

LXXIV.—*Sulphocamphylic Acid and Isolauronolic Acid,* with Remarks on the Constitution of Camphor and of some of its Derivatives.*

By W. H. PERKIN, jun.

INTRODUCTION.

THE constitution of camphor still remains unsolved, in spite of the enormous amount of work which has been done during the last few years in almost every conceivable direction.

It is well known that camphor, $C_{10}H_{16}O$, on oxidation, yields *camphoric acid*, $C_8H_{14}(COOH)_2$, and that this acid, on further oxidation, yields *camphanic acid*, $C_8H_{13}(OH)(COOH)_2$, *camphoronis acid*, $C_6H_{11}(COOH)_3$, and other acids containing a smaller number of carbon atoms, but although the constitution of camphoronic acid has now been conclusively proved, there is still very considerable doubt as to the formulæ of camphoric acid and camphanic acid.

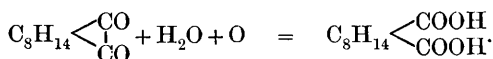
That the relationship existing between camphor and camphoric acid is a very close one is proved, not only by the fact that camphoric acid

* Noyes (*Ber.*, 1895, **28**, 549) proposes to alter the name of this acid to *cis*-campholytic acid, and to reserve the name isolauronolic acid for an isomeric acid which he has prepared. As, however, this is likely to cause much confusion, and there seems, in the meantime, no sufficient reason for the change, it has not been adopted in this paper.

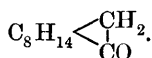
is so readily formed by oxidising camphor, but also by the formation of this acid from camphorquinone.

Claisen and Manasse (*Annalen*, 1893, 274—286) showed that camphor is readily converted into isonitrosocamphor, $C_8H_{14} \begin{smallmatrix} \diagup C \cdot NOH \\ \diagdown CO \end{smallmatrix}$, by treatment with amyl nitrite and sodium methoxide, and from this compound, by treatment with nitrous acid, they obtained camphorquinone, $C_8H_{14} \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix}$.

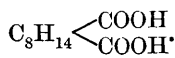
From camphorquinone, camphoric acid is readily obtained by the action of a solution of potash in methylic alcohol, hydrolysis and oxidation (due to the oxygen of the air) taking place simultaneously.



This series of simple reactions fully confirms the view, which has long been held by chemists, that camphor contains the group $-CH_2 \cdot CO-$, and that when it is converted into camphoric acid, this group is oxidised to two carboxyl groups.



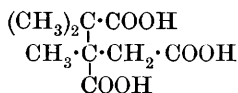
Camphor.



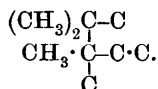
Camphoric acid.

It follows, therefore, that the constitution of camphor could be readily deduced from the constitution of camphoric acid, and this accounts for the great number of experiments which have been carried out with this acid.

Bredt's suggestion (*Ber.*, 1893, 26, 3049), that camphoronic acid has the constitution



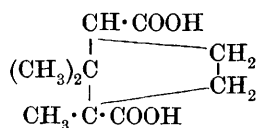
was the first great advance in elucidating the formula of camphoric acid, and now that this constitution of camphoronic acid has been proved by the synthesis of the acid (Perkin and Thorpe, *Trans.*, 1897, 71, 1169), it can be stated with certainty that camphoric acid, $C_{10}H_{16}O_4$, contains 9 of its carbon atoms grouped in the following way.



This fact disposes of a number of formulæ which had been suggested for camphoric acid, such as those of V. Meyer and Ballo, and of Tiemann,

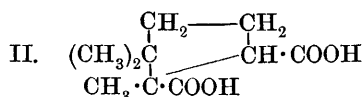
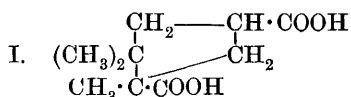
but, on the other hand, it does not afford a sufficient basis on which to build up a constitution for camphoric acid that shall not be open to question.

Arguing from the formula of camphoronic acid, Bretz (*loc. cit.*, p. 3049) has suggested that camphoric acid is probably represented thus.



and this well-known formula does undoubtedly explain a very large number of the reactions of the acid in a comparatively simple manner.

The investigation of sulphocamphylic acid and of isolauronolic acid, on which the author of this paper has been engaged during the last nine years, has, however, brought to light some facts which it seems almost impossible to explain with the aid of Bretz's formula, and this led the author, in 1896 (*Proc.*, 1896, p. 191*), to suggest that the constitution of camphoric acid might equally well be represented by the following formulæ.



An acid having either of these formulæ could, on oxidation, yield camphoronic acid quite as well as an acid of the constitution suggested by Bretz.

It will furthermore be shown that the results obtained in the investigation of isolauronolic acid can only be readily explained on the assumption that formula I is the correct expression for the constitution of camphoric acid, and for this reason this formula has been adopted in this paper.

Among the many remarkable reactions in the camphor group, one of the most interesting is certainly the decomposition which takes place when camphoric acid is gently heated with concentrated sulphuric acid, the camphoric acid being converted almost quantitatively into *sulphocamphylic acid*, with evolution of carbonic oxide.



This decomposition was first observed by Walter (*Ann. Chim. Ph.*, 1843, [iii], 9, 177), and subsequently investigated by Kachler (*Ann-*

* There is an unfortunate printer's error (in the abstract) in the first of these formulæ, two hydrogen atoms having been omitted.

alen, 1873, 169, 179) and Damsky (*Ber.*, 1887, 20, 2959), and for many years the formula for crystallised sulphocamphylic acid was supposed to be $C_9H_{16}SO_6 + 2H_2O$, a formula by which it is represented in the last edition of Beilstein's *Handbuch* (vol. i, p. 905).

During the course of further experiments on this acid, it was, however, clearly proved by Koenigs and Meyer (*Ber.*, 1894, 27, 3466), as well as by the author (*Proc.*, 1895, p. 23), that sulphocamphylic acid in reality has the formula $C_9H_{14}SO_5$, and that it crystallises with $3H_2O$, two of which are given off at 100° and the third at about 110° , and the proof of this fact may be briefly stated as follows.

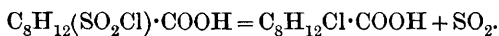
When the silver salt of sulphocamphylic acid is treated with methylic iodide, the dimethylic salt is obtained, and this, on analysis, was shown to have the formula $C_9H_{12}SO_5(CH_3)_2$ (Koenigs and Meyer, *loc. cit.*, p. 3467).

Similarly, the potassium salt of sulphocamphylic acid, when treated with phosphorus pentachloride or pentabromide, yields the *sulphochloride* or *sulphobromide*, and these, on analysis, give numbers agreeing sharply with the formulæ $C_9H_{13}O_2(SO_2Cl)$ and $C_9H_{13}O_2(SO_2Br)$, formulæ which clearly prove that the composition of sulphocamphylic acid must be $C_9H_{13}O_2 \cdot SO_3H$, and not $C_9H_{15}O_3 \cdot SO_3H$, as was at first supposed.

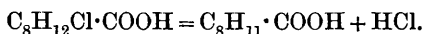
Furthermore, it has been conclusively shown by the analysis of a number of metallic salts, as well as by the formation of the dimethylic salt mentioned above, that sulphocamphylic acid is dibasic, and therefore its formula may be written $C_8H_{12}(SO_3H) \cdot COOH$.

The investigation of the sulphochloride and sulphobromide of sulphocamphylic acid has given very interesting results, some of which are described in this paper; others are reserved for a future communication.

The sulphochloride* is a beautiful, crystalline substance, which melts at 168° , and is at the same time decomposed with evolution of sulphur dioxide and formation of a new acid, $C_8H_{12}Cl \cdot COOH$, melting at 106° .



This acid has been called *chlorodihydro-β-camphylic acid*, because, on prolonged treatment with alcoholic potash, it is converted into β-camphylic acid,† with elimination of hydrogen chloride,

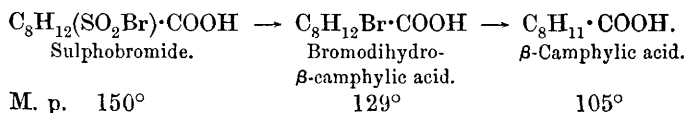


* The decompositions described here are exactly similar to those which Kipping and Pope (*Trans.*, 1895, 67, 371) have used with such success in the preparation of π-halogen derivatives of camphor.

† Compare *Proc.*, 1893, 109; 1895, 23; 1896, 189. A detailed description of this very interesting acid will, it is hoped, form the subject of a future communication.

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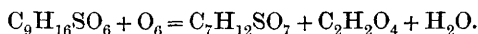
In a similar manner, the sulphobromide of sulphocamphylic acid, when heated above its melting point, decomposes, with evolution of sulphur dioxide and formation of *bromodihydro-β-camphylic acid*, and this acid is decomposed by alcoholic potash in the same way as the corresponding chloro-acid, yielding again *β-camphylic acid*.



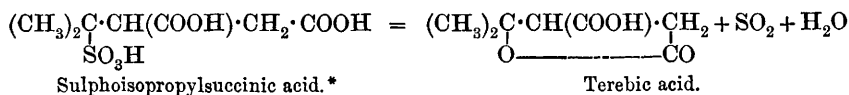
Since, then, it is clear from the above that sulphocamphylic acid must be represented by the formula $\text{C}_8\text{H}_{12}(\text{SO}_3\text{H})\cdot\text{COOH}$, the next important matter is to discuss all the evidence which has a bearing on the further arrangement of the atoms in this molecule.

It has been frequently found in the camphor and terpene series that the study of the behaviour of these substances and their derivatives towards oxidising agents has given valuable clues to their constitution, and in the case of sulphocamphylic acid also, although in a less degree than might have been expected, important results have been obtained in this way.

Kachler (*Annalen*, 1873, 169, 181), who was the first to oxidise sulphocamphylic acid, found that, when heated with nitric acid, it is converted into oxalic acid and a beautifully crystalline tribasic acid, which he called *sulphopimelic acid*, and the formation of which he expressed by the equation



Subsequently, Koenigs and Hoerlin (*Ber.*, 1893, 26, 2045) carefully investigated this sulphopimelic acid, and found that at 160—170° it is decomposed with evolution of sulphur dioxide and formation of terebic acid; they therefore considered that Kachler's acid must be sulphoisopropylsuccinic acid, in which case the formation of terebic acid is readily understood.



These chemists also found that small quantities of dimethylmalonic acid, $(\text{CH}_3)_2\text{C}(\text{COOH})_2$, are produced during the oxidation of sulphocamphylic acid with nitric acid, an important result, since the formation of this acid indicates that sulphocamphylic acid contains the group $-\text{C}\cdot\text{C}(\text{CH}_3)_2\cdot\text{C}-$.

* In studying the possible formulæ for sulphocamphylic acid, it is very difficult to understand how the sulphonic group in sulphopimelic acid can occupy the position given to it here.

Sulphocamphylic acid is also readily oxidised by potassium permanganate in alkaline solution, yielding a variety of very interesting products, which have been carefully investigated by the author of this paper, but the description of these must be reserved for a future communication.

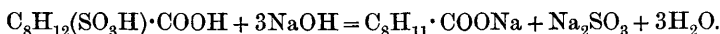
Action of Heat on Sulphocamphylic Acid. Formation of Isolauronic Acid, $C_8H_{13}\cdot COOH$.

When sulphocamphylic acid is heated in small quantities, or distilled with superheated steam, it undergoes a very remarkable decomposition, yielding isolaunonic acid and sulphuric acid (Koenigs and Hoerlin, *Ber.*, 1893, **26**, 813; Perkin, *Centralblatt.*, 1893, ii, 50),

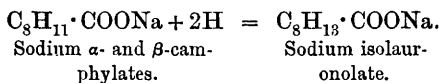


but, unfortunately, at the high temperature necessary for the decomposition, the sulphuric acid formed destroys much of the sulphocamphylic acid, and the yield of isolaunonic acid obtained hardly ever exceeds 10 per cent. of the theoretical. It was subsequently discovered by the author that isolaunonic acid may be obtained in comparatively large quantities by fusing sulphocamphylic acid in a cast iron pot with caustic soda, a remarkable result, which may be explained as follows.

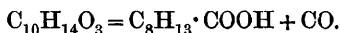
In the first place, the sulphocamphylic acid is decomposed by the fusion with soda, with formation of the sodium salts of the isomeric α - and β -camphylic acids, $C_8H_{11}\cdot COOH$ (Perkin, Proc., 1893, 109; 1895, 23).



The iron of the vessel in which the fusion is carried out then reduces these sodium salts, and the product, which is coloured dark brown by the ferric oxide which it holds in suspension, contains the sodium salt of isolauronic acid.



Although this method is a considerable improvement on the dry distillation of sulphocamphylic acid, it is, nevertheless, a very laborious process, and the best way for preparing isolaunonic acid is undoubtedly that worked out by Blanc (*Bull. Soc. Chim.*, [iii], 15, 1191), which consists in treating a solution of camphoric anhydride in chloroform with aluminium chloride, when the following remarkable decomposition takes place.



Another method of formation of isolauronolic acid direct from camphoric acid, to be discussed later in this paper, is that discovered by Walker (Trans., 1893, **63**, 495). Walker submitted orthoethylic sodium camphorate to electrolysis, and obtained in this way, besides ethylic campholytate, an isomeric ethylic salt boiling at 135—140° (15mm.), which he first called diethylic camphothetate, but which was subsequently (Trans., 1895, **67**, 347) shown to be the ethylic salt of isolauronolic acid.

Lastly, Noyes (*Ber.*, 1894, **65**, 917; 1895, **67**, 549) has obtained isolauronolic acid by the following series of reactions.

The imide of camphoric acid, $C_8H_{14} \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} NH$, when treated with potash, yields *β-camphoraminc acid*, $C_8H_{14}(CONH_2) \cdot COOH$, and this, by the action of sodium hypobromite, is converted into *dihydroaminocampholytic acid*, $C_8H_{14}(NH_2) \cdot COOH$; nitrous acid converts this amido-acid into Walker's *campholytic acid*, which, when boiled with dilute sulphuric acid, undergoes molecular change, yielding isolauronolic acid.

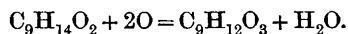
The determination of the constitution of isolauronolic acid is of great importance, for the following reasons.

1. It is formed from camphoric anhydride by elimination of CO.
2. It is formed from sulphocamphylic acid by heat.
3. It is reconverted into sulphocamphylic acid by treatment with sulphuric acid (see p. 835).

From these facts, it will be seen that isolauronolic acid is closely related to camphoric acid on the one hand, and to sulphocamphylic acid on the other, so that the determination of the constitution of this acid must throw much light on the question of the constitution of camphoric and of sulphocamphylic acids.

Oxidation of Isolauronolic Acid. Formation of Isolauronic Acid,
 $C_9H_{12}O_3$.

If a drop of potassium permanganate solution is added to a solution of isolauronolic acid in dilute sodium carbonate, the colour is instantly discharged, even at 0°; and, on investigating this reaction, it is found that the first product of the oxidation is an acid of the formula $C_9H_{12}O_3$.



This new acid, which was first described by Koenigs and Meyer (*Ber.*, 1894, **27**, 3467), and called by them *islauronic acid*, melts at 133°, and differs from isolauronolic acid in being readily soluble in hot water; it is a ketonic acid, and forms the following well characterised derivatives.

<i>Oxime</i>	$\text{COOH} \cdot \text{C}_7\text{H}_{11} \cdot \text{C} : \text{NOH}$	m. p. 222°
<i>Semicarbazone</i>	$\text{COOH} \cdot \text{C}_7\text{H}_{11} \cdot \text{C} : \text{N} \cdot \text{NH} \cdot \text{CONH}_2$	„ 248
<i>Phenylhydrazone</i> *	$\text{COOH} \cdot \text{C}_7\text{H}_{11} \cdot \text{C} : \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$	„ 199

Oxidation of Isolauroic Acid.—Although stable to permanganate at temperatures below 0°, isolauroic acid is readily oxidised by this agent at ordinary temperatures, as also by a mixture of potassium dichromate and sulphuric acid at 90—95°, the principal substances formed being

γ-Dimethylacetylbutyric acid, $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$.

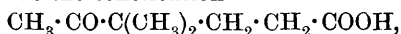
α-Dimethylglutaric acid, $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$.

α-Dimethylsuccinic acid, $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{COOH}$.

All these substances afford important evidence as to the constitution of isolauroic acid, but there can be no doubt, as will be shown later, that it is the first named which is especially valuable in this connection.

Acetyldimethylbutyric acid is identical with the acid which Tiemann (*Ber.*, 1895, 28, 2176) obtained by the oxidation of β-dihydroxydihydrocampholenic acid, and which he named dimethyl-3-hexanon-2 acid.

That this acid has the constitution

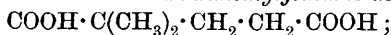


is proved by the following considerations.

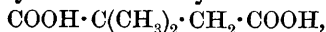
1. It is a ketonic acid, as is shown by the fact that it yields a well characterised oxime and semicarbazone.

2. When reduced with sodium amalgam, it is converted into a lactone, $\text{CH}_3 \cdot \text{CH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2$ (b. p. 239—241°), a fact which indicates that the CO group is either in the γ- or δ- position.

3. Sodium hypobromite readily reacts with the acid, with separation of bromoform and formation of *αα*-dimethylglutaric acid,

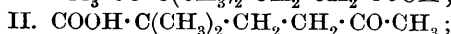
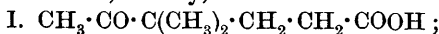


this shows that the ketonic acid contains the group $\text{CH}_3 \cdot \text{CO}$. The dimethylglutaric acid formed in this way melts at 84°, and is isomeric with ββ-dimethylglutaric acid, $\text{COOH} \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{COOH}$ (m. p. 101°; Goodwin and Perkin, *Trans.*, 1896, 69, 1473), and since on oxidation the former yields *αα*-dimethylsuccinic acid,



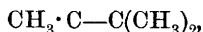
it can only have the constitution $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$.

4. From the formula of *αα*-dimethylglutaric acid, two ketonic acids, $\text{C}_8\text{H}_{14}\text{O}_3$, may be derived, namely,



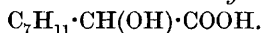
* Carl Meyer (*Inaugural Dissertation Munich*, 1895, p. 38).

but there can be no doubt that formula I represents the constitution of the acid obtained from isolauronic acid, because throughout the whole camphor series there is overwhelming evidence that the three methyl groups contained in this substance and its derivatives are united to neighbouring carbon atoms forming the complex



a condition which is satisfied by formula I, but not by II.

Reduction of Isolauronic Acid to Dihydroisolauronic Acid,



The action of sodium amalgam on isolauronic acid was first investigated by Carl Meyer (*Dissertation Munich*, 1895, p. 45) who obtained in this way two products.

1. A lactone, $\text{C}_9\text{H}_{14}\text{O}_2$, melting at $47-50^\circ$ and yielding on hydrolysis a hydroxy-acid melting at 143° .

2. An acid melting at 81° which does not yield a lactone, and which, on analysis, gave the following numbers.

Found (mean of three analyses) C = 62.95 ; H = 8.66.

$\text{C}_9\text{H}_{14}\text{O}_3$ requires C = 63.53 ; H = 8.23.

$\text{C}_9\text{H}_{16}\text{O}_3$ „ C = 62.71 ; H = 9.30.

These results led Meyer to conclude that the acid melting at 81° was a mixture of two acids, $\text{C}_9\text{H}_{14}\text{O}_3$ and $\text{C}_9\text{H}_{16}\text{O}_3$, which could not be separated by crystallisation.

As the investigation of the behaviour of isolauronic acid on reduction is a matter of fundamental importance in determining the constitution of this acid, a great many experiments on this subject have been made by the author, the results of which differ considerably from those obtained by Carl Meyer. In the first place, Carl Meyer's experiments were repeated exactly as he described them, using isolauronic acid which had been very carefully purified by repeated crystallisation, but no trace of a solid lactone could be detected in the product, which consisted of a beautifully crystalline acid melting at $88-89^\circ$, and on analysis gave numbers agreeing sharply with those required by the formula $\text{C}_9\text{H}_{14}\text{O}_3$.

Found (mean of two analyses) C = 63.36 ; H = 8.21.

$\text{C}_9\text{H}_{14}\text{O}_3$ requires C = 63.53 ; H = 8.23.

The conditions of reduction were then varied, but in all cases it was found that the isolauronic acid had been converted almost quantitatively into the acid $\text{C}_9\text{H}_{14}\text{O}_3$, which, since it is formed by the addition of two atoms of hydrogen to isolauronic acid, has been called *dihydroisolauronic acid*.

The solution of dihydroisolauronic acid in sodium carbonate does

not decolorise permanganate except on long standing, showing that the acid is a saturated acid, and this is confirmed by the fact that the acid does not combine with bromine, or with hydrogen bromide, and that it is not further reduced even when its alkaline solution is boiled with sodium amalgam.

Since dihydroisolauroic acid is formed by the reduction of the ketonic acid isolauroic acid, it is evident that it must be a hydroxy-acid, and the next important point was to determine whether it was capable of forming a lactone, since, in this way, valuable evidence as to the relative positions of the hydroxyl and carboxyl groups, and indirectly as to the position of the CO and COOH in isolauroic acid, might be obtained.

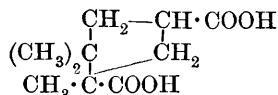
This matter has been most carefully investigated, but it was not found possible to obtain even traces of a lactone by boiling the hydroxy-acid with dilute sulphuric acid; and, indeed, the hydroxy-acid may be distilled without decomposition; it may therefore be safely stated that *dihydroisolauroic acid is incapable of forming a lactone*.

This statement may, at first sight, appear to be at variance with the results obtained by Carl Meyer (*Dissertation*, p. 46), who, by the reduction of isolauroic acid, obtained, as mentioned above, small quantities of a lactone, $C_9H_{14}O_2$, melting at $47-50^\circ$, and which on hydrolysis yielded an acid melting at 143° . The principal product of the reduction was, however, a hydroxy-acid melting at 81° , and yielding on analysis numbers agreeing with those required by a mixture of acids, $C_9H_{14}O_3$ and $C_9H_{16}O_3$, and there can now be no doubt that this acid was simply slightly impure dihydroisolauroic acid (m. p. 88°). Since Meyer's acid melting at 81° was isolated from the product of the reduction of isolauroic acid after this had been boiled with dilute acids, it is evident that his acid is also incapable of forming a lactone, and in this respect Meyer's experiments agree with those of the author. With regard to the nature of the lactone melting at $47-50^\circ$ and yielding, on hydrolysis, the acid melting at 143° , it seems extremely probable that this was *campholactone*, $C_9H_{14}O_2$, which melts at $50-51^\circ$, and which on hydrolysis with baryta yields *campholactonic acid*, $C_9H_{16}O_3$, melting at 143° ;* the few properties of his lactone which Meyer mentions confirm this view. Since, however, campholactone is the lactone corresponding to lauronolic acid (see p. 815), it is exceedingly difficult to understand its formation by the reduction of a derivative of isolauronolic acid.

* According to Woringer (*Annalen*, 1885, **227**, 10) campholactonic acid is precipitated as an oil on acidifying the solution of its barium salt; the author, however, in conjunction with Mr. R. W. Collinson, has obtained the acid by this method in the form of beautiful prismatic crystals melting at 143° . An account of this interesting acid is reserved for a future communication.

The Constitution of Isolaurnolic Acid, of Isolaurnic Acid, and of Sulphocamphylic Acid, with remarks on the Constitution of Camphor and of Camphoric Acid.

It has already been stated that, in the opinion of the author, the results obtained in this investigation can best be explained on the assumption that camphoric acid has the constitution represented by the formula



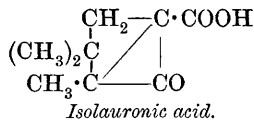
and in giving the reasons for this statement it will be best in the first place to discuss the constitution of isolaurnic acid, in doing which the principal points to be borne in mind are,

1. Isolaurnic acid, on oxidation, yields γ -dimethylacetylbutyric acid, $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$.

2. Isolaurnic acid is a monobasic ketonic acid containing the ketonic group in the β -position relatively to the carboxyl group. This is proved by the fact that the dihydroisolaurnic acid obtained by its reduction is incapable of forming a lactone.

3. Since dihydroisolaurnic acid distils unchanged, it cannot contain the group $-\text{CH} \cdot \text{CH}(\text{OH})-$, because acids containing that group, on distillation, lose water with formation of the corresponding unsaturated acids. Isolaurnic acid itself must, therefore, contain the group $\text{COOH} \cdot \text{C} \cdot \text{CO} \cdot \text{C}$, the free bonds of which must all be united to carbon.

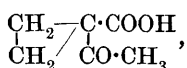
From the formula of camphoric acid given above an expression for the constitution of isolaurnic acid can be easily deduced which will satisfy these conditions and explain all the known properties of the acid, namely,



This formula, which appears to the author to be the only possible formula for isolaurnic acid, represents the acid as a β -ketonic acid, and to this the objection might be raised that the acid gives no coloration with ferric chloride, and that when heated it does not decompose with evolution of carbon dioxide. The reply to the first objection is that β -ketonic acids, or their ethereal salts, which have both α -hydrogen atoms replaced by radicles do not appear to give a coloration with ferric chloride, thus, for example, the author finds that ethylic dimethyl-acetoacetate, $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{COOC}_2\text{H}_5$, does not give a coloration with ferric chloride.

The relatively great stability of isolauroic acid is also quite easily explained. The ease with which β -ketonic acids are decomposed by heat or alkalis with elimination of carbon dioxide depends very much on their constitution.

Thus acetoacetic acid, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COOH}$, and methylacetoacetic acid, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}$, are oils which decompose slowly at ordinary temperatures with evolution of carbon dioxide, whereas dimethylacetoacetic acid, $\text{CH}_3\cdot\text{CO}\cdot\text{C}(\text{CH}_3)_2\cdot\text{COOH}$, is solid, and although still very easily decomposed, it is distinctly more stable than the other two acids. These three acids are furthermore readily decomposed in the same manner by boiling with potash. When, however, the carboxyl and acetyl groups in such compounds are attached to a closed chain, as in the case of acetyltrimethylenecarboxylic acid,

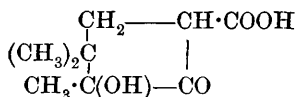


an acid which has a somewhat similar formula to that suggested for isolauroic acid, the stability of the molecule may be, but is not always, enormously increased. Acetyltrimethylenecarboxylic acid, for example, may be boiled with potash for hours without decomposition, and the free acid is only slowly decomposed into carbon dioxide and acetyltrimethylene even at $180\text{--}200^\circ$.

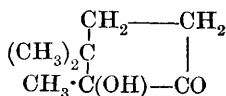
If, then, the introduction of one closed chain into the molecule can bring about such an extraordinary change in stability, it is not remarkable that this stability should be still more pronounced in a substance like isolauroic acid, the formula of which is represented above, not only as containing two closed chains, but also as having no α -hydrogen atoms.

The formation of dimethylacetylbutyric acid from isolauroic acid may be readily explained with the aid of this formula as follows.

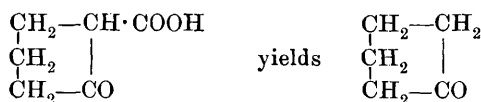
In the first place, the trimethylene ring is split with the addition of the elements of water and formation of an intermediate substance of the formula



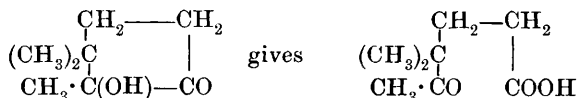
and this being a β -ketonic acid with one α -hydrogen atom not replaced, may be assumed to decompose readily with evolution of carbon dioxide and formation of the substance



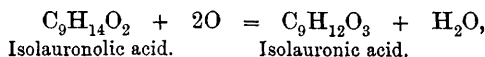
Thus Dieckmann (*Ber.*, 1894, 27, 103) has shown that ethylic β -ketopentamethylenecarboxylate, a substance of very similar constitution to the "intermediate" substance, is readily and quantitatively decomposed on hydrolysis, with formation of ketopentamethylene.



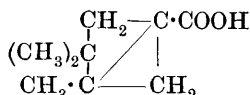
Lastly, the ketonic substance of the formula given above, being produced in the presence of oxidising agents, is readily converted into acetyldimethylbutyric acid.



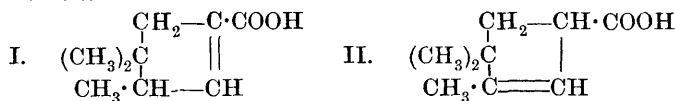
Assuming that the constitution given to isolauronic acid is correct, the next point is to deduce from this the formula for isolauronic acid. This at first sight seems to be a simple matter, since isolauronic acid is formed from isolauronic acid by replacing two hydrogen atoms by an oxygen atom, thus.



and therefore the formula for isolauronic acid, which suggests itself at once, is



But this formula would represent isolauronic acid as a saturated acid, and yet in many of its properties it behaves like an unsaturated acid, so that there are grounds for assuming that one of the alternative formulæ



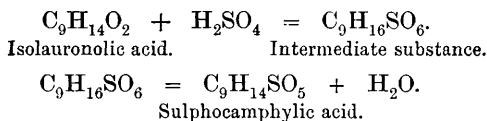
is more probable.

It must, however, be remembered that it is sometimes a matter of the greatest difficulty to distinguish between unsaturated substances and trimethylene derivatives, since the latter frequently form additive compounds with bromine, hydrogen bromide, and, less readily, with hydrogen; but trimethylene derivatives are, as a rule, stable towards permanganate at ordinary temperatures.

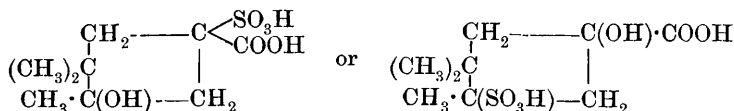
In favour of the unsaturated formula for isolaunonic acid is undoubtedly the fact that this acid instantly reduces permanganate in alkaline solution even at 0° , that it forms a dibrom-additive product when its solution in chloroform is treated with bromine at 0° and in the dark (Noyes, *Ber.*, 1895, **28**, 552), and that it combines with hydrogen bromide;* on the other hand, it is only reduced with difficulty by prolonged treatment with boiling amyl alcohol and sodium, remaining unchanged when its alkaline solution is boiled with sodium amalgam.

But the chief argument against the trimethylene formula is this, that this formula does not explain the fact that isolaunonic acid is obtained from sulphocamphylic acid by the action of heat, and is again converted into this acid by treatment with sulphuric acid.

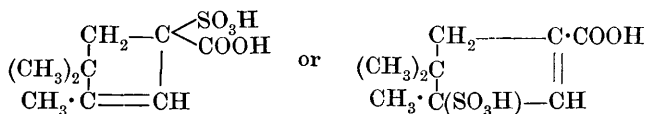
It seems probable that the latter most interesting formation of sulphocamphylic acid takes place in two stages.



Assuming, then, that isolaunonic acid contains a trimethylene ring, the addition of sulphuric acid can only take place by the splitting of the trimethylene ring, and we shall then get for the formula of the intermediate substance either



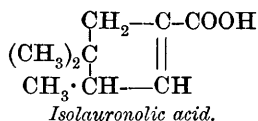
and the constitution of sulphocamphylic acid deduced from these formulæ would be either



If, now, we remove SO_3 from these formulæ to produce isolaunonic acid, we can quite easily see that the acid may have one of the two unsaturated formulæ given on p. 808, but the reconstruction of the trimethylene formula by eliminating SO_3 involves an intramolecular change for the occurrence of which little probability exists.

If, then, isolaunonic acid is an unsaturated acid, the question at once arises whether its constitution is represented by formula I or II (p. 808), and there can be no doubt that the former, that is, the formula

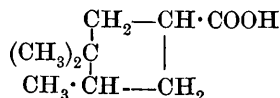
* Noyes (private communication).



best explains the properties of this acid.

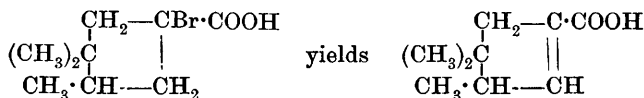
Isolauronolic acid distils without decomposition, and when boiled with dilute sulphuric acid does not yield a lactone. It cannot, therefore, be a $\beta\gamma$ -unsaturated acid such as is represented in formula II, since an acid of this constitution would readily yield a lactone under these conditions; and other properties of this acid, which are explained in more detail in the following pages, lead to the same conclusion, namely, that isolauronolic acid is an $\alpha\beta$ -unsaturated acid.

Perhaps the most striking confirmation of this view of the constitution of isolauronolic acid is the following. When reduced by amyl alcohol and sodium, isolauronolic acid, $\text{C}_9\text{H}_{14}\text{O}_2$, yields dihydroisolauronolic acid, $\text{C}_9\text{H}_{16}\text{O}_2$, the double bond being reduced, and it is obvious that the constitution of this acid will be represented by the formula

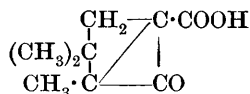


quite independently of whether formula I or II (p. 808) is taken as the constitution of isolauronolic acid.

But it has been shown by Noyes (*Amer. Chem. J.*, 1896, 18, 689), and independently by the author, that dihydroisolauronolic acid, on bromination, behaves quite normally, and yields a monobromo-derivative in which the bromine atom is doubtless in the α -position. Now, when this bromo-derivative is treated with alcoholic potash, isolauronolic acid is quantitatively produced, hydrogen bromide being eliminated between the α - and β -carbon atoms in the usual way.

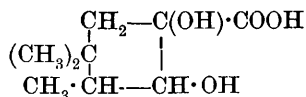


But it must be confessed that, although this formula is so very satisfactory in many ways, it is not quite easy to deduce from it the formula for isolauronolic acid which was advocated on p. 806, namely,

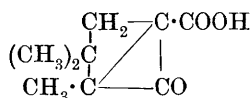


It is, of course, possible to do this by assuming that the oxidation of isolauronolic acid by permanganate takes place in the following stages.

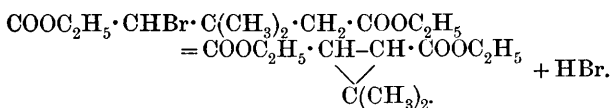
I. The oxidation proceeds in the usual way, with formation of the intermediate dihydroxy-acid of the formula



II. The $\text{CH} \cdot \text{OH}$ group is oxidised to CO , and at the same time water is eliminated, and the trimethylene ring is formed, these changes resulting in the formula of isolauroic acid,

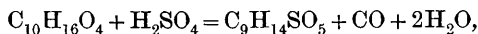


The formation of a trimethylene ring in this way, during the course of an oxidation, is certainly unusual; but there are grounds for assuming that the trimethylene ring may be produced much more easily than used to be thought possible. The above change is, for example, hardly more remarkable than the formation of the *ethylic* salt of *caronic acid* from *ethylic* α -bromo- β -dimethylglutarate, by simply warming with alcoholic potash (Perkin and Thorpe, Trans., 1897, p. 107).

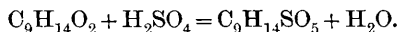


It has already been shown that it is improbable that the relation existing between isolauroic acid and sulphocamphylic acid can be explained on the basis of the trimethylene formula, and it remains to be shown that, with the aid of the unsaturated formula for isolauroic acid, this difficulty can be got over.

Sulphocamphylic acid is formed, as is well-known, by the action of sulphuric acid on camphoric acid or camphoric anhydride,



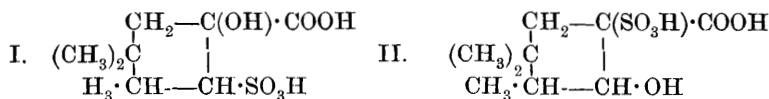
and it is also produced quantitatively when isolauroic acid is warmed with concentrated sulphuric acid,



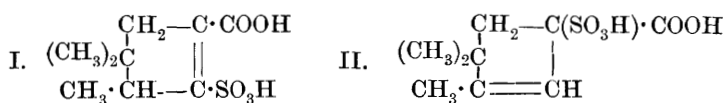
If it be remembered that camphoric anhydride is readily converted into isolauroic acid with evolution of carbon monoxide when its solution in chloroform is treated with aluminium chloride in the cold, it seems very probable that, in the formation of sulphocamphylic acid from camphoric anhydride, isolauroic acid is first produced, and that this then reacts with the sulphuric acid.

The formation of sulphocamphylic acid in this way may be assumed to take place in two stages.

In the first place, the sulphuric acid is added on at the double bond in the isolauronolic acid, a change which may take place in two ways, with the formation of the following substances.

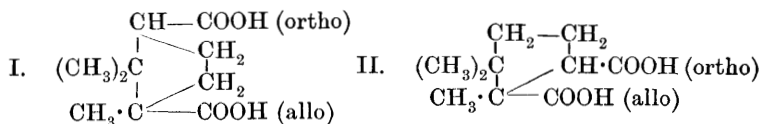


The large excess of sulphuric acid which it is necessary to have present, then acts as a dehydrating agent, water is eliminated, and thus two expressions of the constitution of sulphocamphylic acid are obtained, namely,



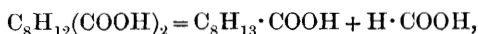
Since, however, the elimination of SO_3 and formation of isolauronolic acid can only be explained by the aid of formula I, this view of the constitution of sulphocamphylic acid has been adopted in this paper. This formula is also in accord with all the known reactions of sulphocamphylic acid, thus, for example, it represents the substance as being an unsaturated acid, and this accounts for the fact that the acid is at once oxidised by permanganate in alkaline solution even at temperatures considerably below 0° .

From the above, it will be seen that the formation and properties of isolauronic, isolauronolic, and sulphocamphylic acids, can be explained with the aid of the author's formula for camphoric acid, and it remains to be shown that the other possible formulæ for camphoric acid, namely, Bredt's formula I and the formula II,



which was at one time considered probable by the author (Proc., 1896, p. 191), do not give an explanation of the formation and properties of these acids.

In the formation of isolauronolic acid from camphoric acid, by the action of sulphuric acid or aluminum chloride, the elements of formic acid are eliminated,



or, in other words, one of the carboxyl groups in the camphoric acid is removed, and the important point is to determine which of the two carboxyl groups remains.

In order to do this, it will be convenient to adopt the nomenclature used by Brühl, Walker, and others, and to represent the carboxyl groups as *ortho* and *allo* in the way shown in the above formulæ.

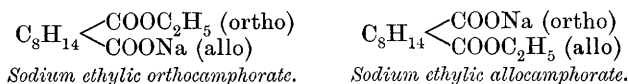
Now there are two series of unsaturated acids which can be obtained from camphoric acid by the elimination of formic acid, according to whether the *ortho*- or the *allo*-carboxyl group is removed during the process, namely.

1. The series the chief member of which is lauronolic acid, $C_8H_{13} \cdot COOH$.

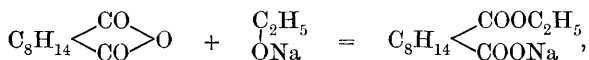
2. The series the chief member of which is isolauronolic acid $C_8H_{13} \cdot COOH$.

And it can be proved that the former series contain the *allo*-the latter the *ortho*-carboxyl group of the original camphoric acid molecule.

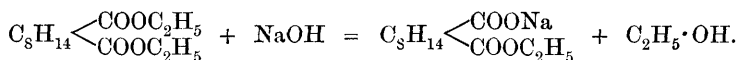
In order to make this clear, it will be necessary to refer briefly to Walker's and Walker and Henderson's important researches on the electrolysis of the sodium and potassium salts of the ethylic *ortho*- and *allo*-camphorates (Trans., 1893, 63, 495; 1895, 67, 337; 1896, 69, 748). Camphoric acid yields two isomeric sodium ethylic salts which may be provisionally represented by the formulæ



The first of these is formed by the addition of sodium ethoxide to camphoric anhydride,



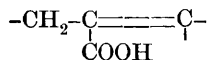
and the second by the partial hydrolysis of ethylic camphorate,



When sodium ethylic *ortho*-camphorate is electrolysed, the product is found to contain the ethereal salts of two isomeric unsaturated acids of the formula $C_8H_{13} \cdot COOH$; one of these acids is isolauronolic acid, and the other has been named campholytic acid. Campholytic acid combines directly with bromine, yielding a dibromide, $C_8H_{13}Br_2 \cdot COOH$, and this when treated with sodium carbonate is decomposed with formation of a bromo-derivative of an unsaturated hydrocarbon,



and since this decomposition is shown only by the dibrom-additive products of $\alpha\beta$ -unsaturated acids, Walker concludes that campholytic acid contains the group



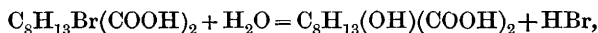
Noyes (*Ber.*, 1895, 28, 548) subsequently showed that campholytic acid is converted into the isomeric isolauronolic acid by boiling with dilute sulphuric acid; it is therefore probable that these two acids have the same structural formula and are simply stereoisomeric.

Similarly, sodium ethylic *allo*-camphorate yields, on electrolysis, the ethereal salts of two isomeric unsaturated acids, $\text{C}_8\text{H}_{13}\cdot\text{COOH}$, namely, *allo*-campholytic acid, and a small quantity of an oily acid which is possibly lauronolic acid. Both *allo*-campholytic acid and lauronolic acid, when boiled with dilute acids, yield the isomeric campholactone; they are therefore probably stereoisomeric, and since the formation of a lactone in this way is characteristic of $\beta\gamma$ -unsaturated acids, it is assumed that both these acids contain the group $\text{>C:C}\cdot\text{C}\cdot\text{COOH}$.

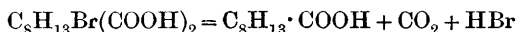
It is obvious from the method of formation that in the two series of unsaturated acids, $\text{C}_8\text{H}_{13}\cdot\text{COOH}$, namely, (*a*) lauronolic acid and *allo*-campholytic acid, (*b*) isolauronolic acid and campholytic acid, the acids all contain one of the carboxyl groups of the original camphoric acid molecule, and that the carboxyl group remaining in series *a* is a different one from that in series *b*.

It has been assumed in the above that the lauronolic series contains the *allo*-carboxyl group, and the isolauronolic series the *ortho*-carboxyl group, and it can be shown in several ways that this is the case, but for the purposes of this paper the formation of lauronolic acid from camphanic acid need only be considered.

When camphoric acid, $\text{C}_8\text{H}_{14}(\text{COOH})_2$, is brominated, the reaction takes place in the normal way with formation of the anhydride of bromocamphoric acid, $\text{C}_8\text{H}_{13}\text{Br}(\text{COOH})_2$, and it is obvious that the substitution must take place at the α -carbon atom connected with the *ortho*-carboxyl group (pp. 812, 815), since the α -carbon atom connected with the *allo*-carboxyl group has no hydrogen attached to it. When bromocamphoric anhydride is treated with dilute alkalis, it undergoes decomposition, yielding *camphanic acid*, the lactone of hydroxycamphoric acid,

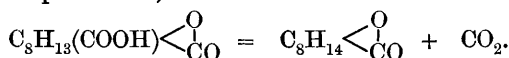


together with lauronolic acid, this acid being produced by the elimination of carbon dioxide and hydrogen bromide, thus,



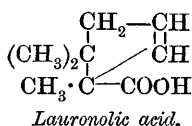
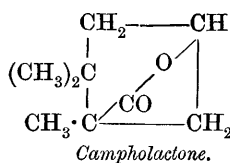
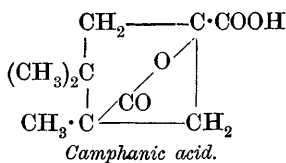
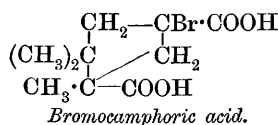
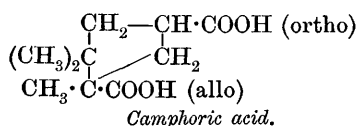
(Aschan, *Ber.*, 1894, 27, 3504).

When camphanic acid* is distilled, it readily loses carbon dioxide and yields campholactone,



In this decomposition, the carboxyl group which is eliminated must be the *ortho*-one, since lactone formation cannot take place between a hydroxy-group and a carboxyl group when both are attached to the same carbon atom. Now lauronic acid is readily converted into campholactone by boiling with dilute sulphuric acid, and therefore in its formation from bromocamphoric anhydride as represented above, it is clear that the carboxyl group which is removed is also the *ortho*-one, or in other words lauronic acid contains the *allo*-carboxyl group of the original camphoric acid molecule.

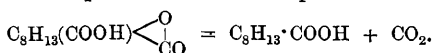
Taking the author's formula for camphoric acid as the basis, it will be seen at once that these changes are all easily understood, the following formulæ representing the constitution of the various substances mentioned above.



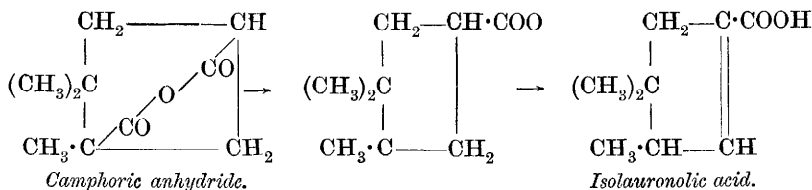
The formula for lauronic acid is in accordance with Walker's views, in so far that it represents this acid as a $\beta\gamma$ -unsaturated acid, and thus accounts for the ease with which it is converted into campholactone on treatment with acid; and since *allo*-campholytic acid also readily yields campholactone with acids, it is very probable, as stated above, that it is stereoisomeric with lauronic acid.

In a similar manner, the constitution of *isolauronic acid* (and of *campholytic acid*) may be deduced from the author's camphoric acid

* Lauronic acid is also produced in this decomposition



formula, either by considering the formation of this acid from sodium ethylic *ortho*-camphorate by electrolysis, or from camphoric anhydride by the action of aluminium chloride. In the latter case, the acid is formed simply by the elimination of CO from the *allo*-position, and thus leads to an intermediate formula, which, by necessary molecular re-arrangement, gives without difficulty the formula for isolauronolic acid.



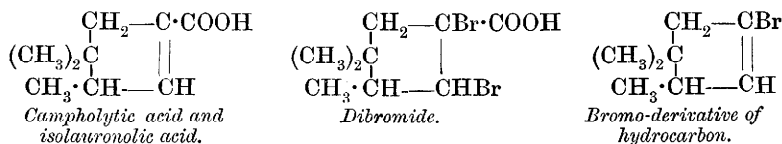
It will be noticed that the formula for isolauronolic acid given here is identical with that which was deduced for this acid on p. 810.

This formula appears to agree well with the known properties of isolauronolic acid; it represents the acid, for example, as an $\alpha\beta$ -unsaturated acid, and thus accounts for the fact that it is not converted into a lactone on boiling with dilute acids.

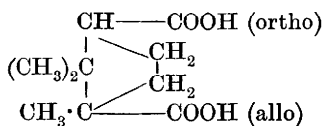
Isolauronolic acid is formed when campholytic acid is boiled with dilute acids, and it is therefore probable, as mentioned before, that these two acids are stereoisomeric. Now campholytic acid, $\text{C}_9\text{H}_{14}\text{O}_2$, yields a dibromide, $\text{C}_9\text{H}_{14}\text{Br}_2\text{O}_2$, which, when treated with sodium carbonate, gives a bromo-derivative of an unsaturated hydrocarbon (see p. 813),*



and this kind of decomposition, which, as Fittig has shown, is confined to the dibrom-additive compounds of $\alpha\beta$ -unsaturated acids, is very well understood with the aid of the above formula for campholytic acid.



It may be easily shown that the formation and properties of lauronolic acid and isolauronolic acid, and the oxidation of the latter to isolauronic acid and dimethylacetylbutyric acid, cannot be satisfactorily explained with the aid of Brecht's formula for camphoric acid.

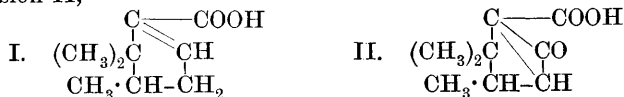


* Isolauronolic acid seems to behave in the same way (Noyes, *Ber.*, 1895, **28**, 552).

If, in proof of this statement, we take the formation of isolaunonic acid by the action of aluminium chloride on camphoric anhydride, a reaction which, as was shown on p. 816, takes place with elimination of CO from the allo-position, we obtain the following result.

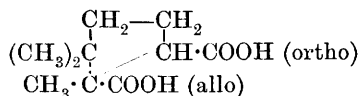


This intermediate formula must now undergo intramolecular change, and the only possible formula for isolaunonic acid which can be derived from this, and at the same time represent the acid as an $\alpha\beta$ -unsaturated acid, is I, and if from this formula we now endeavour to deduce the constitution of isolaunonic acid, $\text{C}_9\text{H}_{12}\text{O}_3$ (p. 806), we get the expression II,



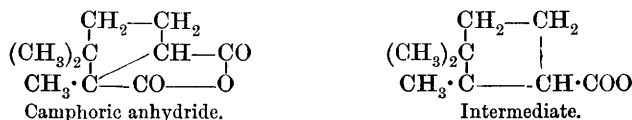
which does not account at all for the properties of this acid, and with the aid of which it seems quite impossible to imagine the formation of dimethylacetylbutyric acid, $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$, by further oxidation.

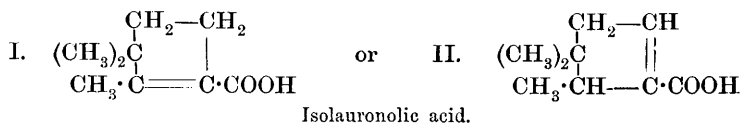
There is still one formula for camphoric acid which must be discussed, especially as it contains the group $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C} - \text{C} - \text{COOH} \\ | \quad | \\ \text{C} - \text{COOH} \end{array}$, which Walker (Trans., 1896, 59, 757), as the result of his investigations, considers must be present in this acid, and that is the formula.



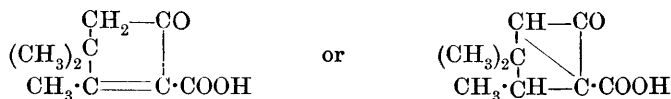
This formula was suggested by the author some time since (Proc., 1896, 191) as possibly being the correct expression for the constitution of camphoric acid.

Using the same arguments as before, the formation of isolaunonic acid from this formula would be expressed thus.

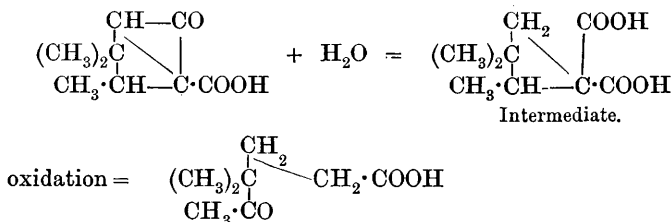




These views of the constitution of isolauronic acid, although much more satisfactory than those derived from Bredt's formula, are nevertheless improbable, since they would lead to formulæ such as

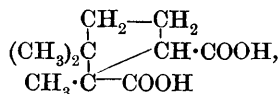


for isolauronic acid, which do not satisfy the condition 3 stated on p. 806. The first of these also could not give acetyldimethylbutyric acid on oxidation, and although the formation of this acid might be explained with the aid of the second formula, if it is assumed that the following changes could take place,



this assumption is highly improbable, since the intermediate trimethyltetramethylenedicarboxylic acid represented here would be a very stable substance, easily capable of isolation, and very difficult to attack by oxidising agents.

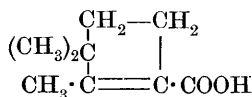
There are also other arguments against the formula,



for camphoric acid, such as, for example, the difficulty in explaining the lactone nature of camphanic acid, which appear to the author to make it much less probable than the formula adopted in this paper.

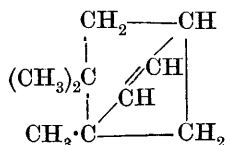
In a paper published a short time since (*Bull. Soc. Chim.*, 1898, [iii], 19, 534), G. Blanc starting with the formula* given just above for camphoric acid, deduces the expression

* This formula, which Blanc calls Bouveault's formula, for camphoric acid was first suggested by the author of this paper (*Proc.*, 1896, 191); Bouveault's communication did not appear till later (compare *Centralblatt*, 1897, ii, 856).



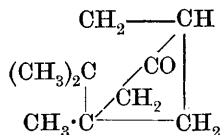
for isolaunonic acid, and states that this may be taken as “fixée avec la plus absolue certitude.” Blanc arrives at this formula (which is identical with that given on p. 818) from the consideration that, as isolaunonic acid is inactive, the asymmetry of the two asymmetric carbon atoms in camphoric acid must have disappeared in the formation of this acid, and he also explains that this formula readily accounts for the formation of acetyldimethylbutyric acid on oxidation.

The results of the examination of the ethylic and methylic salts of isolaunonic acid, which are given on p. 833, make it appear probable that this acid is feebly dextrorotatory,* and in this respect it resembles borneocamphene, which is very feebly dextrorotatory. But, since borneocamphene gives camphoric acid on oxidation, it probably still contains *both* the asymmetric carbon atoms of the original camphor molecule, and its formula, on the basis of the camphor formula given on p. 798, may be represented as



It is well known that comparatively small changes in the structure of a substance often very much affect its rotation, and arguments as to constitution based on optical inactivity are useless until it is satisfactorily proved that the substance in question is really inactive and not merely a racemoid modification.

If the views expressed in this paper are correct, the constitution of camphor will be represented by the formula



which, as will be shown in a future paper, appears to account satisfactorily for the reactions of this substance.

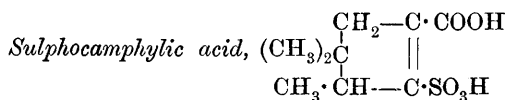
This research was commenced in 1889 in the laboratories of the Heriot Watt College, Edinburgh, and since 1892 it has been continued in the Owens College, Manchester. During the course of the

* In order to decide this point, very careful experiments on the acid itself are in progress.

work, the author has received valuable assistance from Messrs. B. Prentice, W. H. Bentley, E. Haworth, J. L. Heinke, C. T. Abell, F. H. Lees, and others; he is also much indebted to Professors F. S. Kipping and James Walker for reading the manuscript and criticising the theoretical conclusions arrived at in the Introduction to this paper, and also to Prof. Ossian Aschan for valuable suggestions.

The author also wishes to state that the greater part of the heavy expense which is unavoidable in an investigation of this kind has been met by repeated Grants from the Research Fund of the Royal Society, without which it would hardly have been possible to have carried on these experiments.

EXPERIMENTAL.



In preparing small quantities of this acid, Koenigs and Hoerlein (*Ber.*, 1893, 26, 812) heated 20 grams of camphoric acid with 40 c.c. of sulphuric acid for 4—5 hours on a water bath, and after adding water and extracting the unchanged camphoric acid with ether, they evaporated to the crystallising point and purified the crude sulphocamphylic acid by recrystallisation from ethylic acetate. This process gives very good results, but it is not well adapted for preparing the acid in such quantities as were required for the present investigation; and after many experiments, the following method was devised, by which large quantities of sulphocamphylic acid may be obtained in an almost pure condition in a comparatively short time. Five hundred grams of camphoric acid* and 1250 grams of concentrated sulphuric acid are heated in a large, round-bottomed flask on a briskly boiling water bath, when the crystals rapidly dissolve with evolution of much carbon monoxide, which must be carefully led away through a tube into the draught hole of a good draught cupboard, or, better still, into the open air. After 6—7 hours heating, the thick, brown liquid is left until cold, and then mixed with an equal volume of water, and allowed to stand overnight to crystallise, when the whole generally sets to a solid cake. The crystals, which consist of crude sulphocamphylic acid, are collected with the aid of the pump, and freed as far as possible from the dark mother liquors by pressure; these mother liquors were always discarded, as, although by suitable treatment an appreciable amount of

* The whole of the camphoric acid used in this research was obtained from Kahlbaum, and it was always found to be of very excellent quality.

The crude acid obtained from two or three such operations is transferred to a large earthenware pot, and after being mixed with five times its weight of water, steam is passed in until the temperature has been raised to the boiling point and the whole has dissolved. On standing for 24 hours in a cool place, the greenish liquid deposits a quantity of unchanged camphoric acid, which is removed by filtration through canvas bags, and the filtrate is then mixed with a little animal charcoal, and steam again passed in until the boiling point is reached. After filtering through large folded filters, the solution of sulpho-camphylic acid will be nearly colourless; it is now concentrated considerably on the water bath and extracted about eight times with ether, so as to free it completely from unchanged camphoric acid. The solution, after being evaporated to a small bulk, deposits the sulpho-camphylic acid, on standing, as a mass of colourless prisms, which, after removal of the mother liquor with the pump, is almost pure; in this form, it was used in the experiments described in this paper. For the analyses, the acid was once more crystallised from water, and allowed to remain exposed to the air at the ordinary temperature to dry.

$\left\{ \begin{array}{l} 0.9663 \text{ of the air dried crystals lost, at } 95^\circ, 0.1162 = 12.03 \text{ per cent.} \\ 0.7247 \quad " \quad " \quad " \quad 95^\circ, 0.0891 = 12.29 \quad " \\ 0.8101 \text{ of the crystals, dried at } 95^\circ, \text{lost, at } 130^\circ, 0.0610 = 7.53 \text{ per cent.} \\ 0.6356 \quad " \quad " \quad " \quad " \quad 130^\circ, 0.0454 = 7.11 \quad " \end{array} \right.$
 $C_9H_{14}SO_5, 3H_2O$ losing $2H_2O = 12.49$ per cent.
 $C_9H_{14}SO_5, H_2O$ " $H_2O = 7.14$ "

0.1266 gave 0.2147 CO₂ and 0.0689 H₂O. C = 46.25; H = 6.04.
 0.1520 „ 0.2587 CO₂ „ 0.0827 H₂O. C = 46.41; H = 6.04.
 0.6794 „ 0.6653 BaSO₄. S = 13.45.
 0.6098 „ 0.6002 BaSO₄. S = 13.51.

$\text{C}_9\text{H}_{14}\text{SO}_5$ requires C = 46.15 ; H = 5.98 ; S = 13.68 per cent.

These results show that sulphocamphylic acid has the formula $\text{C}_9\text{H}_{14}\text{SO}_5 + 3\text{H}_2\text{O}$, and not $\text{C}_9\text{H}_{16}\text{SO}_6 + 2\text{H}_2\text{O}$, as was supposed by Kachler and others to be the case, and of the 3 molecules of water 2 are given off at 95° and the remaining molecule at 130° .

Sulphocamphylic acid crystallises from water, in which it is excessively soluble, in large, colourless, glistening prisms. Its general properties have already been mentioned in the Introduction to this paper, and many of its derivatives are described in detail in the following pages.

Salts of Sulphocamphylic Acid.

Hydrogen Potassium Sulphocamphylate, $C_9H_{13}SO_5K + H_2O(l)$.—This salt was prepared by dissolving sulphocamphylic acid in water, dividing the solution into two parts, neutralising the one with pure potassium carbonate, and then adding the other. It is readily soluble in water, and crystallises in magnificent tabular crystals which do not become opaque on exposure to the air, and do not lose weight at 100° . When dry, this salt has the appearance of alabaster, and breaks up into flakes on pounding in a mortar. Analysis.

0.4305 gram of the salt gave 0.1320 K_2SO_4 . $K = 13.76$.

$C_9H_{13}SO_5K + H_2O$ requires $K = 13.45$.

$C_9H_{13}SO_5K$ requires $K = 14.33$.

From the results of this analysis, it is possible that this salt crystallises with $1H_2O$.

Potassium Sulphocamphylate, $C_9H_{12}SO_5K_2$.—Considerable quantities of this salt were prepared during the experiments on sulphocamphylic chloride (p. 823) by exactly neutralising an aqueous solution of sulphocamphylic acid with potassium carbonate, and then concentrating on the water bath. The mass of colourless crystals which separated on standing was collected with the aid of the pump, rapidly washed with small quantities of water, and drained on a porous plate. The air dried salt does not appear to contain water of crystallisation, since the loss at 150° only amounted to 0.8 per cent.

0.4328, dried at 150° , gave 0.2493 K_2SO_4 ; $K = 25.82$.

$C_9H_{12}SO_5K_2$ requires $K = 25.16$.

This salt crystallises in small needles, and is very readily soluble in water.

Hydrogen Sodium Salt, $C_9H_{13}SO_5Na + 5H_2O$.—This salt was accidentally prepared during the course of some experiments on the action of sodium hydrogen sulphite on sulphocamphylic acid; a very strong solution of the acid was nearly neutralised with sodium carbonate, and then a saturated solution of sodium hydrogen sulphite was added. On standing, a quantity of iridescent plates separated, which were collected and purified by recrystallisation from water. The crystals, after being allowed to stand on a porous plate exposed to the air for 3 days, were analysed.

I. 0.5556 gram, heated at 100° for $2\frac{1}{2}$ hours, lost 0.1156 $H_2O = 20.8$ per cent., and the residue, on treatment with sulphuric acid, gave 0.1196 Na_2SO_4 . $Na = 6.98$ per cent.

II. 0.4490 gram, heated at 100° until constant, lost 0.0901 $H_2O =$

20·28 per cent. This salt very probably has the formula $C_9H_{13}SO_5Na + 5H_2O$, which contains 6·65 per cent. of sodium, and when heated at 100° it loses $4H_2O$ or 20·81 per cent. of water.

Besides these salts, Koenigs and Hoerlin (*Ber.*, 1893, 26, 813) prepared and analysed the *neutral silver salt*, $C_9H_{12}Ag_2SO_5 + 2H_2O$, the *hydrogen silver salt*, $C_9H_{13}AgSO_5 + 2H_2O$, and a beautifully crystalline *hydrogen lead salt*, $(C_9H_{13}SO_5)_2Pb + 6H_2O$.

Carl Meyer (*Dissertation Munich*, 1895, p. 25) also prepared the *methylic salt*, $C_9H_{12}SO_5(CH_3)_2$ (m. p. 72°), and a *hydrogen methylic salt*, $C_9H_{13}SO_5 \cdot CH_3$ (m. p. 140°).

Sulphocamphylic Chloride, $C_8H_{12}(COOH) \cdot SO_2Cl$.

This substance is formed when dry potassium sulphocamphylate is treated with phosphorus pentachloride. When mixed under ordinary conditions, these two compounds reacted with considerable violence, much heat was developed, and the whole became converted into a carbonaceous mass from which nothing crystalline could be extracted, and for a long time all attempts to prepare sulphocamphylic chloride were unsuccessful.

Ultimately, however, by working at low temperatures, and mixing the substances in small portions at a time, so as to avoid, as far as possible, rise of temperature, it was found possible to isolate sulphocamphylic chloride in sufficient quantities to allow of its properties being carefully investigated. The method of preparation and extraction employed is as follows.

Phosphorus pentachloride (100 grams) is weighed out into a narrow beaker containing a thermometer, and cooled by a freezing mixture to at least -10° , and carefully dried potassium sulphocamphylate (40 grams) is then gradually added in quantities of about 2 grams at a time, the whole being rapidly stirred with the thermometer after each addition, great care being taken during the operation that the temperature does not rise above 0° . When all the potassium salt has been added, the beaker is left in an ice chest overnight, and the dark brown, almost black, product is then stirred with powdered ice; after standing for about an hour, the dark, insoluble precipitate is collected, washed with water, and allowed to remain in contact with porous porcelain in a cool place until quite dry. The almost black product thus obtained is now ground up with sand, transferred to a Soxhlet apparatus, and extracted with dry ether, when the whole of the sulphochloride passes into the ether, leaving a large quantity of an insoluble, black residue. If the brown, ethereal solution is evaporated in a flask to a small bulk, and the flask loosely corked, and allowed to stand in an ice chest, crude sulphocamphylic chloride separates in brown crusts, which may

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be obtained almost colourless by repeated recrystallisation from ether with the aid of animal charcoal.

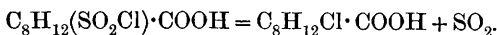
0.1994 gave 0.1124 AgCl. Cl = 13.93.

$C_8H_{12}(COOH) \cdot SO_2Cl$ requires Cl = 14.05 per cent.

Sulphocamphylic chloride melts at 168° , with decomposition. It is readily soluble in alcohol and warm acetic acid, but only sparingly in benzene and light petroleum, and crystallises beautifully either from dilute acetic acid or from dilute alcohol. It dissolves in cold sodium carbonate solution, and may be reprecipitated unchanged on the addition of acids; if, however, the alkaline solution is warmed for a few minutes, the sulphochloride is converted into sulphocamphylic acid, and no precipitation takes place on acidifying.

Chlorodihydro-β-camphylic Acid, $C_8H_{12}Cl \cdot COOH$.

When strongly heated, sulphocamphylic chloride readily undergoes decomposition, with elimination of sulphur dioxide and formation of *chlorodihydro-β-camphylic acid*, thus,



In investigating this decomposition, pure sulphocamphylic chloride, in quantities of about 10 grams, was heated under reduced pressure in a small retort connected with a long glass air condenser* until the evolution of sulphur dioxide had ceased; on rapidly distilling the residue, almost the whole passed over at $195\text{--}200^\circ$ (45 mm.) as a light greenish oil, which, on cooling, solidified completely. The solid distillate, which consisted of almost pure *chlorodihydro-β-camphylic acid*, was dissolved in boiling light petroleum (b. p. $50\text{--}60^\circ$), filtered, and the solution allowed to cool slowly, when beautiful, colourless needles were gradually deposited which, on analysis, gave the following numbers.

0.1354 gave 0.2852 CO_2 and 0.0870 H_2O . C = 57.44; H = 7.14.

0.2044 „ 0.1480 AgCl. Cl = 17.92.

0.2225 „ 0.1651 AgCl. Cl = 18.36.

$C_8H_{12}Cl \cdot COOH$ requires C = 57.32; H = 6.9. Cl = 18.78 per cent.

Chlorodihydro-β-camphylic acid melts at $105\text{--}106^\circ$, and is readily soluble in alcohol, ether, chloroform, acetic acid, and warm light

* In carrying out this operation, it is necessary to use a condenser at least 2 feet long, and to avoid, as far as possible, narrow openings in connecting the apparatus with the vacuum pump, as during the decomposition the *chlorodihydro-camphylic acid* is carried over by the sulphur dioxide to such an extent as to readily block up the connections and cause an explosion.

petroleum, but almost insoluble in water; it is best crystallised from light petroleum or from dilute acetic acid.

It dissolves in dilute sodium carbonate solution without decomposition, and the cold solution instantly decolorises permanganate, but the experiments on this oxidation hitherto made have not given very definite results. The solution of the acid in chloroform does not decolorise bromine, even on long standing, and the acid does not appear to react with hydrogen bromide at ordinary temperatures, since its solution in glacial acetic acid, after being saturated with hydrogen bromide and kept for some days, deposits the unchanged substance when evaporated over potash in a vacuum desiccator.

In chlorodihydro- β -camphylic acid the chlorine is very firmly held, as is shown by the fact that, even if the solution of the acid in sodium carbonate is left in contact with excess of sodium amalgam, very little reduction takes place; if, however, the acid is boiled with sodium amalgam, reduction does take place, with formation of substances which are at present under investigation.

Dibromo-chlorodihydro- β -camphylic acid, $C_8H_{12}Br_2Cl \cdot COOH$.

The action of bromine on chlorodihydro- β -camphylic acid was investigated in order to show that this substance is unsaturated, and thus to obtain indirect evidence of the unsaturated nature of sulphocamphylic acid. Bromine appears to have little action on the solution of chlorodihydrocamphylic acid in chloroform, and although the dry halogen reacts readily, a good deal of hydrogen bromide is evolved, and considerable difficulty was experienced in isolating the product. This was ultimately accomplished as follows. The finely powdered acid, in quantities of half a gram, was exposed on a watch-glass in a desiccator containing bromine and sulphuric acid for about $1\frac{1}{2}$ hours, until the substance had become coloured red throughout by the bromine, care being taken to remove the watch-glass before the mass commenced to become liquid. The product was left exposed to the air until the excess of bromine had evaporated, and the sticky residue was then ground up in a mortar several times with small quantities of light petroleum (b. p. $40-50^\circ$); about half of it dissolved, leaving a residue which was very sparingly soluble in light petroleum. This may be recrystallised from dilute alcohol if the operation is rapidly performed, and in this way beautiful, glistening prisms are obtained which gave the following results on analysis.

0.1656 gave 0.1910 CO_2 and 0.0576 H_2O . C = 31.45; H = 3.86.

$C_8H_{12}Br_2Cl \cdot COOH$ requires C = 30.99. H = 3.73 per cent.

0.1342 gram gave 0.1995 gram of the mixed chloride and bromide of
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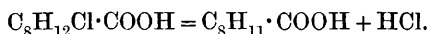
silver, the amount required by the formula $C_8H_{12}Br_2Cl \cdot COOH$ being 0.1994 gram.

Dibromochlorodihydro- β -camphylic acid decomposes rapidly at about $171-172^\circ$. It is readily soluble in alcohol, benzene, chloroform, and acetic acid, almost insoluble in cold light petroleum, and, as stated above, it may be recrystallised from dilute alcohol if the operation be rapidly performed, otherwise the acid decomposes, with formation of a substance, not yet investigated, which melts at about $100-102^\circ$ and decomposes with evolution of gas at $150-160^\circ$.

Dibromochlorodihydrocamphylic acid dissolves in dilute caustic soda, and the solution, on gently warming, rapidly deposits bromoform; if this be removed and the aqueous solution acidified, an oily acid separates which, on standing, gradually solidifies.

β -Camphylic Acid, $C_8H_{11} \cdot COOH$.

This acid is formed when chlorodihydro- β -camphylic acid is digested with alcoholic potash, hydrogen chloride being eliminated according to the equation



The pure acid was dissolved in a little alcohol, the solution heated to boiling in a reflux apparatus, and then a large excess of strong alcoholic potash added in small quantities at a time; decomposition takes place slowly, with separation of potassium chloride. After boiling for 2 hours, water was added, the solution evaporated until free from alcohol, cooled well, and acidified with hydrochloric acid, when an almost colourless, crystalline acid separated; this, after recrystallisation from dilute acetic acid, melted at $103-105^\circ$, and on examination proved to be β -camphylic acid.

0.1505 gave 0.3896 CO_2 and 0.1064 H_2O . $C = 70.60$; $H = 7.85$.

$C_8H_{11} \cdot COOH$ requires $C = 71.05$; $H = 7.89$ per cent.

β -camphylic acid has been obtained in quantity by the fusion of sulphocamphylic acid with caustic soda, and a detailed description of the properties, and the discussion of the constitution of this interesting substance, is reserved for a future communication.

Sulphocamphylic Bromide, $C_8H_{12}(COOH) \cdot SO_2Br$.

This can be prepared by treating dry potassium sulphocamphylate with phosphorus pentabromide, the reaction being much less violent than is the case with phosphorus pentachloride (p. 823). The dry potassium salt (16 grams) is gradually mixed in a mortar with the pentabromide (60 grams), when a vigorous action sets in, torrents of

hydrogen bromide are evolved, and the mass becomes quite pasty. After standing for 2 hours, the product is stirred with powdered ice until the crude sulphobromide has become quite hard, the whole is then collected, and the ochre-coloured precipitate washed well with water, and dried on a porous plate at the ordinary temperature. The product is purified by recrystallisation from ether, exactly as in the case of the corresponding sulphochloride, and the sample employed for analysis was also recrystallised from dilute alcohol.

0.1598 gave 0.2120 CO_2 and 0.0603 H_2O . $\text{C} = 36.18$; $\text{H} = 4.20$.

0.1846 „ 0.1146 AgBr. $\text{Br} = 26.45$.

$\text{C}_8\text{H}_{12}(\text{COOH})\text{SO}_2\text{Br}$ requires $\text{C} = 36.36$; $\text{H} = 4.37$. $\text{Br} = 26.93$ per cent.

When heated in a capillary tube, sulphocamphylic bromide softens at about 147° and melts at 150° with decomposition, due to elimination of sulphur dioxide. It is readily soluble in alcohol and in boiling benzene, but only sparingly in the latter solvent, and also in ether or light petroleum in the cold.

Bromodihydro- β -camphylic Acid, $\text{C}_8\text{H}_{12}\text{Br}\cdot\text{COOH}$.

At temperatures slightly above its melting point, sulphocamphylic bromide decomposes rapidly with evolution of sulphur dioxide and formation of *bromodihydro- β -camphylic acid*; but at the same time a quantity of carbonaceous matter is formed, and unless care is taken in carrying out the decomposition, it is almost impossible to extract the product and obtain it in a crystalline condition. The best results were obtained in the following way. Test tubes containing each about 2 grams of sulphocamphylic bromide were gradually heated in a sulphuric acid bath until the temperature reached 155° , when decomposition rapidly set in, with evolution of sulphur dioxide. After remaining for a few seconds at this point, the temperature was allowed to sink to about 140° , and kept at this until no more sulphur dioxide was evolved.

If the uninviting-looking, black, tarry product be now digested with light petroleum (b. p. 60°) the brominated acid will be extracted, the tarry impurity remaining undissolved, and the yellow solution, on standing in flat basins at the ordinary temperature, deposits ochre-coloured, crystalline crusts as the solvent gradually evaporates.

The crude product was purified by recrystallisation from dilute formic acid, with the aid of animal charcoal, an operation which must be rapidly carried out, as prolonged boiling with the formic acid decomposes the substance.

The pale, ochre-coloured, crystalline precipitate, which separates

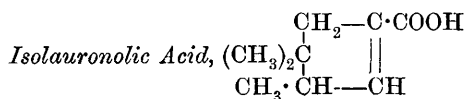
from the hot formic acid solution on rapidly cooling and stirring with a glass rod, gave the following results on analysis.

0.1518 gave 0.2580 CO_2 and 0.0775 H_2O . $\text{C} = 46.35$; $\text{H} = 5.67$.

0.2050 „ 0.1648 AgBr . $\text{Br} = 34.18$.

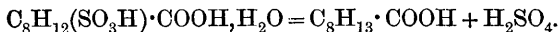
$\text{C}_8\text{H}_{12}\text{Br}\cdot\text{COOH}$ requires $\text{C} = 46.34$; $\text{H} = 5.57$; $\text{Br} = 34.33$ per cent.

Bromodihydro- β -camphylic acid melts at $128\text{--}129^\circ$, and when heated rapidly in small quantities, distils with very little decomposition. It dissolves readily in alcohol, benzene, acetic acid, and ether, but is only sparingly soluble in light petroleum. When digested with alcoholic potash, it behaves in the same way as chlorodihydro- β -camphylic acid, yielding β -camphylic acid.



The isolauronolic acid required for this research was nearly all prepared by the two following methods.

I. *The Action of Heat on Sulphocamphylic Acid*.—When rapidly heated, crystallised, air dried sulphocamphylic acid is decomposed into isolauronolic acid and sulphuric acid, according to the equation



Unfortunately, at the temperature of the reaction the sulphuric acid formed decomposes much of the product, so that the yield of isolauronolic acid actually obtained is not more than 8—10 per cent. of the theoretical. The decomposition of sulphocamphylic acid was carried out under reduced pressure in small retorts connected by rubber joints with a long air condenser fitting into an ordinary distilling flask, the latter being connected with the water pump. On heating the sulphocamphylic acid (10 grams), the mass froths up without actually melting, and becomes black at a comparatively low temperature, white fumes coming over which partially condense in the condenser tube in beautiful, feathery groups like snow crystals, and partially pass over into the receiver in the form of an oil which rapidly solidifies. The distillation is stopped when oil ceases to come over; and the retort, which is filled with a voluminous mass of carbon, is replaced by a fresh one. It was found best to distil the acid in quantities of not more than ten grams, as, if larger quantities are employed, the frothing, which is always most troublesome, becomes unmanageable.

The product, which smells strongly of sulphur dioxide and oil of turpentine, is dissolved in ether, the ethereal solution separated from

the water present, dried over calcium chloride, evaporated, and the solid residue, which contains oily impurity, allowed to remain in contact with porous porcelain until dry and nearly colourless. The crude isolauronic acid thus obtained is then very easily purified by recrystallisation, either from dilute alcohol or from dilute acetic acid, from which solvents it separates in the form of beautiful, glistening prisms which melt at 133—135°. The analysis gave the following results.

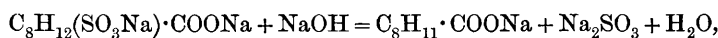
I. 0.1455 gave 0.3726 CO₂ and 0.1203 H₂O. C = 69.89 ; H = 9.18.

II. 0.1160 „ 0.2984 CO₂ „ 0.0961 H₂O. C = 70.16 ; H = 9.19.

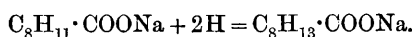
C₈H₁₃·COOH requires C = 70.13 ; H = 9.09 per cent.

II. *Fusion of Sulphocamphylic Acid with Caustic Soda in Cast Iron Pots.*—When fused in cast iron vessels with caustic soda, sulphocamphylic acid undergoes a remarkable decomposition, yielding isolauronic acid in considerable quantities, a reaction which, as explained in the introduction to this paper, evidently takes place in the following two stages.

In the first place, the sodium salts of α - and β -camphylic acids* are formed.



and these salts are then reduced by the iron of the cast iron vessel, with formation of the sodium salt of isolauronic acid,



As this reaction was employed for preparing the greater portion of the isolauronic acid used in this research, the following description of the process is given in detail.

Caustic soda (450 grams), mixed with about 250 c.c. of water in the outer vessel of an ordinary large glue-pot, is heated on a Fletcher ring burner until dissolved, and sulphocamphylic acid (150 grams) is added in small quantities at a time, and with constant stirring ; the temperature is then raised slowly to about 240°, and maintained at that point for 45 minutes. During this operation, pungent vapours are evolved, and with some practice the end of the reaction may be readily detected by the appearance of the melt, which becomes granular and nearly solid. The product, which is coloured dark reddish-brown by the ferric oxide which it contains, is dissolved out by hot water, and transferred to a large porcelain pot ; and when about 2 kilos. of sulphocamphylic acid have been fused in this way, the liquid is acidified and allowed to stand overnight, when the oil which separates will have become semi-solid.

* A description of these interesting acids is reserved for a future communication.

This dark-brown, semi-solid mass is collected, washed with water, and stirred up with ether in large beakers until the organic matter is entirely dissolved; the ethereal solution is then decanted, filtered from the ferric oxide, dried over calcium chloride, and the ether distilled off. The oily residue, which usually weighs about 350 grams, is next twice fractionated under reduced pressure, when nearly the whole passes over between 170—190° (60 mm.) as a pale greenish oil, which on cooling solidifies completely. The crystalline cake is broken up and digested with excess of sodium carbonate and some animal charcoal, filtered, the filtrate acidified, and the crystalline precipitate collected and washed. In this way, a small quantity of a neutral substance smelling strongly of peppermint, and much colouring matter, is removed. In order to purify the crude isolauronolic acid thus obtained, it is dissolved in excess of ammonia, and submitted to distillation in steam, when the ammonium salt of isolauronolic acid dissociates, causing the acid to separate out in the flask, and to be partially carried over with the steam and ammonia. The distillate is acidified, and the precipitate, together with the acid which has separated in the flask, is collected, dissolved in sodium carbonate, heated on the water bath with purified animal charcoal for half an hour, and, after filtering, the acid is reprecipitated and purified by recrystallisation from dilute acetic acid or dilute alcohol, until the melting point rises to 133—135°. The analysis of three different preparations gave the following results.

0·1485 gave 0·3792 CO₂ and 0·1206 H₂O. C = 69·61; H = 9·02.

0·1500 „ 0·3865 CO₂ „ 0·1235 H₂O. C = 70·27; H = 9·28.

0·1489 „ 0·3826 CO₂ „ 0·1218 H₂O. C = 70·05; H = 9·08.

C₈H₁₃·COOH requires C = 70·13; H = 9·09 per cent.

In preparing isolauronolic acid by this method, a quantity of oily impurity is removed from the crude crystals during the crystallisation from dilute acetic acid, and in order to investigate the nature of this, the mother liquors from a very large number of different preparations were mixed with water and extracted with ether. The ethereal solution was several times washed with water to remove the acetic acid, dried over calcium chloride, and evaporated; in this way, about 50 grams of a thick, yellow oil was obtained, which was carefully fractionated, first under reduced pressure, and then under ordinary pressure.

Rather more than 30 grams of the oil distilled between 230° and 245° (750 mm.), and this, on standing for some months in an ice chest, deposited a few crystals of isolauronolic acid. The oil was decanted from these crystals and again distilled, when nearly the whole passed over at 230—235° as a colourless oil, which on analysis gave the following results.

0.1436 gave 0.3548 CO_2 and 0.1236 H_2O . $\text{C} = 67.45$; $\text{H} = 9.63$.

0.1584 „ 0.3905 CO_2 „ 0.1391 H_2O . $\text{C} = 67.23$; $\text{H} = 9.75$.

$\text{C}_7\text{H}_{13}\cdot\text{COOH}$ requires $\text{C} = 67.60$; $\text{H} = 9.86$ per cent.

The silver salt of this acid was prepared by precipitating a slightly alkaline solution of the ammonium salt with silver nitrate; and the white, caseous precipitate was analysed, with the following results.

0.1943 gave 0.2693 CO_2 , 0.0860 H_2O , and 0.0855 Ag.

$\text{C} = 37.80$; $\text{H} = 4.91$; $\text{Ag} = 44.00$.

$\text{C}_7\text{H}_{13}\cdot\text{COOAg}$ requires $\text{C} = 38.55$; $\text{H} = 5.22$; $\text{Ag} = 43.38$ per cent.

From these results, it seems probable that this oil, boiling at $230\text{--}235^\circ$, is an acid of the composition $\text{C}_7\text{H}_{13}\cdot\text{COOH}$, but, as its examination did not give any results which seemed likely to be of value in the present inquiry, its systematic investigation was not undertaken.

Properties and Salts of Isolaunonic Acid.—Isolaunonic acid melts at $133\text{--}135^\circ$, and distils without decomposition at about 250° under the ordinary pressure; it is readily volatile in steam. It dissolves readily in alcohol, ether, chloroform, benzene, carbon bisulphide or ethylic acetate, but is only very sparingly soluble in water. The solution of the acid in sodium carbonate is oxidised by potassium permanganate instantly at the ordinary temperature, but bromine is not decolorised by the solution of the acid in chloroform except on warming or long standing, and then with evolution of hydrogen bromide. Isolaunonic acid is not readily attacked by hydrogen bromide, since it does not form an additive compound when its solution in glacial acetic acid is saturated with hydrogen bromide and allowed to stand overnight; this is shown to be the case by adding water to the solution, when the acid is reprecipitated unchanged.

Noyes (*Ber.*, 1895, 28, 552) succeeded in obtaining a dibromide of isolaunonic acid, $\text{C}_8\text{H}_{13}\text{Br}_2\cdot\text{COOH}$, melting at $138\text{--}140^\circ$, by treating the solution of the acid in dry chloroform with bromine, in the dark, at temperatures below 0° , and he has also prepared a crystalline hydrobromide, $\text{C}_8\text{H}_{14}\text{Br}\cdot\text{COOH}$ (m. p. $127\text{--}130^\circ$), which he obtained by shaking the acid with fuming aqueous hydrobromic acid and light petroleum.* Isolaunonic acid is not reduced when treated with a large excess of sodium amalgam, but it yields a *dihydro-derivative*, $\text{C}_8\text{H}_{15}\cdot\text{COOH}$, when its solution in amyl alcohol is heated with sodium (see p. 836).

Isolaunonic acid does not form a lactone when boiled with dilute acids. This point has been very carefully investigated by heating

* Private communication.

the acid with sulphuric acid of varying concentration and under various conditions, but in no case could a lactone be isolated.

The dissociation constant of isolauronolic acid has been determined by Walker (Trans., 1893, 63, 505) who found the very low value $k = 0.0018$.

Isolauronolic acid dissolves in dilute ammonia and in sodium hydrogen carbonate, but it is a very feeble acid, since its ammonium salt readily dissociates into ammonia and the free acid on evaporating its solution on the water bath. Koenigs and Hoerlin (*Ber.*, 1893, 26, 814) state that the solution of the calcium salt of the acid is decomposed by carbon dioxide into calcium carbonate and the free acid, a decomposition seldom met with in organic calcium salts.

Silver isolauronolate, $C_8H_{13} \cdot COOAg$, was obtained, on adding silver nitrate to a neutral solution of the ammonium salt, as a white, caseous, and very voluminous precipitate which on analysis gave the following results.

I. 0.1967 gave 0.2976 CO_2 , 0.0884 H_2O , and 0.0815 Ag.

C = 41.26 ; H = 4.99 ; Ag = 41.43.

II. 0.1625 gave 0.0672 Ag. Ag = 41.35.

$C_8H_{13} \cdot COOAg$ requires C = 41.38 ; H = 4.98 ; Ag = 41.38.

A neutral dilute solution of the ammonium salt of isolauronolic acid gives, with *copper sulphate*, a light blue, apparently crystalline, and very insoluble precipitate, and with *lead acetate* or *zinc sulphate*, a white, amorphous, caseous precipitate, but no precipitation with *barium* or *calcium chlorides*.

Koenigs and Hoerlin (*loc. cit.*) have prepared and analysed a *calcium salt* of isolauronolic acid, $(C_9H_{13}O_2)_2Ca + H_2O$ (?),* and the *potassium salt*, $C_9H_{13}KO_2 + H_2O$; both of these salts are crystalline and soluble in water; according to Noyes (*Ber.*, 1895, 28, 550), the calcium salt of isolauronolic acid crystallises with $3\frac{1}{2}H_2O$.

Walker (this Journal, 1893, 63, 506) has described the *barium salt* of isolauronolic acid as a soluble, crystalline substance, which appears to have the formula $(C_9H_{13}O_2)_2Ba + 5H_2O$.

Ethereal Salts of Isolauronolic Acid.—The methylic and ethylic salts of isolauronolic acid were prepared by dissolving the acid in the corresponding alcohol, adding concentrated sulphuric acid, allowing the mixture to stand for 12 hours, and then heating for 2 hours at 60–80°, etherification taking place very readily under these conditions. After adding water, the oily ethereal salts were extracted three times with ether, the ethereal solutions were well washed with water and dilute

* The formula, $C_9H_{13}CaO_2 + H_2O$, given for this salt in Koenigs and Hoerlin's paper is obviously a slip.

sodium carbonate, dried over anhydrous potassium carbonate, and after distilling off the ether, the residue was purified by fractionation under the ordinary pressure. The determination of the densities, magnetic rotation, refraction, &c., of these ethereal salts was carried out by W. H. Perkin, sen.

Methylic isolauronolate, $C_8H_{13} \cdot COOCH_3$, a colourless liquid possessing a rather characteristic odour, boils at $204-204.5^\circ$ without decomposition.

0.1114 gave 0.291 CO_2 and 0.0962 H_2O . C = 71.24; H = 9.60.

$C_8H_{13} \cdot COOCH_3$ requires C = 71.43; H = 9.52 per cent.

The density determinations gave

$d\ 4^\circ/4^\circ = 0.9835.$	$d\ 15^\circ/15^\circ = 0.9747.$
$d\ 10^\circ/10^\circ = 0.9784.$	$d\ 25^\circ/25^\circ = 0.9681.$

Prepared in the way described above, this methylic salt has a slight permanent rotation, which was found to be $+7' 48''$ for a length of 10.2 cm. at 30° .

	<i>t.</i>	Sp. rotation.	Mol. rotation.
Magnetic rotation	30°	1.1696	11.312
Refraction	$t = 17.5^\circ$	$d\ 17.3^\circ/4^\circ = 0.97207.$	

	$\mu.$	$\frac{\mu - 1}{d.}$	$\frac{\mu - 1}{d} p.$
A.....	1.46278	0.47607	79.981
Li	1.46575	0.47913	80.494
Ha	1.46634	0.47974	80.596
Na	1.46970	0.48319	81.176
H β	1.47795	0.49168	82.603
H γ	1.48517	0.49911	83.851

Ethylic isolauronolate, $C_8H_{13} \cdot COOC_2H_5$. B. p. 216° .

0.1170 gave 0.3112 CO_2 and 0.1049 H_2O . C = 72.60; H = 9.96.

$C_8H_{13} \cdot COOC_2H_5$ requires C = 72.53; H = 9.89 per cent.

The density determinations gave

$d\ 4^\circ/4^\circ = 0.9645.$	$d\ 10^\circ/10^\circ = 0.9596.$	$d\ 15^\circ/15^\circ = 0.9560.$
$d\ 20^\circ/20^\circ = 0.9527.$	$d\ 25^\circ/25^\circ = 0.9494.$	

This ethereal salt had a slight permanent rotation which was found to be $+10' 12''$ for a length of 10.2 cm. at 29° .

	<i>t.</i>	Sp. rotation.	Mol. rotation.
Magnetic rotation.....	28.5°	1.1623	12.405
Refraction	$t = 17.2^\circ$	$d\ 17.2^\circ/4^\circ = 0.95339.$	

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	μ .	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
A	1.45950	0.48197	87.718
Li	1.46238	0.48498	88.267
Ha ...	1.46307	0.48571	88.400
Na.....	1.46624	0.48903	89.004
H β ...	1.47429	0.49748	90.541
H γ ...	1.48127	0.50478	91.870

The results obtained in the examination of the magnetic rotation of methylic and ethylic isolauronolates are interesting. The difference in the values of the two ethereal salts is 1.093 and is normal, that is to say, it is the same as between the ethylic and methylic salts in the fatty series; thus, for example, the difference between the ethylic and methylic salts of butyric acid is 1.090.

Again, the values obtained afford important evidence that isolauronolic acid is an unsaturated acid, as the following comparison of ethylic isolauronolate with ethylic nonate shows. The magnetic rotation of ethylic nonate, $C_8H_{17} \cdot COOC_2H_5$, is 11.590, and assuming that ethylic isolauronolate is unsaturated, and at the same time a closed chain compound, its magnetic rotation may be approximately calculated.

From the examination of a large number of closed chain compounds, it has been found that these differ from the corresponding open chain saturated compounds by about -0.47 , and also that unsaturated compounds have a higher rotation than the corresponding saturated compounds by about 1.112.

We have, therefore,

Magnetic rotation of ethylic nonate	= 11.590
Add value for unsaturation	= 1.112
	<hr/>
	12.702
Deduct value for ring formation	= 0.471
	<hr/>

Calculated magnetic rotation of ethylic isolauronolate = 12.231

The value thus calculated agrees well with that actually found, namely, 12.405.

The refractions of the methylic and ethylic salts of isolauronolic acid are very high, showing their unsaturated nature, as is evident from the following comparison between the values found and those calculated.

	Found.	Calculated.	Difference.
Methylic salt.....	80.596	77.0	+ 3.504
Ethylic salt	88.400	84.6	+ 3.800

Methylic dibromisolauronolate, $C_8H_{13}Br_2 \cdot COOCH_3$.—The action of

bromine on methylic isolauronolate was investigated in order to obtain further evidence as to the unsaturation of the acid. Methylic isolauronolate (3 grams) was dissolved in carefully dried chloroform (3 grams), and after cooling the solution to 0° , dry bromine (3 grams) dissolved in chloroform (10 grams) was slowly added, the apparatus being covered up so as to exclude light during the operation. The bromine was rapidly, but not instantaneously, absorbed, and as soon as the whole had been decolorised, the product, which, owing to the presence of traces of hydrogen bromide, fumed slightly, was freed from chloroform by passing a current of dry air through it for some hours. The thick oil thus obtained, after standing for some time over solid paraffin wax in a vacuum desiccator, gave the following results on analysis.

0.2171 gave 0.2994 CO_2 and 0.0931 H_2O . C = 37.61; H = 4.76.

0.1899 „ 0.2536 CO_2 „ 0.0772 H_2O . C = 36.40; H = 4.50.

0.3329 „ 0.3696 AgBr; Br = 47.24.

0.4172 „ 0.4650 AgBr; Br = 47.42.

$\text{C}_8\text{H}_{13}\text{Br}_2 \cdot \text{COOCH}_3$ requires C = 36.6; H = 4.87; Br = 48.77.

These results show that very little hydrogen bromide is eliminated when methylic isolauronolate is treated with the calculated quantity of bromine at 0° in the dark, since the product contains almost the quantity of bromine theoretically required for the dibrom-additive compound.

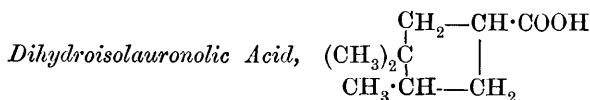
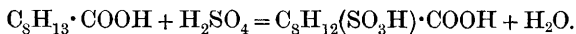
Conversion of Isolauronic Acid into Sulphocamphylic Acid.

When isolauronic acid, in quantities of 0.5 gram, is added to 10 times its weight of concentrated sulphuric acid, it dissolves with development of some heat, and formation of a yellow solution from which water precipitates the acid unchanged. If, however, the solution is gradually heated to 75° , it darkens and becomes brownish-black, a small amount of sulphur dioxide is liberated, and after heating some time no isolauronic acid is deposited on adding water. After about 20 minutes heating at 75° , and as soon as a drop of the solution gave no precipitate on diluting with water, the well-cooled product was gradually mixed with an equal bulk of water, and the greenish solution left for some hours, when crystals separated; these were collected with the aid of the pump, dissolved in a little water, the solution warmed with animal charcoal, filtered, and evaporated nearly to dryness on the water bath. On standing in the ice chest, beautiful crystals of sulphocamphylic acid gradually formed; after draining these on a porous plate and subsequently drying at 130° , they gave the following results on analysis.

0.5547 gave 0.5451 BaSO_4 . $S = 13.43$.

$\text{C}_8\text{H}_{12}(\text{SO}_3\text{H})\cdot\text{COOH}$ requires $S = 13.68$ per cent.

The careful examination of the properties of these crystals proved conclusively that they consisted of sulphocamphylic acid, and this acid, which is produced almost quantitatively in this way, is evidently formed from isolauronolic acid by the addition of sulphuric acid and elimination of water thus.



In the first experiments on the reduction of isolauronolic acid, it was treated with sodium amalgam under varied conditions, but no reduction took place even when its solution in sodium carbonate was boiled with a large excess of the amalgam; ultimately, it was found that the acid could be reduced, although with difficulty, when its solution in amylic alcohol was treated with sodium at the boiling temperature.

Pure isolauronolic acid (35 grams) was dissolved in isoamylic alcohol ($1\frac{1}{2}$ litres), the solution heated to boiling on a sand bath in a flask connected with a long reflux condenser, and then 10 grams of sodium, in small pieces, was added all at once; as soon as the violent action had moderated somewhat, 20 grams more sodium was added, and the whole boiled vigorously until the sodium had dissolved. After allowing the mixture to cool, water was added, the product acidified with hydrochloric acid, the oily layer separated, and the aqueous liquid extracted twice with small quantities of isoamylic alcohol. The extract was then added to the main bulk, the whole distilled until the thermometer rose to 125° , when it was treated again with 30 grams of sodium exactly as in the first instance. After this process had been repeated three times, the product was extracted with water three times, the isoamylic alcohol distilled down to a small bulk, the remainder removed by distillation with steam, and the aqueous solution thus obtained added to the previous extracts. The whole was then heated on the water bath until quite free from isoamylic alcohol, acidified, and repeatedly extracted with ether; after drying over calcium chloride and evaporating off the ether, 35 grams of an almost colourless oil was obtained which, on standing for some days in an ice chest, deposited about 5 grams of unchanged isolauronolic acid. These crystals were removed by filtration, and the filtrate distilled; almost

the whole passed over at 165° (at 30 mm.) as a colourless oil which gave the following results on analysis.

0.1292 gave 0.3284 CO_2 and 0.1163 H_2O . $\text{C} = 69.27$; $\text{H} = 10.00$.

$\text{C}_8\text{H}_{15}\cdot\text{COOH}$ requires $\text{C} = 69.23$; $\text{H} = 10.25$ per cent.

Although this analysis agrees well with the numbers required by dihydroisolauroic acid, it was found that when a drop of the substance dissolved in dilute sodium carbonate was mixed with a trace of permanganate, the colour was instantly discharged, showing that it still contained some unchanged isolauroic acid, and since, for subsequent experiments, it was necessary that this should be removed, the following process of purification was resorted to.

The acid was dissolved in dilute sodium carbonate and oxidised by dilute permanganate in a vessel fitted with a turbine, the temperature being kept at 0° by means of powdered ice, and a rapid current of carbonic anhydride being passed during the whole operation. As soon as the pink colour remained permanent for several minutes, the excess of permanganate was destroyed by sodium hydrogen sulphite, the whole heated to boiling, filtered, and the filtrate and washings from the manganese precipitate evaporated to dryness. The residue was acidified, distilled in a current of steam,* the oily acid extracted from the distillate in the usual way, and purified by distillation under reduced pressure, when nearly the whole passed over at 144° (22 mm.).

0.1272 gave 0.3221 CO_2 and 0.1168 H_2O . $\text{C} = 69.04$; $\text{H} = 10.22$.

$\text{C}_8\text{H}_{15}\cdot\text{COOH}$ requires $\text{C} = 69.23$; $\text{H} = 10.25$ per cent.

Dihydroisolauroic acid is a colourless, moderately mobile oil which smells like a high boiling fatty acid. It dissolves readily in sodium carbonate, and the solution of the sodium salt does not decolorise permanganate in the cold. The acid is, in fact, characterised by extraordinary stability, as even when boiled with permanganate it is only very slowly attacked, and all attempts to oxidise it with nitric acid were unsuccessful, since, after boiling it for a week with 50 per cent. nitric acid, more than 75 per cent. of the acid was recovered unchanged.

Salts of Dihydroisolauroic Acid.—The silver salt, $\text{C}_8\text{H}_{15}\cdot\text{COOAg}$, obtained as a white, gelatinous precipitate by adding silver nitrate to a slightly alkaline solution of the ammonium salt, was washed well with water and once with methylic alcohol.

0.2338 gave 0.0950 Ag. $\text{Ag} = 40.64$.

$\text{C}_8\text{H}_{15}\text{COOAg}$ requires $\text{Ag} = 41.06$ per cent.

* A considerable quantity of isolauroic acid separated from the residue in the distilling flask on standing.

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This salt is very sparingly soluble in water, but it dissolves moderately readily in alcohol.

The *ammonium salt*, which separates in colourless crystals when the acid is mixed with moderately concentrated ammonia, is readily soluble in water, and dissociates when its solution is evaporated on the water bath. A slightly alkaline solution of the ammonium salt shows the following behaviour with reagents.

Barium chloride, no precipitate in the cold, but on boiling a crystalline barium salt separates, the crystals dissolving again on cooling.

Calcium chloride gives no precipitate with dilute solutions, but with moderately concentrated solutions a white calcium salt separates as an amorphous mass which becomes crystalline on warming.

Copper acetate gives at once a very pale blue, amorphous precipitate.

Bromination of Dihydroiselaurnolic Acid, and its Reconversion into Iselaurnolic Acid.

This experiment, which has such an important bearing on the constitution of iselaurnolic acid (p. 810), was conducted as follows.

Dihydroiselaurnolic acid (3 grams) was mixed in a reflux apparatus with phosphorus pentabromide (8 grams), and after the reaction, which commenced at once, had ceased, the mixture was heated for 10 minutes on the water bath. Bromine (3 grams) was then added to the well cooled product, and the whole very gently heated until the evolution of hydrogen bromide had practically ceased, and the colour of the bromine had disappeared.

The mixture of bromacid bromide and phosphorus oxybromide thus obtained was poured in a thin stream into excess of methylic alcohol; water was added, and the methylic salt, extracted with ether in the usual way, was washed with dilute sodium carbonate, dried, and fractionated under reduced pressure. Almost the whole of it (6 grams) distilled at 123—126° (30 mm.) as a colourless oil, and with liberation of traces of hydrogen bromide, which accounts for the analytical results being a little low.

0.3134 gave 0.2230 AgBr. Br = 30.27.

0.2904 „ 0.2050 AgBr. Br = 30.03.

$C_8H_{14}Br \cdot COOCH_3$ requires Br = 32.12 per cent.

When this *methylic bromodihydroiselaurnolate* * is mixed with warm alcoholic potash, a vigorous action takes place, accompanied by separation of potassium bromide, and if, after boiling for some minutes,

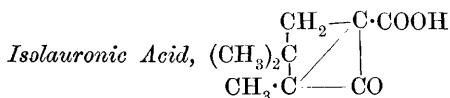
* The free acid, called by Noyes α -bromodihydro-*cis*-campholytic acid, is crystalline and melts at 124–125° (*Journ. Amer. Chem. Soc.*, 1896, **18**, 689).

water is added and the alcohol removed by evaporation, a residue is obtained which, on acidifying, gives a crystalline precipitate; this, after being freed from traces of oily impurity by spreading it on porous porcelain, crystallises beautifully from dilute alcohol, and consists of pure isolauronic acid (m. p. 133°).

0.1474 gave 0.1205 H_2O and 0.3793 CO_2 . $\text{C} = 70.18$; $\text{H} = 9.08$.

$\text{C}_8\text{H}_{13}\cdot\text{COOH}$ requires $\text{C} = 70.13$; $\text{H} = 9.09$ per cent.

The yield of isolauronic acid obtained in this way appears to be almost quantitative.



This acid was first described by Koenigs and Meyer (*Ber.*, 1894, 27, 3467), who obtained it by oxidising isolauronic acid with potassium permanganate at 0°.

Almost at the same time, and quite independently, the author carried out a series of experiments on the oxidation of isolauronic acid, and after preparing a quantity of isolauronic acid, carefully investigated it, with the result that many fresh facts were discovered which throw important light on the constitution both of this acid and of isolauronic acid.

The isolauronic acid used in these experiments was prepared as follows. Pure isolauronic acid (5 grams) was dissolved in a slight excess of warm dilute potash, the solution transferred to a large porcelain beaker fitted with a turbine, and a rapid stream of carbon dioxide passed through the liquid. After adding powdered ice, and cooling the beaker externally by a freezing mixture, so that the temperature of the solution never exceeded -3° , a well cooled saturated solution of potassium permanganate was slowly run in until the colour, which at first instantly disappeared, just remained permanent, the whole being stirred continuously, and a rapid current of carbon dioxide passed during the operation.*

After the excess of permanganate had been destroyed by adding a little sodium hydrogen sulphite, the product was heated on the water bath, filtered from the manganese precipitate, and the filtrate, together with the washings of the precipitate, evaporated to a small bulk. On acidifying the deep yellow solution thus obtained, it deposited a mass of yellow crystals of isolauronic acid,† which were collected with

* If these precautions are not taken, the yield of isolauronic acid is very much reduced.

† The mother liquors from these crystals contain considerable quantities of γ -dimethylacetylbutyric acid (see p. 844).

the aid of the pump, washed with water, and purified by recrystallisation from this solvent.

0.1730 gaev 0.4069 CO_2 and 0.1141 H_2O . $\text{C} = 64.16$; $\text{H} = 7.32$.

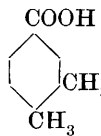
0.1557 „ 0.3667 CO_2 „ 0.1029 H_2O . $\text{C} = 64.22$; $\text{H} = 7.34$.

$\text{C}_9\text{H}_{12}\text{O}_3$ requires $\text{C} = 64.22$; $\text{H} = 7.14$ per cent.

Isolauronic acid crystallises from water in long, glistening, straw-yellow prisms and melts at 133° . It is readily soluble in hot water, ether, and alcohol, but only sparingly in light petroleum and cold water; it dissolves readily in sodium carbonate, and although the solution does not decolorise permanganate below 0° , it does so readily at the ordinary temperature. Isolauronic acid does not appear to form an additive compound with hydrogen bromide, since the solution of the acid in acetic acid saturated with hydrogen bromide, even on long standing, gives a precipitate of the unchanged acid on the addition of water. A solution of bromine in caustic potash oxidises the acid particularly easily on warming, with separation of bromoform and formation of an oily acid, which is at present under investigation.

Bromine vapour converts isolauronic acid into a red liquid, which gradually solidifies on standing over potash in a vacuum; the crystals, however, are very deliquescent, and as the substance could not be purified by recrystallisation from solvents, it was not further investigated.

When heated with concentrated aqueous hydrochloric acid at 170° for 3 hours, isolauronic acid is completely changed, with separation of a certain amount of carbonaceous matter. In order to find out what had been formed during this decomposition, the product was extracted with ether, the ethereal extract evaporated, the solid residue dissolved in sodium carbonate, and the solution, after boiling with animal charcoal and filtering, evaporated to a small bulk and acidified with hydrochloric acid. The almost colourless, sparingly soluble, sandy precipitate, which melted at 165° , after crystallisation from acetic

acid, was, on investigation, found to be paraxylic acid, , an

acid which Koenigs and Meyer (*Ber.*, 1894, 27, 3468) had already obtained from isolauronic acid by treatment with sulphuric acid.

Salts of Isolauronic Acid.—The silver salt, $\text{C}_9\text{H}_{11}\text{AgO}_3$, is obtained by adding silver nitrate to a warm neutral solution of the ammonium salt, as a colourless, crystalline precipitate, which dissolves moderately readily in hot water, and separates again on cooling as a beautiful, silky mass of crystals.

0.1732 gave 0.2492 CO_2 , 0.0642 H_2O and 0.0684 Ag.

C = 39.24 ; H = 4.12 ; Ag = 39.48.

$\text{C}_9\text{H}_{11}\text{AgO}_3$ requires C = 39.27 ; H = 4.00 ; Ag = 39.27 per cent.

A dilute neutral solution of the ammonium salt of isolauronic acid gives no precipitate with *barium* or *calcium* chlorides even on boiling ; the addition of *copper* sulphate produces no precipitate in the cold, but on boiling a very pale blue, apparently crystalline, salt separates ; *lead* acetate gives at once a white, caseous precipitate which is soluble in hot water.

Oxime of Isolauronic Acid, $\text{C}_7\text{H}_{11}(\text{C}:\text{NOH})\cdot\text{COOH}$.—The action of hydroxylamine on isolauronic acid has been studied by Carl Meyer (*Dissertation Munich*, 1895, p. 39), who obtained in this way the oxime which he describes as a pale yellow powder which softens at 215° and decomposes at $228\text{--}230^\circ$. In preparing this substance in considerable quantities for experiments in connection with this research, the following method was always used. The pure acid (5 grams) was dissolved in moderately strong potash (15 grams), a solution of hydroxylamine hydrochloride (7 grams) added, and the whole after standing overnight was acidified, when the oxime was precipitated as a voluminous, amorphous precipitate somewhat resembling a precipitate of alumina. The whole was extracted 20 times with ether, and the ethereal solution, after being rapidly dried over calcium chloride, was evaporated until crystalline crusts of the oxime commenced to separate. After standing for some time, these were collected, washed with ether, and analysed.

0.1240 gave 8 c.c. of nitrogen at 18° and 762 mm. N = 7.47.

$\text{C}_9\text{H}_{13}\text{NO}_3$ requires N = 7.65 per cent.

When heated in a capillary tube, the oxime of isolauronic acid turns brown at 210° , and melts with vigorous decomposition at 222° .

Semicarbazone of Isolauronic Acid, $\text{C}_7\text{H}_{11}(\text{C}:\text{N}_2\text{H}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{COOH}$.—This very characteristic derivative is readily prepared by warming isolauronic acid with a slight excess of semicarbazide hydrochloride and sodium acetate on the water bath for a few minutes. The very sparingly soluble precipitate which separates rapidly on cooling was collected, washed with water, recrystallised from alcohol, and analysed, with the following result.*

0.1444 gave 23.9 c.c. nitrogen at 20° and 740 mm. N = 18.42.

0.2178 „ 36.1 c.c. „ 18° „ 745 mm. N = 18.70.

$\text{C}_{10}\text{H}_{15}\text{N}_3\text{O}_3$ requires N = 18.66 per cent.

* Carl Meyer (*Dissertation Munich*, 1895, p. 39), who has also prepared this semicarbazone, states that he always found 1 per cent. too much nitrogen in his analyses.

The *semicarbazone* of isolauronic acid melts at about 247—248° with decomposition.

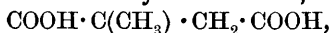
Oxidation of Isolauronic Acid. Formation of γ -Dimethylacetylbutyric Acid, $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$, and α -Dimethylsuccinic Acid, $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{COOH}$.

I. *α -Dimethylsuccinic Acid.*—In the first experiments on the oxidation of isolauronic acid, 3 grams of the pure acid were dissolved in hot water, the solution heated to boiling in a reflux apparatus and then potassium dichromate and sulphuric acid run in through a tap funnel until very little further oxidation appeared to take place. The green solution, after saturating with ammonium sulphate, was extracted 10 times with ether, and the ethereal solution dried over calcium chloride and evaporated, when nearly 2 grams of a thick oil were obtained, which deposited crystals on standing; these were collected, drained on a porous plate, recrystallised from concentrated hydrochloric acid, and analysed, with the following result.

0.1520 gave 0.274 CO_2 and 0.0958 H_2O . C = 49.15; H = 7.0.

$\text{C}_6\text{H}_{10}\text{O}_4$ requires C = 49.31; H = 6.85 per cent.

This substance melted at 138—140°, and it seemed probable that it was identical with the α -dimethylsuccinic acid,



which Leuckart (*Ber.*, 1885, 18, 2250) and Bischoff and Jaunsnicker (*Ber.*, 1890, 23, 3400) had obtained by the hydrolysis of the product of the action of ethylic α -bromoisobutyrate on the sodium compound of ethylic malonate. In order to decide this point, the acid obtained from isolauronic acid was carefully compared with a sample of the synthetical acid which Professor Bischoff kindly sent the author, and in this way the identity of the two acids was clearly proved.

As it is a matter of importance, particularly for those working in the camphor group, to be able quickly to identify small quantities of α -dimethylsuccinic acid, a short account of the more characteristic properties of this acid, together with a description of some new derivatives which were prepared during the above experiments, is given here.

α -Dimethylsuccinic acid is best purified by dissolving it in a little water, and saturating the well cooled solution with hydrogen chloride; on cooling, the acid rapidly separates in small crystals, which, after collecting on an asbestos filter, washing with hydrochloric acid, and draining on a porous plate, melt at 138—140°.

A characteristic of dimethylsuccinic acid, which is often very valuable in separating the acid from a mixture with other acids, is

the property that, when its aqueous solution is made strongly alkaline with ammonia and then mixed with excess of calcium chloride solution, no precipitate is formed in the cold, but on boiling a very sparingly soluble calcium salt separates, which, after collecting, washing with water, decomposing with hydrochloric acid and extracting with ether, yields at once the pure acid.*

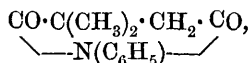
α-Dimethylsuccinanic acid is readily prepared by heating the acid with excess of acetyl chloride for a few minutes, and after evaporating the excess of the chloride, dissolving the residue in benzene and adding aniline. In a short time, the anilic acid separates in crystals, which, after collecting and purifying by recrystallisation from dilute methylic alcohol, melt, when rapidly heated, at about 187° with rapid decomposition. The following analyses were made.

I. (From isolauroic acid) 0.1796 gave 9.8 c.c. of nitrogen at 16° and 755 mm. N = 6.32.

II. (From synthetical acid) 0.2695 gave 14.8 c.c. of nitrogen at 15° and 752 mm. N = 6.36.

$C_{12}H_{15}NO_3$ requires N = 6.33 per cent.

This anilic acid is readily decomposed by heating at 200—210°, with elimination of water and formation of *α-dimethylsuccinil*,



a colourless, crystalline substance which, after recrystallisation from light petroleum (boiling point, 80—100°), melts at 87°. The following analyses were made.

I. (From isolauroic acid) 0.1801 gave 10.6 c.c. of nitrogen at 17° and 756 mm. N = 6.80.

II. (From synthetical acid) 0.2420 gave 14.9 c.c. of nitrogen at 15° and 760 mm. N = 7.21.

$C_{12}H_{13}NO_2$ requires N = 6.89 per cent.

* This property has been made use of with great success in preparing *α*-dimethylsuccinic acid from the product of the action of ethylic *α*-bromoisobutyrate on the sodium compound of ethylic malonate. When the product of this reaction is hydrolysed, a mixture of *α*-dimethylsuccinic acid and *α*-methylglutaric acid, $\text{COOH} \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$, is obtained, and these two acids can only be separated with difficulty by crystallisation. If, however, the mixed acids are dissolved in excess of ammonia, calcium chloride added, and the clear solution heated to boiling, the whole of the calcium dimethylsuccinate is precipitated, whereas the calcium salt of methylglutaric acid remains in solution.

II. *γ*-Dimethylacetylbutyric Acid, $\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$.

In oxidising isolauronic acid in the way just described, it was observed that the mother liquors from which the crude dimethylsuccinic acid had separated, and from which the last traces of this acid had been removed by calcium chloride, contained an oily acid which gave a precipitate of bromoform on treatment with bromine and caustic potash. In order to find out what this acid was, the oxidation was repeated under various conditions, but without result until ultimately the following process was devised.

Isolauronic acid (10 grams), in quantities of 1 gram, was oxidised on the water bath by means of potassium dichromate and sulphuric acid in such a way that, on cooling the solution, a small quantity of unchanged isolauronic acid always separated.* The product from the 10 oxidations was left in an ice chest overnight, filtered from the long crystals of isolauronic acid which separated, the green solution evaporated at 50° to a small bulk, and extracted 10 times with pure ether. On evaporating the ether, a dark brown oil was obtained, which, although it was readily soluble in water, contained besides dimethylsuccinic acid and the new ketonic acid, also appreciable quantities of isolauronic acid. The whole was dissolved in a slight excess of ammonia, boiled with calcium chloride to precipitate the calcium dimethylsuccinate, filtered, acidified, and again repeatedly extracted with ether; after drying over calcium chloride, the ether was distilled off, and a light yellow, oily residue was left, which, even after standing for some weeks, did not show any signs of crystallising.

The crude oil was dissolved in water, mixed with a large excess of semicarbazide hydrochloride and the corresponding quantity of sodium acetate, and heated on a water bath at 60° for about 15 minutes, when a brownish semicarbazide rapidly separated, and on standing overnight a further quantity of a much paler coloured, crystalline precipitate was deposited. The whole was collected, washed with water, and boiled with a large quantity of water; about half the semicarbazide dissolved,† and on filtering while hot and allowing the filtrate to stand for some days, a brown, sandy precipitate gradually crystallised out. This was collected, purified by recrystallisation from large quantities of alcohol, and the colourless, crystalline precipitate thus obtained analysed, with the following results.

* The isolauronic acid recovered from these oxidations crystallised from water in beautifully glistening needles which were nearly colourless, whereas this acid prepared as described in this paper, is always obtained in straw-yellow crystals; the yellow colour is therefore obviously due to impurity.

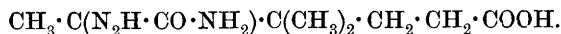
† The portion which remained undissolved was found on examination to consist of the semicarbazide of isolauronic acid.

0·1381 gave 0·2537 CO₂ and 0·0974 H₂O. C = 50·07 ; H = 7·83.

0·1314 „ 22·4 c.c. nitrogen at 17° and 758 mm. N = 19·72.

C₉H₁₇N₃O₃ requires C = 50·24 ; H = 7·9 ; N = 19·53 per cent.

The subsequent examination showed that this was the *semicarbazide* of γ -acetyldimethylbutyric acid,



γ -Acetyldimethylbutyric acid was obtained from the semicarbazide by heating it on the water bath with dilute hydrochloric acid (1 vol. HCl to 2 vols. H₂O) until the crystals had entirely dissolved, and then extracting the liquid repeatedly with pure ether. The ethereal solution, when dried over calcium chloride and evaporated, deposited a nearly colourless oil, which solidified when left over sulphuric acid for some days ; on leaving the crystalline mass in contact with porous plates, the traces of oily impurity were completely absorbed, and colourless crystals were left, which, on analysis, gave the following results.

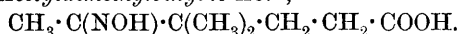
0·1572 gave 0·3487 CO₂ and 0·1236 H₂O. C = 60·49 ; H = 8·73.

0·1415 „ 0·3145 CO₂ „ 0·1126 H₂O. C = 60·62 ; H = 8·83.

CH₃ · CO · C(CH₃)₂ · CH₂ · CH₂ · COOH requires C = 60·76 ; H = 8·86.

γ -Acetyldimethylbutyric acid melts at about 50—51°, and is so readily soluble in organic solvents that it could not be satisfactorily recrystallised. This acid is identical with dimethyl-3-hexanon-2 acid, which Tiemann (*Ber.*, 1895, 28, 2176) prepared by the oxidation of β -dihydroxydihydrocampholenic acid with chromic acid mixture, and the melting point of which he found to be 48—49°.

Oxime of γ -Acetyldimethylbutyric Acid,



—In order to prepare this derivative, the acid (3 grams) was dissolved in dilute potash (4 grams), a strong solution of hydroxylamine hydrochloride (3 grams) added, and the whole allowed to stand overnight ; on acidifying, a viscid mass separated, which, on shaking, rapidly solidified ; this was collected, dried on a porous plate, purified by recrystallisation from hot water, and analysed.

0·1556 gave 0·3196 CO₂ and 0·1242 H₂O. C = 56·01 ; H = 8·87.

0·2432 „ 18 c.c. of nitrogen at 20° and 760 mm. N = 8·46.

C₈H₁₅NO₃ requires C = 55·49 ; H = 8·67 ; N = 8·09 per cent.

This oxime is readily soluble in hot water, sparingly in cold water, and crystallises in long, colourless needles which melt at 97—98°.

Reduction of γ -Acetyldimethylbutyric Acid. Formation of the Lactone of γ -Dimethyl- δ -hydroxycaproic Acid, $\text{CH}_3 \cdot \underset{\text{O}}{\underset{|}{\text{CH}}} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \underset{\text{CO}}{\underset{|}{\text{CH}_2}}$.

The reduction of acetyldimethylbutyric acid was investigated, as it was thought possible that the hydroxy-acid formed might be of value in connection with some synthetical experiments which are being carried out in the camphor series.

About 15 grams of the acid was dissolved in dilute sodium carbonate, and treated at the ordinary temperature with 500 grams of 3 per cent. sodium amalgam; after standing overnight, 200 grams more amalgam was added, and the whole heated on the water bath to complete the reduction. The alkaline solution, separated from the mercury, was acidified, saturated with ammonium sulphate, and extracted 10 times with ether; the ethereal solution was then dried with calcium chloride, evaporated, and the oily residue of hydroxy-acid submitted to fractional distillation. During this distillation, much water is eliminated, the thermometer then rises to 235° , almost the whole passing over between 235° and 245° , and, on again distilling, the lactone is easily obtained pure as a colourless oil possessing a faintly camphor-like odour, and boiling at $239\text{--}241^\circ$.

I. 0.1235 gave 0.3074 CO_2 and 0.1056 H_2O . C = 67.88; H = 9.50.

II. 0.1358 „ 0.3366 CO_2 „ 0.1189 H_2O . C = 67.60; H = 9.72.

$\text{C}_8\text{H}_{14}\text{O}_2$ requires C = 67.60; H = 9.85 per cent.

The lactone of dimethylhydroxycaproic acid is isomeric with, and closely related to, the lactone of γ -ethyl- δ -hydroxycaproic acid, $\text{CH}_3 \cdot \underset{\text{O}}{\underset{|}{\text{CH}}} \cdot \text{CH}(\text{C}_2\text{H}_5) \cdot \text{CH}_2 \cdot \underset{\text{CO}}{\underset{|}{\text{CH}_2}}$, which Fittig and Christ (*Annalen*, 1892, 268, 122) obtained by the reduction of γ -ethyl- γ -acetylbutyric acid, and which boils at $254\text{--}255^\circ$.

It is insoluble in water, and dissolves only very slowly on boiling with sodium carbonate solution. Caustic alkalis, however, readily dissolve it, with formation of the salts of the hydroxy-acid.

Oxidation of Acetyldimethylbutyric Acid. Formation of α -Dimethylglutaric Acid, $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$.

When treated with bromine and caustic potash, acetyldimethylbutyric acid is readily oxidised, with separation of bromoform or tetrabromomethane, and formation of α -dimethylglutaric acid.

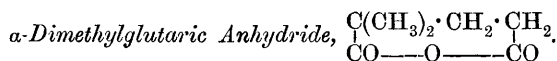
In investigating this decomposition, the pure acetyl acid was dissolved in a large excess of moderately concentrated aqueous potash,

the solution cooled to 0° , and bromine added, until, so far as could be seen, no further deposition of tetrabromomethane took place, and the solution, after standing for some minutes, was found to contain excess of hypobromite. After destroying the excess of hypobromite by passing sulphur dioxide into the solution, it was acidified with hydrochloric acid, saturated with ammonium sulphate, and extracted five times with pure ether; the ethereal solution, dried over calcium chloride, was then evaporated, when an oily residue was left, which, on standing in a vacuum over sulphuric acid, rapidly solidified.* The crystalline mass was dissolved in a little water, and the well cooled solution saturated with hydrogen chloride, when, in a few hours, colourless, needle-shaped crystals separated; these, after draining on a porous plate and drying in a desiccator over potash and sulphuric acid, gave the following results on analysis.

I. 0.1408 gave 0.2701 CO_2 and 0.0956 H_2O . $\text{C} = 52.32$; $\text{H} = 7.53$.

II. 0.1126 „ 0.2168 CO_2 „ 0.0765 H_2O . $\text{C} = 52.51$; $\text{H} = 7.62$.
 $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ requires $\text{C} = 52.50$; $\text{H} = 7.50$ percent.

α -Dimethylglutaric acid melts at about 84° , and is readily soluble in water, alcohol, and most organic solvents, but only very sparingly in cold concentrated hydrochloric acid, separating from its hot solution in this solvent in woolly masses of fine needles. This acid has also been prepared by Tiemann (*Ber.*, 1895, 28, 2176), who showed that, when oxidised by nitric acid, it yields α -dimethylsuccinic acid, $\text{COOH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{COOH}$.

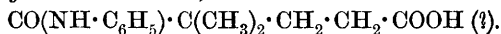


This was prepared by digesting the pure acid with excess of acetic anhydride for half an hour, and allowing the solution to evaporate over potash in a vacuum desiccator, when a colourless, syrupy residue was obtained, which soon solidified on being rubbed with a glass rod. The crystalline mass, after draining on a porous plate, melted at 38° , and consisted of α -dimethylglutaric anhydride, as the following analysis shows.

0.1088 gave 2365 CO_2 and 0.0698 H_2O . $\text{C} = 59.27$; $\text{H} = 7.13$.

$\text{C}_7\text{H}_{10}\text{O}_3$ requires $\text{C} = 59.15$; $\text{H} = 7.04$ per cent.

α -Dimethylglutaranilic Acid,



—When a solution of dimethylglutaric anhydride in pure benzene is

* If the oil does not solidify rapidly, the treatment with potash and bromine must be repeated.

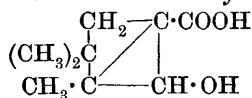
mixed with the calculated quantity of aniline, the corresponding anilic acid rapidly separates in crystals. These were collected, drained on a porous plate, and purified by recrystallisation from dilute alcohol, from which the substance separates in lustrous plates melting at 144° without decomposition.

0.2205 gave 11.5 c.c. of nitrogen at 16.5° and 768 mm. $N = 6.07$.

$C_{13}H_{17}NO_3$ requires $N = 5.96$ per cent.

α -Dimethylglutaranilic acid is readily soluble in alcohol, but only sparingly so in water, benzene, or light petroleum.

Reduction of Isolauronic Acid. Formation of Dihydroiselauronic Acid,



The reduction of iselauronic acid was first studied by Carl Meyer (*Dissertation Munich*, 1895, p. 45), who treated the solution of the acid (1 gram) in sodium carbonate at ordinary temperatures with 40—50 grams of 3 per cent. sodium amalgam, a slow current of carbon dioxide being passed during the operation. After 24 hours, he acidified the product, digested it with dilute sulphuric acid for 1 hour, and then extracted with ether; the ethereal solution, after shaking with sodium carbonate to remove an acid (which is mentioned below) and evaporating off the ether, deposited a crystalline lactone, $C_9H_{14}O_2$, which melted at $47-50^{\circ}$, and gave on hydrolysis a hydroxy-acid melting at 143° ; it had, in fact, as mentioned in the Introduction, the properties of campholactone. On acidifying the soda solution from which the lactone had been extracted with ether, Carl Meyer obtained an oily acid which gradually solidified; this crystallised from light petroleum in nodular masses, and melted at $80-81^{\circ}$, the melting point not being altered by repeated crystallisation from light petroleum.

The analysis of this substance gave numbers which Carl Meyer thought indicated that it was a mixture of two acids, $C_9H_{14}O_3$ and $C_9H_{16}O_3$.

Found, as a mean of four analyses, $C = 62.95$; $H = 8.66$ per cent.

$C_9H_{14}O_3$ requires $C = 63.53$; $H = 8.23$ per cent.

$C_9H_{16}O_3$ „ $C = 62.71$; $H = 9.30$ „

This acid was not further reduced on treatment with sodium amalgam for several hours on the water bath; and, although no experiment seems to have been made with the object of determining whether it

was capable of forming a lactone, its method of isolation would seem to show that this is not the case.

In assigning the relative positions of the CO and COOH groups in isolauronic acid, it is obvious that it is a matter of the greatest importance to determine whether the acid formed by reducing this ketonic acid is capable of forming a lactone, and, for this reason, a very large number of experiments were instituted on the reduction of isolauronic acid under varied conditions. In the first place, Carl Meyer's experiment was repeated several times exactly as he described it, and using very pure isolauronic acid; but no trace of lactone could be obtained, and the hydroxy-acid, after extraction with ether and evaporating the solvent, solidified at once, and crystallised from light petroleum (b. p. 40—45°) in colourless leaflets which soften at 84—85° and melt at 88—89°.

The analysis gave numbers agreeing sharply with the formula $C_9H_{14}O_3 = C_7H_{11}(CH \cdot OH) \cdot COOH$.

0.1478 gave 0.3429 CO₂ and 0.1090 H₂O. C = 63.27; H = 8.19.

0.1332 „ 0.3099 CO₂ „ 0.0985 H₂O. C = 63.45; H = 8.22.

C₉H₁₄O₃ requires C = 63.53; H = 8.23 per cent.

This acid, for which the name *dihydroisolauronic acid* is proposed, was formed in all the experiments on the reduction of isolauronic acid, even when very varying conditions of temperature, concentration of solution, and quantities of reagents were employed, and it was the only product of reduction which the author could isolate. Dihydroisolauronic acid is moderately easily soluble in hot water, and crystallises from it, under certain conditions, in beautiful, colourless, glistening, prismatic needles which melt at 88—89°; it is very readily soluble in most organic solvents, and crystallises fairly well from light petroleum.

The solution of dihydroisolauronic acid in dilute sodium carbonate does not decolorise permanganate, except on long standing, and since it does not react with hydrobromic acid at the ordinary temperature, and its solution in chloroform does not decolorise bromine, it appears to be a saturated acid; this is confirmed by the fact, noticed by Carl Meyer, that the acid is not further reduced by sodium amalgam, even at 100°.

Dihydroisolauronic acid dissolves in concentrated sulphuric acid at 30°, forming a yellow solution, and at 40—50° decomposition sets in, with evolution of sulphur dioxide. If, after heating for a few minutes on the boiling water bath, the dark-coloured solution is poured into water, a yellow precipitate separates, which, on recrystallisation from acetic acid, melts at 164—165° and shows all the properties of paraxylic acid.

Attempts to Convert Dihydroiselauronic Acid into a Lactone.

For reasons stated in the Introduction to this paper, it was most important to determine whether dihydroiselauronic acid was capable of forming a lactone, and many experiments were made to decide this point.

I. In three experiments, the pure acid was digested with sulphuric acid of 10, 15, and 20 per cent. for 1 hour. The products from the first two experiments were extracted with ether, and the ethereal solution, after treatment with sodium carbonate, evaporated, but no trace of a lactone was obtained in either case, and on acidifying the sodium carbonate solution, the hydroxy-acid was recovered unchanged.

In the third experiment, in which 20 per cent. sulphuric acid had been used, the solution, on standing overnight, became filled with beautiful, glistening plates which melted at 87° with slight previous softening, and on examination were found to consist of the unchanged hydroxy-acid.

II. Dihydroiselauronic acid was heated in a sealed tube with water at 220° for 3 hours. On opening the tube, there was no pressure, and the light yellow oil which had separated below the water, on being touched with a crystal of the acid, solidified at once, and the crystals, after spreading on a porous plate, melted at $85-87^{\circ}$.

III. When heated in small quantities in a test-tube, dihydroiselauronic acid distils at a high temperature and condenses on the cooler portion of the tube as an oil which rapidly solidifies; the crystals, after being freed from traces of impurity by spreading on a porous plate, melt at $80-85^{\circ}$ and consist of the unchanged acid, showing that the hydroxy-acid undergoes very little decomposition when distilled under the ordinary pressure. In order to clearly prove that dihydroiselauronic acid does not yield a lactone on heating, about 5 grams of the carefully dried acid was slowly distilled under reduced pressure (65 mm.); no elimination of water was observed, and the thermometer at once rose to 215° , the whole passing over between this temperature and 220° as a colourless oil which, on touching with a crystal of the original acid, immediately and completely solidified. This distilled acid, without further purification, gave the following results on analysis.

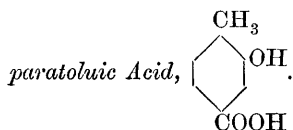
0.1771 gave 0.4152 CO_2 and 0.1341 H_2O . $\text{C} = 63.93$; $\text{H} = 8.42$.

Dihydroiselauronic acid, $\text{C}_9\text{H}_{14}\text{O}_3$, requires $\text{C} = 63.53$; $\text{H} = 8.23$ per cent.

This distilled acid melted at about $78-84^{\circ}$, dissolved completely in dilute sodium carbonate solution, and, as the analysis shows, consisted of unchanged dihydroiselauronic acid.

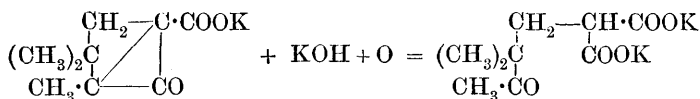
These experiments appear to the author to prove conclusively that *dihydroisolauroic acid is incapable of forming a lactone*.

Fusion of Isolauroic Acid with Potash. Formation of Hydroxy-



The behaviour of isolauroic acid on fusion with potash was investigated, because it was thought probable that in this way a more direct product of hydrolysis and oxidation might be obtained than had been found possible by submitting it to oxidation alone.

It was conceivable, for example, that the reaction might take the following course.



Isolauroic acid (1 gram) was dissolved in strong aqueous potash (10 grams), and the solution, which, on warming, rapidly became dark brown, was gradually heated at 130—140° until the frothing had subsided; the temperature was then raised to 230° for 10 minutes.

On acidifying, a milky solution smelling strongly of isobutyric acid was obtained, and on shaking it, a dark, resinous mass separated; this was extracted five times with ether, the ethereal solution evaporated, and the residue, which on standing overnight partially solidified, boiled with about 200 c.c. of water and filtered. The filtrate, decolorised by boiling with purified animal charcoal, was evaporated to a small bulk on the water bath, and on standing it deposited glistening plates, which were collected, recrystallised twice from water, and analysed, with the following result.

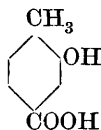
0.1291 gave 0.2978 CO₂ and 0.0642 H₂O. C = 62.91; H = 5.52.

C₈H₈O₃ requires C = 63.15; H = 5.26 per cent.

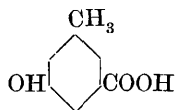
This acid melts at about 203—205° without decomposition, and when cautiously heated sublimes in feathery crystals; it dissolves readily in warm, sparingly in cold water, and crystallises from the hot solution, on slowly cooling, in beautiful, colourless, glistening prisms. When heated with acetic anhydride, it yields an acetyl compound, which crystallises from dilute alcohol in colourless needles and melts at 163—164°, but the amount obtained was too small for analysis.

As the results of the analysis and general properties of the acid clearly showed that it must be an aromatic compound, a search was

made among known hydroxy-acids of this composition, when two acids of similar properties were found, namely,



2-Hydroxyparatoluic acid,
m. p. 206—207°.



5-Hydroxymetatoluic acid,
m. p. 208.

Mr. J. L. Rose, B.Sc., a student of Owens College, kindly prepared for me a specimen of the former of these acids, using the method described by Weinreich (*Ber.*, 1887, 20, 981), which consists in sulphonating paratoluic acid and fusing the sulphonic acid with potash. The acid thus obtained, which melted at 206—207°, was digested with acetic anhydride for 1 hour, and when cold mixed with water and allowed to stand until it had completely solidified; this acetate, when purified by recrystallisation from benzene, separated in beautiful, colourless needles which melted at 162°, and gave the following result on analysis.

Found C = 61.99; H = 5.19.

$\text{CH}_3 \cdot \text{C}_6\text{H}_3(\text{O} \cdot \text{C}_2\text{H}_3\text{O}) \cdot \text{COOH}$ requires C = 61.85; H = 5.16 per cent.

The properties of the acid obtained by fusing isolauronic acid with potash agree, so far as they have been investigated, with those of hydroxyparatoluic acid, but as it is still possible that the acid may be hydroxymetatoluic acid, a specimen of the latter acid is being prepared in order that this point may be decided.