oxidation.—*l-Bornylene-2-carboxylic acid* is quickly oxidised by nitric acid, and, in studying this oxidation, the pure acid (0.5 gram) was warmed with nitric acid (25 c.c. of D 1.24) in a reflux apparatus, when a vigorous reaction set in, and some of the acid distilled with the nitric acid and crystallised in the condenser. After boiling for an hour a further quantity (15 c.c.) of the same acid was added, and the boiling continued for twelve hours; the product was then repeatedly evaporated with the addition of water, and the crystalline mass extracted with chloroform. The residue separated from water in glistening plates melting at 185°, and, on titration, 0.0894 neutralised 9.03 c.c. *N*/10-NaOH, whereas this amount of a dibasic acid, C₁₀H₁₆O₄, should neutralise 8.94 c.c. *N*/10-NaOH. Since the acid yielded an anhydride melting at 216—218°, there can be no doubt that it was *d-camphoric acid*.

l-Camphane-2-carboxylic Acid.—This acid is readily obtained by reducing bornylene-2-carboxylic acid, in dilute methyl-alcoholic solution, with hydrogen in the presence of palladium and gum arabic under the conditions already described in the case of the corresponding reduction of bornylene-3-carboxylic acid to camphane-3-carboxylic acid (p. 2199).

The product was distilled in steam, the distillate made alkaline

* The rotation of *d-bornylene-3-carboxylic acid*, in benzene solution, at a concentration of 13.1506 is $\alpha_D + 149.5^\circ$.

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with sodium carbonate, evaporated until free from methyl alcohol, mixed with powdered ice and a little permanganate, and allowed to remain for an hour, but the addition of hydrogen had evidently been practically complete, since there was hardly any reduction of the permanganate.

After the removal of the permanganate, the acid was precipitated by hydrochloric acid, washed well, and dried on porous porcelain.

Owing to the fact that it is so very soluble in the usual organic solvents, the recrystallisation of this acid is a matter of difficulty, and the best plan seems to be to dissolve it in warm dilute acetic acid, and then to cool the solution below 0° , when the pure acid separates well in long, colourless needles, which are collected on a filter surrounded by a freezing mixture:

0.1343 gave 0.3560 CO_2 and 0.1198 H_2O . $\text{C}=72.3$; $\text{H}=9.9$.

$\text{C}_{11}\text{H}_{18}\text{O}_2$ requires $\text{C}=72.5$; $\text{H}=9.9$ per cent.

0.7489, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D -37.8^{\circ}$.

L-Camphane-2-carboxylic acid melts at $78-80^{\circ}$, and distils at about $155^{\circ}/15$ mm.; it is very sparingly soluble in cold, but dissolves somewhat in boiling water, and separates, on cooling, in glistening needles.

It is mentioned on p. 2194 that this acid had already been prepared by Houben and Kesselkaul (*Ber.*, 1902, **35**, 3696; compare Houben, *Ber.*, 1905, **38**, 3799), who named it "hydropinenecarboxylic acid," and state that it melts at $72-74^{\circ}$, and by Zelinsky (*Ber.*, 1902, **35**, 4417), who gives the melting point $69-71^{\circ}$, and called it "camphanecarboxylic acid."

Conversion of l-Bornylene-2-carboxylic Acid into d-Camphor.

The interesting conversion of l-bornylene-2-carboxylic acid—and indirectly of epicamphor—into camphor was brought about through the agency of l-bornylene-2-hydroxamic acid (compare p. 2206). Hydroxylamine hydrochloride (12 grams), carefully dried and powdered, was dissolved in anhydrous methyl alcohol (100 c.c.), and mixed in the cold with a solution of sodium (3.5 grams) in methyl alcohol. Methyl l-bornylene-2-carboxylate (30 grams) was then added, and afterwards sodium (3.5 grams) dissolved in methyl alcohol (50 c.c.), and the whole allowed to remain for two days, during which no crystallisation of the sodium salt of the hydroxamic acid took place. After heating for four hours in a thermostat at 50° the product was divided into the halves (A) and (B). The portion (A) was mixed with water, a small quantity of unchanged ester (1.5 grams) extracted with ether, the aqueous solution was just acidified with hydrochloric acid and extracted three times with ether, and,

after washing well, drying, and evaporating carefully, the ethereal solution deposited a syrup which did not crystallise. This syrupy acid, which gave an intense claret coloration when ferric chloride was added to its alcoholic solution, was dissolved in a slight excess of potassium hydroxide, and the pale blue copper salt precipitated by the addition of excess of copper acetate; the precipitate was washed, dried, suspended in ether, and decomposed by hydrogen sulphide. After filtering, the ethereal solution yielded, on evaporation, an almost colourless syrup, which did not crystallise even after several days' exposure over sulphuric acid, but analysis indicated that this syrup was practically pure *l-bornylene-2-hydroxamic acid*:

0.1480 gave 9.1 c.c. N_2 at 17° and 755 mm. $N=7.2$.

$C_{11}H_{17}ON_2$ requires $N=7.2$ per cent.

Conversion of l-Bornylene-2-hydroxamic Acid into d-Camphor by Heat.—This conversion was brought about by heating the syrupy hydroxamic acid in a reflux apparatus at about 120° , when decomposition commenced and continued, after the flame had been removed, so vigorously that the temperature rose to about 200° ; a good deal of ammonia was formed, and some camphor crystallised in the neck of the flask and in the condenser. The product was mixed with concentrated hydrochloric acid and distilled in steam, and the semi-solid mass, which smelt strongly of camphor, was extracted with ether. The ethereal solution yielded, on evaporation, a buttery mass, which was left for some hours in contact with methyl-alcoholic potassium hydroxide ($KOH=5$ grams)*; water was then added, and the crystalline precipitate extracted with ether.

After washing thoroughly, the ethereal solution was dried and carefully evaporated, when a nearly solid mass remained, which, in contact with porous porcelain, became quite dry, and consisted of nearly pure *d*-camphor, a fact which was proved by recrystallising it from a little very light petroleum (b. p. $35-40^\circ$), when it melted at $174-176^\circ$, had $\alpha_D +46.9^\circ$ in ethyl acetate solution, and yielded camphoroxime melting at 119° .

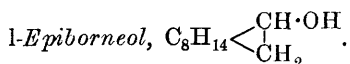
Conversion of l-Bornylene-2-hydroxamic Acid into d-Camphor with the Aid of Toluene-p-sulphonyl Chloride.—The second portion (B) of the solution of the sodium salt of *l*-bornylene-2-hydroxamic acid, obtained as described above, was mixed with twice its volume of water, and shaken for twelve hours on the machine with finely-powdered toluene-*p*-sulphonyl chloride (25 grams). The product was extracted with ether, the ethereal solution washed, dried, and

* The alkaline solution, after the methyl alcohol has been removed by evaporation, yielded, on acidifying, crude bornylene-2-carboxylic acid (2 grams).

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evaporated, and shaken for half an hour with concentrated hydrochloric acid. Water was then added, and the whole distilled in steam, when a semi-solid mass passed over, and a brown button and some crystals containing nitrogen and sulphur were left in the distillation flask (compare p. 2208). The distillate was extracted with ether, the ethereal solution evaporated, and the residual crude camphor mixed with methyl-alcoholic potassium hydroxide (5 grams KOH) and warmed on the steam-bath for half an hour in order to hydrolyse some bornylene-2-carboxylic ester which was present. Water was then added, the camphor extracted with ether, the ethereal solution very thoroughly washed, dried, and evaporated, and the *d*-camphor left on porous porcelain until quite dry, and then twice recrystallised from light petroleum (b. p. 30–40°). It was then quite pure, since it melted at 176°, and, when treated with hydroxylamine under the conditions given on p. 2208, yielded camphoroxime melting at 119°. Furthermore, there was no alteration in melting point when these preparations were mixed with ordinary *d*-camphor, which had been recrystallised from light petroleum, and with *d*-camphoroxime. The determination of the rotation gave the following result: 0.4002, dissolved in ethyl acetate and made up to 20 c.c., gave $\alpha_D + 47.7^\circ$, whereas the rotation of ordinary *d*-camphor, after crystallisation from light petroleum, was $\alpha_D + 48.0^\circ$ under the same conditions.

The yield of camphor obtained in the above experiment was more than 40 per cent. of that theoretically possible.



In order to obtain this substance, *l*-epicamphor, dissolved in ten times its weight of ethyl alcohol, was reduced, in a reflux apparatus, with an equal weight of sodium, which was added as rapidly as possible in order that the whole might pass into solution. If any sodium remains it is removed by the addition of ice; the whole is then distilled in steam, when the epiborneol passes over much in the same way, but not so readily, as epicamphor, and a considerable portion solidifies in the condenser, and must be removed from time to time by solution in ether.

The ethereal solution is combined with the ether extract of the distillate, washed thoroughly with water to remove the alcohol, dried, and evaporated, when *l*-epiborneol remains as a crystalline mass, which melts at 179–181°, and, after purification with the aid of the phenylurethane, at 181–182.5°:

0.1550 gave 0.4415 CO_2 and 0.1695 H_2O . $\text{C}=77.7$; $\text{H}=12.2$.

0.1392 „ 0.3975 CO_2 „ 0.1495 H_2O . $\text{C}=77.8$; $\text{H}=11.9$.

$\text{C}_{10}\text{H}_{18}\text{O}$ requires $\text{C}=77.9$; $\text{H}=11.7$ per cent.

It is remarkable that all the specimens of *l*-epiborneol which we have obtained have proved to be inactive.

The *phenylurethane*, $\text{C}_{10}\text{H}_{17}\cdot\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, was prepared by dissolving epiborneol (6 grams) in a little light petroleum (b. p. 35–40°), adding phenylcarbimide (5 grams), and allowing the mixture to remain for several days in a sealed tube, during which some of the phenylurethane separated in white crystals, and the addition of more light petroleum precipitated a further quantity of the same substance:

0.1607 gave 0.4402 CO_2 and 0.1238 H_2O . $\text{C}=74.7$; $\text{H}=8.6$.

0.1910 „ 9.4 c.c. N_2 at 17.5° and 733.5 mm. $\text{N}=5.5$.

$\text{C}_{17}\text{H}_{23}\text{O}_2\text{N}$ requires $\text{C}=74.7$; $\text{H}=8.5$; $\text{N}=5.1$ per cent.

l-Epibornylphenylurethane separates from light petroleum in groups of long needles, and melts at 82°; it is readily decomposed by distillation with dilute hydrochloric acid, and pure epiborneol passes over with the condensed water.

Preparation of l-Epiborneol from Sodium l-Epibornylxanthate.

When sodium epibornylxanthate (see below) is dissolved in hot water and mixed with hydrochloric acid a precipitate of epiborneol is at once produced, and, after distilling in steam, extracting with ether, and evaporating, the solid was recrystallised from light petroleum several times, but the melting point remained constant at 176–176.5°, whereas the substance obtained from *l*-epicamphor by reduction with sodium and alcohol had melted at 181–182.5°:

0.1822 gave 0.5176 CO_2 and 0.191 H_2O . $\text{C}=77.5$; $\text{H}=11.7$.

$\text{C}_{10}\text{H}_{18}\text{O}$ requires $\text{C}=77.9$; $\text{H}=11.7$ per cent.

It was at first thought that these two substances were stereoisomeric, and corresponded with borneol and isoborneol, which, as is well known, occur together in the product of the reduction of camphor. That this is probably not the case is indicated by the fact that both preparations were inactive, and that, in spite of the difference in melting points, both gave the same phenylurethane.

Conversion of l-Epiborneol into l-Bornylene by the Method of Tschugaev.

This interesting conversion of inactive *l*-epiborneol into active *l*-bornylene was carried out under the following conditions: In the first place, sodium epibornylxanthate was prepared by adding sodium ribbon (3 grams) to the solution of *l*-epiborneol (15 grams)

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in absolute ether (150 c.c.) in a flask protected from moisture and carbon dioxide by a calcium chloride and soda-lime tube, when a slow and regular evolution of hydrogen set in, and was complete after remaining over-night. The unchanged sodium ribbon was easily removed, and the solution of sodium borneol was then mixed with carbon disulphide (15 grams), when a yellow precipitate separated immediately and the contents of the flask became nearly solid. The precipitate of sodium *l*-epibornylxanthate was collected and recrystallised from water, when about 70 per cent. separated as a very pale yellow, almost white, crystalline mass, and, from the mother liquors, epiborneol was recovered by treatment with hydrochloric acid. The sodium salt was converted into methyl *l*-epibornylxanthate, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{O} \cdot \text{CS}_2\text{Me} \\ \text{CH}_2 \end{smallmatrix}$, by suspending it in ether, adding methyl iodide, and boiling in a reflux apparatus, the whole being repeatedly shaken to ensure complete decomposition. After ten hours the product was mixed with water, the ethereal solution dried and evaporated, when the methyl ester remained as a rather mobile, yellow oil.

This oil was now heated in a small distillation flask by means of a small flame, and the gases evolved (methyl mercaptan and carbonyl sulphide) ignited, so that the progress of the decomposition could be judged by the size of the jet. After a short time bornylene commenced to distil over, and crystallised in the receiver as a colourless mass. The distillation was repeated, and the *l*-bornylene then distilled over sodium, when it melted sharply at 113–114°, but did not exhibit constant rotation, since different portions of the distillate had values varying between $\alpha_D - 16.93^\circ$ and -19.58° . After a further distillation over sodium, the solution of two different specimens in benzene gave the values:

Melting point.	Concentration.	α_D .
113–114°	4.771	-18.45°
114.5–115	4.345	-18.41

Oxidation.—In carrying out this experiment, the above *l*-bornylene (2 grams) was dissolved in benzene and shaken with 700 c.c. of 1 per cent. permanganate on the machine for twenty hours; the excess of permanganate was then decomposed by sulphur dioxide, and the filtrate and washings from the manganese precipitate concentrated, acidified, and the precipitated acid extracted with ether. After distilling off the ether, the mass was boiled with chloroform, decanted, and the residue recrystallised from water, when an acid was obtained, which melted at 188°, and proved on examination to consist of pure *d*-camphoric acid.

l-Bornylene had been previously obtained by Bredt (*Annalen*,

1909, **366**, 52) by the decomposition of sodium β -bromodihydro-bornylene-3-carboxylate (compare p. 2191), and was found to have the constants: m. p. 113° ; b. p. 146° ; rotation, in toluene solution at a concentration of 10.45, $\alpha_D - 21.69^{\circ}$. More recently, Tschugaev and Budrick (*Annalen*, 1912, **388**, 288) prepared *d*-bornylene from methyl *l*-bornylxanthate (from *l*-borneol) by heating at $176-177^{\circ}$, and this specimen melted at $109-109.5^{\circ}$, distilled at $146.5^{\circ}/750$ mm., and, in toluene solution at a concentration of 12.75, had $\alpha_D + 19.29^{\circ}$.

On oxidation with permanganate it yielded *l*-camphoric acid.

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