LX.—*Derivatives of Camphoric acid.* Part I.

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THE simple mono-substitution products of camphor, such as α -bromo-, α -nitro-, and α -amido-camphor, are oxidised to camphoric acid, by boiling nitric acid, without much difficulty, whereas the halogen and nitro- di-substitution products cannot be oxidised, as a rule, under ordinary conditions; for these reasons it is usually assumed that the two hydrogen atoms of the $-\text{CH}_2\text{CO}-$ group are successively displaced when camphor is converted into any of the ordinary di-derivatives by direct substitution.

Whether this be invariably true or not, the fact remains that, in consequence of this general behaviour of the best-known substitution products of camphor, all attempts to determine the constitution of the ketone by oxidising it step by step to simpler compounds, have, until quite recently, been necessarily confined to a study of the oxidation products of camphoric acid; derivatives of this acid, produced by the oxidation of substitution products of camphor are not known, and the only compounds which have hitherto been prepared directly from the acid appear to be *w*-bromocamphoric anhydride and the corresponding chloro-derivative (*Aschan, Acta Soc. Scient. fenn.*, **21**, [5], 1—227; compare *Ber.*, 1895, **28**, Ref. 922).

In his investigation of the campholenic acids (*Ber.*, 1895, **28**, 1079, 2168), Tiemann has broken entirely new ground and, since the products of oxidation of these acids are very different from those of camphoric acid, their study has materially increased the store of facts on which the constitutional formula of camphor will be ultimately securely established; unfortunately, however, the formation of the campholenic acids themselves involves reactions which are both novel and obscure, and this uncertainty as to the nature of the initial products diminishes for the time the theoretical value of the results.

Now the discovery of the π -halogen derivatives of camphor (Kipping and Pope, *Trans.*, 1895, **67**, 371) appeared to offer a possibility of obtaining a new series of oxidation products; these halogen compounds are produced by simply heating the sulphonic chlorides or bromides of camphor and its derivatives at a temperature below about 160° ,

(X = H, Cl, or Br; Y = Cl or Br) and, since the compounds thus obtained are not identical with the ordinary halogen derivatives of the same composition, the π -atom cannot be situated in the $-\text{CH}_2\text{CO}-$ group of camphor. Of these π -derivatives, the well-defined $\alpha\pi$ -di-

bromocamphor seemed to be the most suited for further investigation, more particularly because it is formed from bromocamphorsulphonic bromide in practically theoretical quantity, and the sulphonic bromide itself is prepared without very much difficulty.

The first idea was to prepare an unsaturated compound from $\alpha\pi$ -dibromocamphor by eliminating the π -bromine atom as hydrogen bromide, and then to submit this product to oxidation; these experiments, however, were abandoned owing to the fact that the π -halogen atom resists the action of quinoline, alcoholic potash, &c., in much the same way as does the α -atom in ordinary bromocamphor.* It thus became necessary to submit $\alpha\pi$ -dibromocamphor itself to the action of oxidising agents, and it is an account of work in this direction which is now communicated.

The results, unfortunately, are not of such a nature as to ensure the final dismissal of a number of camphoric acid formulæ which have been proposed at different times, and which are still regarded with a certain amount of favour; they may, in fact, be explained more or less satisfactorily with the aid of one of several of these formulæ. Before proceeding to describe these results, for the clear understanding of which the use of some graphic formula is imperative, the following brief statement may, therefore, be made in support of that which is chosen for the purpose.

The conversion of homocamphoric acid into camphor (Bredt, *Annalen*, 1895, 289, 1) having shown that Collie's views of the relation between camphoric acid and camphor cannot be maintained, there remain only three or four formulæ for camphoric acid, which can be considered as at all in accordance with present knowledge, namely those of V. Meyer, Armstrong, Bredt, and Tiemann.

Of these, the first two do not account for the formation of tri-

* $\alpha\pi$ -Dibromocamphor is slowly acted on by a boiling methyl alcoholic solution of sodium methoxide, giving a crystalline compound; this action is now being investigated by Mr. Revis and the author, and the behaviour of α -bromocamphor and of other halogen derivatives of camphor is likewise being studied.

methylsuccinic acid on oxidising camphoric acid, and they are not in other ways so fully in agreement with recent experimental data as are those of Brecht and Tiemann. Finally, since Tiemann's formula may be regarded as a modified form of Brecht's, and, as Brecht himself has pointed out (*loc. cit.*), the necessity for such modification has not been established, Brecht's formula, in the author's opinion, holds the field.

Against this formula no really damaging facts have yet been advanced. Walker (*Trans.*, 1893, **63**, 495) and Noyes (*Ber.*, 1894, **27**, 917; 1895, **28**, 547), from the results of a study of the campholytic acids, have, it is true, come to conclusions which are not reconcilable with Brecht's formula, but inasmuch as these conclusions are chiefly based on the assumption that cycloid unsaturated acids and lactones must necessarily behave in exactly the same way as the open-chain compounds so carefully studied by Fittig,—an assumption which is clearly unsound,—their arguments lose much in importance. This is also true with regard to Aschan's objections which are founded on the formation of lauronic acid from *w*-bromocamphoric acid.

Brecht's formula for camphoric acid is, therefore, adopted in this paper, for the reasons already stated, and because it also accounts in a simple and satisfactory manner, and better than other formulæ, for the existence and properties of the various compounds obtained in the course of this investigation.

$\alpha\pi$ -Dibromocamphor is oxidised by boiling nitric acid giving an acid of the composition $C_{10}H_{15}BrO_4$, which is named π -bromocamphoric acid, and an $\alpha\pi$ -dibromo- α -nitrocamphor of the composition, $C_{10}H_{13}Br_2O_4 \cdot NO_2$.

This behaviour is clearly analogous to that of α -bromocamphor, which, under similar conditions, yields camphoric acid and α -bromonitrocamphor. The results of the investigation of the dibromonitrocompound have recently been recorded by Dr. Lapworth and the author (*Trans.*, 1896, **69**, 304).

π -Bromocamphoric acid, an isomeride of *w*-bromocamphoric acid (*Trans.*, 1896, **59**, 61), is a simple bromo-substitution product of ordinary *d*-camphoric acid, since it yields the latter on reduction with zinc dust and acetic acid; it is dextrorotatory, the introduction of the π -bromine atom into the camphoric acid molecule having produced very little change in the specific rotation; like *w*-bromocam-

phoric acid, it is very easily converted into a well-defined anhydride, $C_{10}H_{13}BrO_3$.

Although the π -bromine atom in $\alpha\pi$ -dibromocamphor is so firmly held, this same bromine atom in π -bromocamphoric acid can be eliminated with the greatest ease; when an aqueous solution of the sodium salt of the acid is boiled, sodium bromide is formed, together with the sodium salt of an acid of the composition $C_{10}H_{14}O_4$.

This acid is isomeric with *w*-camphanic acid,* and is a saturated compound; its method of formation and its properties show, that like *w*-camphanic acid, it contains a lactone ring and a carboxyl group. For these reasons, and also to avoid the necessity of coining a new trivial name, this substance is called *trans*- π -camphanic acid; it is derived from a *trans*- π -hydroxycamphoric acid, just as ordinary *w*-camphanic acid is derived from the as yet unknown *w*-hydroxycamphoric acid, corresponding with *w*-bromocamphoric acid.

trans- π -Camphanic acid crystallises in transparent prisms, and is dextrorotatory; its *amide*, $C_9H_{13}O_2 \cdot \text{CO} \cdot \text{NH}_2$, prepared by treating methylic π -bromocamphorate with ammonia, crystallises in colourless octahedra.

trans- π -Camphanic acid is, in some respects, comparatively unstable, and when it is boiled with excess of an aqueous alkali, it is rapidly converted into a salt of *trans*- π -hydroxycamphoric acid, the lactone ring undergoing hydrolysis.

The *trans*- π -hydroxycamphoric acid, $C_{10}H_{16}O_5$, obtained from this salt is a crystalline dicarboxylic acid, readily soluble in water, and,

* In order to avoid ambiguity in referring to the structurally isomeric camphanic acids now known, that obtained from Wreden's bromocamphoric anhydride is named *w*-camphanic acid (compare *Trans.*, 1896, 59, 61); the letter *w* is also used in other cases to distinguish any substituent which is in the position occupied by the bromine atom in *w*-bromocamphoric anhydride.

like *trans*- π -camphanic acid, it is dextrorotatory; it shows no tendency to pass again into a lactonic acid with loss of the elements of water. This last fact might be interpreted as showing that the π -hydroxyl group cannot be in the γ -position relatively to either of the carboxyl groups; such a conclusion, however, would hardly be warranted, and that it would be false is proved by the facts stated later. The presence of a hydroxyl group in the acid in question is shown by the formation of *π -acetoxycamphoric anhydride*,

this acetyl derivative crystallises in monosymmetric plates, and seems to be dimorphous.

When *trans*- π -hydroxycamphoric acid is distilled under atmospheric pressure, it yields small quantities of a neutral lacto-anhydride, $\text{C}_{20}\text{H}_{26}\text{O}_7$, but the principal product is a crystalline saturated acid of the composition $\text{C}_{10}\text{H}_{14}\text{O}_4$. This acid is, therefore, isomeric with *trans*- π -camphanic acid, and, like the latter, it is a lactone as well as a monocarboxylic acid. Nevertheless, the two isomerides differ in properties in a very striking manner; whereas the lactone ring in *trans*- π -camphanic acid is readily hydrolysed by alkalis, as already stated, and even by hot mineral acids, the π -hydroxy-acid being formed, the isomeride is precipitated unchanged on acidifying its solution in strong potash, even after this solution has been boiled. On fusion with potash, however, this stable isomeride is converted into *trans*- π -hydroxycamphoric acid.

Now unless, during distillation, *trans*- π -hydroxycamphoric acid undergoes some change in *structure* which is exactly reversed on fusing the more stable lactonic acid with potash, an assumption which is highly improbable, it must be concluded that both these lactonic acids are derived from, structurally, one and the same π -hydroxycamphoric acid. There are, therefore, two possibilities: firstly, since the hydroxy-acid contains two carboxyl groups, the isomerism of the two lactones might be structural, the elimination of the elements of water taking place in different ways in the two cases; secondly, the isomerism might be due to a difference in configuration such as is met with in the case of the camphoric acids themselves, and in that of other camphor derivatives.

The first alternative seems highly improbable. On boiling an aqueous solution of sodium π -bromocamphorate, the carboxyl group which, structurally and stereochemically is in the more favourable position, would take part in lactone formation, and the lactonic acid which would thus be formed, either as sole or as principal product, would be the more stable of the two structural isomerides in question;

but *trans*- π -camphanic acid, the substance actually formed under these conditions, is by far the less stable of the two, and therefore this alternative must be dismissed.

Further, since the position of the hydroxy-group in *trans*- π -hydroxycamphoric acid is either structurally or stereochemically not very favourable to lactone formation, whereas it is so in the structurally identical π -hydroxy-acid from which the stable lactonic acid is derived, it follows that the two isomerides in question differ in *con-figuration* only, and are respectively derived from *trans*- and *cis*-modifications of π -hydroxycamphoric acid, as represented in the following formulæ.

In accordance with this view, the unstable lactonic acid has already been named *trans*- π -camphanic acid to distinguish it from the stable isomeride, which will be referred to as *cis*- π -camphanic acid.

Judging from the behaviour of the camphoric acids, which are known to undergo stereoisomeric change very readily (compare Aschan, *loc. cit.*), it is probably the carboxyl and not the $\text{-CH}_2\text{OH}$ group, which changes its position in the conversion of the π -camphanic acids one into the other; in other words, *trans*- π -camphanic acid and *trans*- π -hydroxycamphoric acid are probably stereochemically as well as structurally derived from ordinary *cis*-*d*-camphoric acid, and not from the *trans*-isomeride (isocamphoric acid). Notwithstanding this probability, it seems better to use the prefixes *cis*- and *trans*- in the sense already adopted, as in the case of these π -derivatives they apply to the position of the π -substituent relatively to one of the carboxyl groups. As indicated in the above formulæ, it is probably the carboxyl group nearer to the *w*-hydrogen atom which takes part in the formation of the lactone ring, as will appear from the results to be described later.

cis- π -Camphanic acid can be obtained by various methods besides that already mentioned, as, for example, by distilling the *trans*-isomeride under atmospheric pressure; it is also formed when π -bromocamphoric acid is heated with quinoline or with hydrobromic acid. *cis*- π -Camphanic acid is an unusually interesting substance in many ways; it separates from solvents in a great variety of beautiful and characteristic crystalline habits, and is easily obtained in well-

defined crystals. Unlike the *trans*-isomeride, which is feebly dextro-rotatory, it is strongly lævorotatory in solution; it also shows circular polarisation in the solid state. In some respects, *cis*- π -camphanic acid resembles the isocamphanic acid described by Reyher (*Inaug. Dissert., Leipzig*, 1891), but the two substances are not identical. *Methylic cis*- π -camphanate, $C_9H_{13}O_2 \cdot COOMe$, and *cis*- π -camphanic anhydride are described; *cis*- π -hydroxycamphoric acid, apparently, does not exist under ordinary conditions, but immediately passes into its lactone when set free from its salts.

The *cis*- and *trans*-modifications of π -camphanic acid show an extraordinary difference in behaviour towards oxidising agents generally. The *cis*-acid seems to be unaltered by boiling concentrated nitric acid, and it is only very slowly oxidised by a boiling solution of chromic acid, or by a boiling alkaline solution of potassium permanganate; when treated with the last named agent, it yields a *w*-hydroxy-*cis*- π -camphanic acid, $C_{10}H_{14}O_5$, which is a lactonic monocarboxylic acid derived from a *w*- π -dihydroxycamphoric acid, $C_{10}H_{16}O_6$, the formation of which is doubtless due to the oxidation of a tertiary hydrogen atom to hydroxyl.

w-Hydroxy-*cis*- π -camphanic acid. *w*- π -Dihydroxycamphoric acid.

This *w*-hydroxy- π -camphanic acid doubtless contains the same lactone ring as *cis*- π -camphanic acid, the hydroxyl group occupying the position of the bromine atom in *w*-bromocamphoric acid, as indicated in the formulæ (compare *Proc.*, 1895, 211).

w-Hydroxy-*cis*- π -camphanic acid dissolves freely in water, but is less soluble and crystallises more readily than π -hydroxycamphoric acid; when heated with acetyl chloride, it gives *w*-acetoxy-*cis*- π -camphanic acid, $AcO \cdot C_9H_{12}O_2 \cdot COOH$, a well-defined crystalline substance, and a small quantity of a neutral compound, possibly an anhydride of the acetoxy-acid. The fact that the *w*-hydroxy-acid is not converted into a neutral dilactone, $C_{10}H_{12}O_4$, under these conditions cannot be regarded as throwing any light on the structural position of the hydroxyl relatively to the free carboxyl group, the case of the isomeric π -camphanic acids having shown that lactone formation may be rendered very difficult by unsuitable configuration alone. The great stability of *w*-hydroxy-*cis*- π -camphanic acid frustrated all endeavours to oxidise it.

trans- π -Camphanic acid, unlike the *cis*-acid, is readily oxidised by

nitric acid, and, under suitable conditions, is converted almost quantitatively into a beautiful crystalline compound of the composition $C_{10}H_{14}O_6$; analyses of this product, of its silver salt, and of its anhydride show it to be a tricarboxylic acid, and it is named *trans-camphotricarboxylic acid*.

trans-Camphotricarboxylic acid, $C_{10}H_{14}O_6$, is also produced when *trans*- π -hydroxycamphoric acid, $C_{10}H_{16}O_5$, is oxidised with nitric acid, so that evidently its formation from *trans*- π -camphanic acid is preceded or accompanied by hydrolysis of the lactone ring; in both cases, therefore, the process really consists in the substitution of one atom of oxygen for two atoms of hydrogen.

Considering the origin and nature of the substances concerned, this at first sight appears to be a remarkable reaction; as already indicated in the above formulæ, however, it is easily explained in the following manner. If it be assumed that in the sulphonation of α -bromocamphor (and of camphor also) the sulphonic group displaces an atom of hydrogen from a methyl group, then the π -bromine atom (which comes from the $-SO_2Br$ group) is a constituent of a $-CH_2Br$ group, and π -hydroxycamphoric acid is a *primary alcohol*, as well as a dicarboxylic acid. Hence in the oxidation of this π -hydroxy-acid, the primary alcohol group $-CH_2\cdot OH$ merely undergoes the normal change, and is converted into carboxyl, probably with formation of an aldehyde as an intermediate product.

Unless this view be accepted, it is impossible to explain the formation of *trans*-camphotricarboxylic acid except by assuming that what is apparently a simple process of oxidation is in reality a complex reaction, in the course of which a 6-carbon ring is converted into a 5, or a 5 into a 4, by oxidation and subsequent ring formation, as indicated in the following scheme.

Against such an assumption it may be urged, firstly, that the conversion of *trans*- π -camphanic acid into *trans*-camphotricarboxylic acid takes place almost quantitatively, no other product being formed in quantities sufficient for its detection. Secondly, that the same change is brought about by oxidising agents other than nitric acid, as, for example, by chromic acid and by bromine in presence of water. Thirdly, that there is some evidence of the formation of an aldehyde as an intermediate product. Fourthly, that accepting the formula for camphoric acid which appears to be most in accordance

with facts, the assumed change would involve the conversion of a penta- into a tetra-methylene ring, which in itself is very improbable under the conditions.

It must be concluded, therefore, that π -hydroxycamphoric acid contains the group $-\text{CH}_2\cdot\text{OH}$, and that the π -substituent in all these compounds has displaced hydrogen from a methyl group.

Now *trans*-camphotricarboxylic acid passes into its anhydride when it is heated at about 200° , and it does not lose carbonic anhydride when its aqueous solution is heated at 250° ; it follows, therefore, that the three carboxyl groups in the acid are all united with different carbon atoms, and consequently also the $-\text{CH}_2\cdot\text{OH}$ group in π -hydroxycamphoric acid is not combined with carbon, which already carries one of the carboxyl groups in camphoric acid.

In accordance with this conclusion, the constitution of *trans*-camphotricarboxylic acid may be represented by the formula,

and, as will be evident, the position assigned to the substituted methyl group in all the foregoing formulæ rests on the same basis.

trans-Camphotricarboxylic acid crystallises from water in massive, hexagonal pyramids, and is dextrorotatory in solution, a fact which indicates its relation to *trans*- rather than to *cis*- π -camphanic acid. It is an extraordinarily stable substance, and up to the present it has resisted all the efforts which have been made to oxidise it by successive stages: on prolonged treatment with potassium permanganate, it yields small quantities of oxalic acid.

trans-Camphotricarboxylic anhydride, $\text{C}_{10}\text{H}_{12}\text{O}_6$, forms well-defined crystals, and has the properties of a carboxylic acid as well as those of an anhydride. Since, of the three carboxyl groups in camphotricarboxylic acid, the two which are already contained in camphoric acid very readily enter into anhydride formation, it may be taken for granted that the same two do so in the case of this compound.

The only derivatives of *trans*-camphotricarboxylic acid which have been prepared from it by substitution are two isomeric compounds of the composition $\text{C}_{10}\text{H}_{12}\text{O}_6$. These substances are formed when a mixture of the tricarboxylic acid and amorphous phosphorus is heated with bromine at 100° , and the product then warmed with water. The method of formation shows that they are both derived from a hydroxycamphotricarboxylic acid of the composition $\text{C}_{10}\text{H}_{14}\text{O}_7$, with elimination of one molecule of water.

One of these substances, which may be referred to as the β -lactone, appears to be the primary product; the other, which is henceforth called the γ -lactone, is formed when the β -lactone is boiled with water, or heated with excess of aqueous alkali and the solution acidified. Respecting the formulæ by which these substances may be represented, there is, in the first place, the fact that one of the hydrogen atoms in the molecule of camphoric acid and of π -bromocamphoric acid is known to be displaceable by bromine, giving rise to *w*-bromocamphoric anhydride and πw -dibromocamphoric anhydride (Proc., 1895, 211); further, it is very probable that it is this particular, probably a tertiary hydrogen atom, which is oxidised to hydroxyl in the conversion of *cis*- π -camphanic acid into *w*-hydroxy-*cis*- π -camphanic acid. Moreover, since *trans*-camphotricarboxylic acid still contains this particular *w*-hydrogen atom it may be assumed with some confidence that the two lactones in question are derived from a *w*-hydroxycamphotricarboxylic acid, which may be represented by the formula,

As to the lactones themselves, for obvious reasons it is impossible with the facts at disposal to attempt to put forward constitutional formulæ. One fact bearing on this question may be mentioned, however, namely, that the γ -lactone is not altered when it is boiled with acetyl chloride for some time; since *trans*-camphotricarboxylic acid is readily converted into its anhydride under these conditions, the non-formation of an anhydride from the γ -lactone might be interpreted as showing that the carboxyl group, to which the hydroxyl is in the γ -position (in the above formula) has taken part in the lactone formation. Although this is merely speculation, the two substances have been called β - and γ -lactones respectively on these grounds, simply for want of a better means of distinguishing them by name.

The β -lactone of *w*-hydroxycamphotricarboxylic acid crystallises in six-sided plates which are probably orthorhombic and sphenoidally hemihedral. The γ -lactone crystallises in prisms, and is much more readily soluble in water than the isomeride; like the tricarboxylic acid from which it is prepared, it is extremely stable towards oxidising agents.

Although it was found impossible to oxidise *cis*- π -camphanic acid directly to a tricarboxylic acid in a manner similar to that in which *trans*- π -camphanic acid may be converted into *trans*-camphotricarb-

oxylic acid, an isomeride of the last-named compound is easily obtained by other methods; when, for example, the *trans*-tricarboxylic acid is strongly heated, it is partially transformed into *cis*-camphotricarboxylic anhydride, a change recalling that of *trans*- into *cis*- π -camphanic acid; the *cis*-anhydride is also formed when the *trans*-tricarboxylic acid is heated with concentrated sulphuric acid.

cis-Camphotricarboxylic acid, $C_{10}H_{14}O_6$, is formed when the *trans*-isomeride is fused with potash, and under these conditions the conversion appears to be complete, which is the more noteworthy since under similar conditions *cis*-camphanic acid is converted into *trans*- π -hydroxycamphoric acid.

cis-Camphotricarboxylic acid resembles its isomeride in ordinary properties, and separates from water in magnificent transparent prisms which contain water of crystallisation; when heated it is readily converted into its *anhydride*, $C_{10}H_{12}O_6$, without melting. It is not oxidised by nitric acid, and its behaviour towards alkaline potassium permanganate is analogous to that of its isomeride.

The relationship between the more important compounds which have now been referred to is shown in the table.

As will be evident from what has already been stated, one of the main objects of this work has, so far, been defeated owing to the extraordinary stability of many of the compounds which have been examined. Camphoric acid itself is, no doubt, very difficult to oxidise, but in this respect it is certainly surpassed by some of these π -derivatives, which seem to be as resistant as the saturated compounds derived from hexamethylene; to assume that this behaviour is inconsistent with the view that camphoric acid contains a closed chain of five carbon atoms would, of course, be absurd, since at present there is no evidence to show that pentamethylene derivatives are less stable than those of hexamethylene.

Many of the compounds prepared in the course of this work, like most of the π -derivatives previously described (Kipping and Pope, *Trans.*, 1895, **67**, 371) have been obtained in crystals of exceptional beauty, and their crystallographic properties have been examined by Mr. W. J. Pope, Instructor of Crystallography in this College; some of the results of his investigations are recorded in this paper, to which they add much in interest and importance, and the author desires here to express his indebtedness to his colleague for the work which he so kindly undertook.

The crystallographic and optical properties of two of the compounds, namely, *cis*- π -camphanic acid and *trans*-camphotricarboxylic acid, are of such particular interest as to merit a separate and detailed description, which is given by Mr. Pope in the following paper.

Mr. C. Revis, Assoc. C.G.I., has rendered great assistance, more

particularly in preparing large quantities of π -bromocamphoric acid, a task of no slight difficulty; without this assistance, the progress of the work would have been considerably delayed.

EXPERIMENTAL.

The production of π -bromocamphoric acid, the starting point of this investigation, involves four distinct preliminary operations, which are indicated below.

The principal loss occurs in the preparation and isolation of the ammonium α -bromocamphorsulphonate, the yield of which seems to vary considerably when comparatively slight alterations in the conditions are made; as, for example, when carbon tetrachloride is used instead of chloroform in the process of sulphonating. In each of the other preliminary operations (all of which have been previously described), the yield is at least 85—95 per cent. of the theoretical if the materials are carefully purified.

In preparing π -bromocamphoric acid, $\alpha\pi$ -dibromocamphor (40 grams) is placed in a large flask provided with a reflux condenser, and covered with a mixture of nitric acid of sp. gr. 1.42 (300 grams) and water (90 grams); the flask is then heated on a sand bath, and, as soon as the acid begins to boil, acetic acid is added in sufficient quantity (20—30 c.c.) to cause the whole of the dibromocamphor to pass into solution. Oxidation soon sets in, and oxides of nitrogen, together with bromine, are evolved; a small quantity of a very volatile substance is produced after a short time, and appears as an oil in the condenser. After boiling during 3 to 3½ hours—although the evolution of ruddy fumes has then by no means ceased—the clear solution is allowed to cool slowly, whereupon it soon becomes turbid and deposits a considerable quantity of a yellow oil; shortly afterwards, but while still warm, it becomes clear again, and at this stage it is decanted into a large retort, the heavy oily deposit being kept apart.

The contents of the retort are now distilled until the volume has diminished to about one-quarter, and the residual solution is then poured out and left for some hours. The crystals which are slowly deposited are separated by filtration, and, after having been washed, first with nitric acid and then with water, are dried on porous earthen-

ware; the nitric acid mother liquors are further concentrated by distillation, and then diluted with a little water in order to obtain a second, but smaller, crop of crystals, which, however, is impregnated with oil. After repeating these processes once more, the acid mother liquors contain a considerable quantity of oily matter which is deposited on the addition of a large volume of water, and also those products of oxidation which are readily soluble in water; the latter are present in insignificant quantity, and have not been examined.

The crude product is a colourless, crystalline powder, consisting of π -bromocamphoric acid, mixed with variable quantities of α -nitro- $\alpha\pi$ -dibromocamphor either in a crystalline or pasty form; sometimes, also, it contains a little $\alpha\pi$ -dibromocamphor which has escaped oxidation. As soon as it is thoroughly air dried it is well agitated with a small quantity of chloroform which dissolves the nitrodibromo- and the dibromo-camphor, but in which the acid is practically insoluble; the latter is then separated by filtration and repeatedly washed with chloroform until a portion dissolves in sodium carbonate solution, leaving only a minute residue. The acid is now sufficiently purified if it is to be used for the preparation of *trans*- π -camphanic acid or other derivatives; but it still contains traces of silica and of nitrodibromocamphor.

The oil referred to above, which separates from the hot nitric acid, consists for the most part of nitrodibromocamphor, and this substance is also obtained in large quantities on evaporating the chloroform filtrate and washings from the bromocamphoric acid; it is also the main constituent of the oil which is finally deposited from the last nitric acid mother liquors on adding water to them. This oil, from the first- and last-named sources, contains a little bromo-acid which can be separated with the aid of chloroform as before; the preparation of crystalline nitrodibromocamphor from the oil, and the results of the investigation of this compound have been communicated in a recent paper (Lapworth and Kipping, *Trans.*, 1896, **69**, 304).

The yield of purified bromocamphoric acid under the above conditions is, unfortunately, comparatively small, namely, only about 15 grams from 40 grams of dibromocamphor, the principal product being the nitrodibromo-compound. Numerous attempts were made on a small scale to improve the process by using nitric acid of a different concentration and by varying the time of oxidation, but in vain; this is probably owing to the fact that when weaker acid is used oxidation takes place much more slowly; so that, even if the production of the acid at the expense of the nitro-compound is actually increased, this is counterbalanced by the larger amount of the acid which undergoes decomposition as the result of more prolonged boiling with the dilute mineral acid.

Attempts were also made to prepare π -bromocamphoric acid in quantity from the nitrodibromocamphor which is obtained as a by-product; for this purpose the latter was first converted into α -nitro- α -bromocamphor by treatment with alcoholic potash (Lapworth and Kipping, *loc. cit.*), and then oxidised by boiling it for a short time with nitric acid of sp. gr. 1.5. The acid can be prepared in this way, but the process was so troublesome that it was only used to a limited extent.

For analysis, a sample of the bromo-acid, obtained by the first method, was recrystallised from acetone and dried at 100°.

0.1654 gave 0.2620 CO₂ and 0.0802 H₂O. C = 43.2; H = 5.4.

C₁₀H₁₅BrO₄ requires C = 43.0; H = 5.4 per cent.

π -Bromocamphoric acid separates from acetone in lustrous, elongated, flattened prisms having pointed ends, but crystals suitable for measurement were not obtained. It seems to sinter slightly at about 210°, and melts at 216–217° (when heated quickly from about 200°), effervescing vigorously, but darkening only very slightly; if heated for a short time at 210–220°, and allowed to solidify, it melts below 150° on heating again. It is practically insoluble in cold chloroform, and very little more soluble in the hot liquid, but it dissolves freely in ether, acetone, acetic acid, and alcohol, from all of which it is usually deposited in ill-defined, rosette-shaped or nodular crystals; it crystallises from ethylic benzoate in small needles.

It is comparatively sparingly soluble in boiling water, from which it is deposited on cooling in beautiful, fern-like crystals and in small prisms; if the aqueous solution be boiled for some time and then cooled, it gives a precipitate of silver bromide at once on the addition of a solution of silver nitrate acidified with nitric acid; on prolonged boiling with water the bromo-acid is completely converted into an acid which is readily soluble in water—doubtless the π -hydroxycamphoric acid described later.

π -Bromocamphoric acid is dextrorotatory. A solution of 1.030 grams of the acid in absolute alcohol, diluted to 25 c.c. and measured at 20° in a 2-dm. tube, gave $\alpha_D = +3.36^\circ$; the specific rotation is, therefore, $[\alpha]_D = +40.8^\circ$. The specific rotatory power of *d*-camphoric acid in 10 per cent. alcoholic solution is $[\alpha]_D = +49.7^\circ$ (Aschan, *loc. cit.*), so that the introduction of the bromine atom has had but little effect on the rotatory power.

π -Bromocamphoric acid has all the properties of a strong carboxylic acid; it reddens litmus, and dissolves rapidly in cold dilute sodium carbonate solution from which it is precipitated unchanged if the solution be quickly acidified. Its metallic salts were not prepared because, owing to the readiness with which the acid loses the ele-

ments of hydrogen bromide, it would probably have been impossible to obtain them free from impurity. A freshly prepared cold solution of the acid in a slight excess of dilute ammonia does not give a precipitate at once on the addition of silver nitrate, but it does so on warming gently; on keeping the ammoniacal solution at ordinary temperatures, ammonium bromide is slowly formed, but, even after 24 hours, the solution still contains some unchanged ammonium bromocamphorate. It is interesting to note that although the bromo-acid is changed fairly rapidly by boiling water, it may be heated at 100° with nitric acid of sp. gr. 1.42 for a long time without undergoing any appreciable decomposition; after three hours of such treatment, the solution gives no precipitate with silver nitrate; on cooling, the bromo-acid slowly separates, unchanged, in fern-like crystals.

The action of alkalis on π -bromocamphoric acid is described later; when heated with concentrated sulphuric acid at 110 – 120° the acid is oxidised and charred, hydrogen bromide being evolved; it does not seem to be acted on by an ethereal solution of bromine, even on exposure to direct sunlight.

Methylic π -bromocamphorate, $C_8H_{13}Br(COOMe)_2$, was prepared by passing hydrogen chloride into a solution of the acid in methylic alcohol; on subsequently allowing this solution to evaporate spontaneously, the product was deposited in colourless, lustrous, transparent prisms. It melts at 114 – 115° , and is readily soluble in cold chloroform, ether, and methylic alcohol, but only sparingly in boiling light petroleum, and is, practically, insoluble in cold water. It is readily hydrolysed, and then further changed, by boiling dilute alkalis in alcoholic solution; when treated with cold concentrated aqueous ammonia, it gives the amide of *trans*- π -camphanic acid. It may be distilled in small quantities at a time under atmospheric pressure without suffering much decomposition.

The effervescence which is observed on heating π -bromocamphoric acid at its melting point is due to the escape of water vapour, the acid being converted into its anhydride; for the preparation of the anhydride, however, it is better to treat the acid with acetic chloride, in which it dissolves slowly on heating; after boiling the solution for a short time, the acetic chloride is evaporated, and the solid residue recrystallised from a mixture of chloroform and ether.

0.1408 gave 0.2371 CO_2 and 0.0654 H_2O . C = 45.92; H = 5.16.

$C_{10}H_{13}BrO_3$ requires C = 45.97; H = 4.98 per cent.

π -Bromocamphoric anhydride separates from cold chloroform in

transparent, rhomboidal plates, and from a mixture of ether and chloroform in large, opaque, well-defined prisms; it melts at $155-156^{\circ}$, sublimes readily in long, slender needles, and, when heated in small portions at a time, can be distilled under atmospheric pressure without appreciably decomposing; its vapour has an intensely irritating action on the eyes and nose. It is readily soluble in cold chloroform and benzene, and freely so in hot ethylic acetate and methylic alcohol, but it is comparatively sparingly soluble in boiling light petroleum, from which it separates, on cooling, in moss-like needles. It is insoluble in cold dilute sodium carbonate solution, and is only slowly hydrolysed by boiling water. When strongly heated with resorcinol, it gives a reddish-brown product, which dissolves in aqueous sodium hydroxide, yielding a deep reddish-brown solution; on diluting with water, a distinct, but not very intense, greenish fluorescence is observed.

It has been recently shown (Kipping, Trans., 1896, 69, 61) that *w*-bromocamphoric anhydride may be converted into the corresponding *w*-bromocamphoric acid by heating it at 100° for a short time with concentrated nitric acid, whereas hydrolysis with water or with aqueous alkalis, as is well known, does not give the bromo-acid, but its decomposition product, *w*-camphanic acid. π -Bromocamphoric anhydride, which, doubtless, would also lose the elements of hydrogen bromide if heated with aqueous alkalis, may be transformed into the acid in a similar manner, namely, by dissolving it in hot nitric acid of sp. gr. 1.42 and then cooling the solution; the crystals which are deposited melt at $216-217^{\circ}$, both when heated alone or in admixture with π -bromocamphoric acid. In this case, the conversion into the acid seems to be far more easily accomplished and much more complete than in that of *w*-bromocamphoric anhydride.

Reduction of π -Bromocamphoric acid.

As the chief object of this investigation was to add to our knowledge of the structure of camphor, it was necessary, before proceeding further, to establish beyond question the supposed relation between π -bromocamphoric acid and ordinary *d*-camphoric acid; in other words, to prove that, in spite of the numerous operations through which the camphor had passed in its conversion into π -bromocamphoric acid, the net result had been simply the substitution of bromine for hydrogen, and the oxidation of the $\begin{smallmatrix} -CH_2 \\ | \\ -CO \end{smallmatrix}$ group to $\begin{smallmatrix} -COOH \\ -COOH \end{smallmatrix}$.

The simplest way of doing this was evidently to reduce the brominated acid and compare the reduction product with *d*-camphoric

acid. For this purpose, therefore, the purified π -bromocamphoric acid was dissolved in dilute acetic acid and reduced with zinc dust; after the lapse of two or three hours, the solution was partly evaporated and filtered from a slight crystalline precipitate, consisting of the zinc salt of camphoric acid. On adding excess of dilute hydrochloric acid to the filtrate and allowing it to cool, a crystalline acid was deposited in transparent prisms. This melted at $185\text{--}186^\circ$, and proved to be *d*-camphoric acid, with which it was directly compared; a mixture of *d*-camphoric acid with the acid thus obtained also melted at $185\text{--}186^\circ$. These facts, in ordinary cases, would be sufficient to establish the identity of the two substances; as, however, at the time, Aschan had not published his exhaustive investigation of the camphoric acids (*Acta soc. scient. fenn.*, **21**, No. 5, 1), of which 13 had been described, it seemed advisable to obtain further evidence on this point. For this reason, the acid obtained by the reduction of π -bromocamphoric acid was converted into the anhydride by treatment with acetic chloride and directly compared with *d*-camphoric anhydride;* the two preparations proved to be identical. Finally, the optical properties of the crystals both of the acid and of the anhydride were examined, and the result was to prove conclusively that π -bromocamphoric acid is converted into *d*-camphoric acid on reduction under the above conditions.

Clearly, therefore, any conclusions drawn from the behaviour of the brominated acid may be made use of in considering the constitution of camphoric acid.

The fact that the bromine atom in π -bromocamphoric acid is so readily displaced by hydrogen was hardly to be expected, inasmuch as $\alpha\pi$ -dichlorocamphor in aqueous alcoholic solution is simply converted into π -chlorocamphor on treatment with sodium amalgam at ordinary temperatures (Kipping and Pope, *Trans.*, 1895, **67**, 371). The behaviour of $\alpha\pi$ -dibromocamphor, on reduction, has been recently investigated (Revis and Kipping, *Proc.*, 1896, **163**, 77), and here also the α -halogen atom is eliminated more readily than the π -atom.

The first product of the action of dilute alkalis on π -bromocamphoric acid is the salt of an unstable lactonic acid, which is derived

* It is to be regretted that Aschan (*loc. cit.*) should have applied the designation *l*-camphoric anhydride to the anhydride of *d*-camphoric acid, and *d*-camphoric anhydride to that of the *l*-acid simply because the compounds are levorotatory and dextrorotatory respectively; in these and similar cases it is much better to fall in with E. Fischer's suggestion in spite of the apparent contradiction.

from a π -hydroxycamphoric acid of the composition $C_{10}H_{16}O_5$; the formation of *trans*- π -camphanic acid, however, is not preceded by that of the hydroxy-compound, but is due to simple elimination of sodium bromide from the sodium salt of the bromo-acid,

In preparing this compound, π -bromocamphoric acid is covered with water, the mixture heated on a water bath, and a dilute solution of the theoretical quantity (1 mol.) of sodium carbonate added in small quantities at a time, the operation occupying about an hour; the solution is then cooled, and filtered, if necessary, from traces of silica and nitrotribromocamphor, which are usually present when crude π -bromocamphoric acid has been used (p. 925). The clear solution is afterwards concentrated by evaporation, and, when cold, treated with dilute sulphuric acid as long as a precipitate is produced; this precipitate should be readily and completely soluble in a small quantity of boiling water, otherwise π -bromocamphoric acid is present, owing to incomplete action. After about an hour's time, the colourless product is separated by filtration, washed with water, and recrystallised from dilute alcohol, in order to free it from a little oily impurity.

The yield of purified *trans*- π -camphanic acid is, on the average, about 80 per cent. of the theoretical, the rest being accounted for by the production of small quantities of π -hydroxycamphoric acid and by slight loss on recrystallising. If more than one molecular proportion of sodium carbonate be used for dissolving the bromo-acid, the yield may be materially diminished, a larger proportion of the readily soluble hydroxy-acid being formed; if, on the other hand, rather less than that quantity of alkali carbonate be employed, the yield does not seem to be altered, but some of the *trans*- π -camphanic acid crystallises from the solution on cooling, before adding sulphuric acid.

The aqueous and alcoholic mother liquors from the *trans*-camphanic acid yield, on evaporation and extraction with ether, small quantities of an oil—a mixture of the hydroxy- and lactonic acids—which may be conveniently used for the preparation of *cis*- π -camphanic acid (p. 944); in one or two experiments, the aqueous acid mother liquors, after having been concentrated, deposited traces of the *cis*-acid, but in a far greater number of cases the presence of this substance was not observed.

For analysis, a sample was recrystallised from anhydrous solvents and dried at 100°.

0.1583 gave 0.3504 CO_2 and 0.1010 H_2O . C = 60.37; H = 7.09.

$C_{10}H_{14}O_4$ requires C = 60.60; H = 7.07 per cent.

trans- π -Camphanic acid separates from water and from dilute methylic alcohol in transparent prisms and in fern-like crystals, which contain 1 mol. of water of crystallisation.

1.8890 air-dried substance lost 0.1632 at 100°; $H_2O = 8.59$.

$C_{10}H_{14}O_4 + H_2O$ requires $H_2O = 8.33$ per cent.

When a capillary tube containing these hydrated crystals is placed in sulphuric acid at 140–150°, the substance melts in its water of crystallisation, but immediately solidifies again, and then begins to sinter at about 157°, liquefying completely at about 163°; on re-heating the solidified mass, it melts at temperatures ranging from 150° to 160°, this indefinite melting point being possibly due to slight hydrolysis having occurred. The anhydrous acid melts sharply at 164–165°, and does so also on re-heating; it crystallises from ether and from chloroform in transparent prisms, and from benzene in fern-like masses; it is readily soluble in boiling water, alcohol, and in most of the ordinary organic solvents, with the exception of light petroleum, in which it is insoluble, or nearly so.

trans- π -Camphanic acid is dextrorotatory, like the bromo-acid from which it is derived, but its specific rotation is much lower than that of the latter; an alcoholic solution of 1.307 gram of the acid, diluted to 25 c.c. and examined in a 2-dm. tube at 20°, gave $\alpha_D = +1.03^\circ$, from which $[\alpha]_D = +9.85^\circ$.

Crystals of *trans*- π -camphanic acid deposited from ethylic acetate solution were examined by Mr. Pope; it may be noted that these crystals become opaque at 100°, doubtless owing to the loss of included solvent or water.

"*Trans*- π -camphanic acid crystallises in large, colourless, transparent, and very lustrous monosymmetric prisms (Fig. 1). The pinacoid $a\{100\}$ is the dominant form, and usually gives good results on measurement; the forms $r\{\bar{1}01\}$ and $c\{001\}$ are very variable in size and are often very curved. The dome $p\{110\}$ is small but gives better reflections than do most of the other forms. Two other dome or pyramid forms are usually present, these possibly have the indices $\{011\}$ and $\{\bar{1}11\}$ but the faces are too corroded to allow of accurate measurements.

"The plane of symmetry is the optic axial plane; one optic axis emerges almost perpendicularly through

$a(100)$, and the other can be seen through $c(001)$ to make a small angle with the normal to that face. The double refraction is strong and the optic axial dispersion slight. There is a perfect cleavage parallel to $a\{100\}$.

“Crystalline system. Monosymmetric.

$$a : b : c = 1.366 : 1 : 1.785.$$

$$\beta = 69^\circ 1'.$$

“Forms present:

$$a\{100\}, c\{001\}, r\{\bar{1}01\}, p\{110\}.$$

“The following angular measurements were obtained:—

Angle.	Number of measurements.	Limits.	Mean.	Calculated.
$ac = 100 : 001$	19	$67^\circ 52' - 69^\circ 48'$	$69^\circ 1'$	—
$cr = 001 : \bar{1}01$	11	$65^\circ 59' - 67^\circ 21'$	$66^\circ 49'$	$66^\circ 26'$
$ar = \bar{1}00 : \bar{1}01$	24	$43^\circ 23' - 45^\circ 47'$	$44^\circ 33'$	—
$ap = 100 : 110$	19	$52^\circ 37' - 54^\circ 50'$	$53^\circ 48'$	—
$pp = 110 : \bar{1}10$	7	$70^\circ 59' - 73^\circ 49'$	$72^\circ 19'$	$72^\circ 24'$

The lactonic ring in the acid is very easily hydrolysed; when the substance is boiled for a short time with moderately dilute (1:1) sulphuric acid, it is converted into π -hydroxycamphoric acid (p. 938), and on leaving the solution at ordinary temperatures, the last-named compound is deposited in transparent plates. A similar change occurs when *trans*- π -camphanic acid is heated with fairly concentrated hydrochloric acid for some time, but it may be boiled with water for several hours without being completely hydrolysed. Alkalis act even more rapidly than mineral acids, giving a salt of the π -hydroxy-acid.

Trans- π -camphanic acid is comparatively easily changed in other ways: when heated with concentrated sulphuric acid at about 130° it rapidly chars and sulphur dioxide is evolved, but definite products are not easily isolated from the solution; in one experiment, however, a small quantity of *cis*- π -camphanic acid (p. 943) was obtained, a change in configuration having occurred similar to that observed in the case of *trans*-camphotricarboxylic acid under like conditions. The behaviour of *trans*- π -camphanic acid towards bromine and certain oxidising agents is described later, but it may be stated here that its solution in dilute aqueous sodium carbonate, or in acetic acid, does not destroy the colour of potassium permanganate at ordinary temperatures, and even on boiling the alkaline solution oxidation takes place extremely slowly. On prolonged boiling with a solution of chromic acid and dilute sulphuric acid, it is gradually converted into *trans*-camphotricarboxylic acid, but this change is brought about much more quickly by hot nitric acid.

Before it was known that the lactonic acid underwent hydrolysis with such ease, it seemed desirable to analyse one of its salts in order to confirm the results of the combustion; for this purpose, the barium salt was prepared by boiling the acid with excess of barium hydroxide solution, treating with carbonic anhydride, and then evaporating; the crystalline residue was finally dried in the air on porous earthenware.

0.3724 lost 0.0310 H_2O at 160° and 0.3414 anhydrous salt gave 0.2261 BaSO_4 . $\text{H}_2\text{O} = 8.32$; $\text{Ba} = 38.94$.

$\text{C}_{10}\text{H}_{14}\text{O}_5\text{Ba}$ requires $\text{Ba} = 39.03$ per cent.

This result showed that the salt contained water of crystallisation ($1\frac{3}{4}$ mol. = 8.54 per cent.), and that it was derived from a hydroxydicarboxylic acid of the composition $\text{C}_{10}\text{H}_{16}\text{O}_6$, and not from *trans*- π -camphanic acid. On acidifying a concentrated solution of the barium salt with hydrochloric acid, no precipitate was produced, but on extracting the acid solution with ether and evaporating the extract, there remained a colourless syrup which gradually deposited crystals of π -hydroxycamphoric acid.

That *trans*- π -camphanic acid is a lactonic monocarboxylic acid is shown by its behaviour on titration; at ordinary temperatures it neutralises one molecular proportion of sodium hydroxide, whereas on boiling, double this quantity of alkali is required.

A freshly prepared solution of the acid in a quantity of dilute aqueous ammonia just sufficient for neutralisation, does not give a precipitate on the addition of barium chloride, calcium chloride, magnesium sulphate or lead acetate, but with ferric chloride it yields a light-buff, apparently amorphous precipitate which does not dissolve on boiling. The *silver* salt is precipitated from concentrated solutions in an amorphous state; it dissolves on boiling, but without darkening, and is deposited again on cooling. The *ammonium* salt is very soluble in cold water and in methylic alcohol, from both of which it crystallises in plates or prisms; from a solution of this salt, *trans*- π -camphanic acid is precipitated on acidifying with a mineral acid, so that the salts just mentioned are derived from the lactonic monocarboxylic acid, and not from π -hydroxycamphoric acid.

When a solution of *trans*- π -camphanic acid in acetic anhydride is boiled for some hours, and the excess of anhydride then distilled off, there remains a colourless liquid from which crystals are slowly deposited on keeping it over potash and sulphuric acid. These crystals, purified by washing with benzene, are short, transparent

prisms and have not a definite melting point; when heated fairly quickly from about 200° , they begin to sinter at $205-210^{\circ}$ and melt at about 230° , whereas when the capillary tube is plunged into the bath already heated to 230° , the crystals do not liquefy until the temperature rises to about 240° . This behaviour is not due to the presence of impurity, and is, therefore probably the result of decomposition, although there is no appreciable charring; on reheating, the substance begins to melt at temperatures below 140° .

An analysis gave results which show that the compound is derived from two molecules of the lactonic acid.

0.1432 gave 0.3322 CO_2 and 0.0931 H_2O . $\text{C} = 63.27$; $\text{H} = 7.22$.

$\text{C}_{20}\text{H}_{26}\text{O}_7 = 2\text{C}_{10}\text{H}_{14}\text{O}_4 - \text{H}_2\text{O}$ requires $\text{C} = 63.49$; $\text{H} = 6.88$ per cent.

trans- π -Camphanic anhydride is practically insoluble in ether and is only very sparingly soluble in boiling benzene and in chloroform, separating from the last-named solvent in microscopic plates; it dissolves slowly, but in considerable quantities in boiling acetic acid, by which, however, it is converted into *trans*- π -camphanic acid; it is practically insoluble in cold water, but, on boiling, the solution soon acquires an acid reaction owing to hydrolysis having occurred.

Distillation of trans- π -Camphanic acid.

When *trans*- π -camphanic acid is heated in quantities of 2 or 3 grams at a time under atmospheric pressure it distils as a yellowish oil, leaving only a small quantity of carbonaceous residue; traces of water vapour pass over together with the oil, but qualitative tests give no indication of the evolution of carbonic anhydride.

The distillate solidifies immediately to a hard, crystalline mass which contains a little oily matter, and which in parts has a brilliant green hue; this distillate is a mixture of two substances, the principal constituent being the *cis*- π -camphanic acid described later; the other compound, which is formed in small quantities only, is probably a lacto-anhydride of the composition, $\text{C}_{20}\text{H}_{26}\text{O}_7$ (p. 942).

Bromination of trans- π -Camphanic acid.

In the course of some preliminary experiments on the bromination of *trans*- π -camphanic acid, a small quantity of the purified, but not specially dried, acid was dissolved in chloroform and mixed with a little bromine; as no visible action occurred the solution was left for some time, and then allowed to evaporate spontaneously. The thick, yellow, oily residue was gently warmed with water to expel chloroform and, after cooling, gradually treated with excess of dilute sodium carbonate solution, in which part of it dissolved with effervescence, leaving a crystalline powder. The latter was insoluble in

cold sodium carbonate solution, and in cold water, but soluble in alcohol, from which it crystallised in long needles melting at about 230° ; it did not contain bromine, and it was rapidly dissolved by hot potassium hydroxide solution, the subsequent addition of a mineral acid causing the separation of a heavy, colourless oil. The original sodium carbonate extract of the crude bromination product gave, on acidifying, a crystalline precipitate of a compound which melted at about 130° after recrystallisation from alcohol.

On attempting to prepare these two substances again in larger quantities, only oily or resinous acids were obtained as, unfortunately, the conditions under which the first experiment had been made, had not been noted with sufficient care.

In view of the now well-known fact that the course of such actions is often completely altered by a slight change in the conditions *trans*- π -camphanic acid was treated with bromine in a great many different ways in order, if possible, to again obtain the products just mentioned. Some experiments were made in the dark, some in diffused light or in direct sunlight; in some cases ether, in others chloroform was used as a solvent; in some cases all the materials were carefully dried, in others small quantities of water were purposely added. The results of these experiments may be summarised as follows:—

When the acid was mixed with bromine (1 mol.) in chloroform solution, in the dark and in absence of water, no visible action took place for some days, and then a brown, jelly-like mass began to separate; after several weeks the colour of the bromine had gone, the jelly had increased in bulk, and traces of hydrogen bromide were evolved on opening the vessel. The gelatinous product gave off hydrogen bromide at 100° , and became friable, but it was hygroscopic and could not be obtained in crystals; when treated with water, it gave an oil which was practically insoluble in water, and which did not crystallise.

In presence of water, and in direct sunlight, the action was much more rapid and an oily product was obtained, but in no case was the formation of the above-mentioned neutral crystalline substance observed, except, perhaps, in minute quantities; when other solvents were used or the acid alone, and the proportion of bromine was varied, the results were similar.

Two experiments were made at higher temperatures; in one case *trans*- π -camphanic acid was heated with water and bromine (2 mols.) at about 150° for some hours; on opening the tube, hydrogen bromide escaped, but bromine was still present. On evaporation, the contents of the tube yielded a small quantity of a crystalline acid, readily soluble in cold water, and identical with the camphotricarboxylic acid (p. 951) obtained on oxidising *trans*- π -camphanic acid with nitric

acid; under these conditions, therefore, the bromine, in presence of water, had simply acted as an oxidising agent. In another experiment, a concentrated solution of *trans*- π -camphanic acid in a little glacial acetic acid was heated with bromine (2 mols.) at about 180° for six hours; all the bromine had entered into combination, and part of the acid had become converted into a carbonaceous mass. On adding water and evaporating the filtered solution, the pungent odour of bromacetic acid was observed, and the solution, on cooling, deposited crystals; these were found to consist of *cis*- π -camphanic acid, the *trans*-acid having undergone stereoisomeric change, doubtless owing to the action of the hydrobromic acid; traces of an oily product were also present, but in quantities too small to investigate.

Finally, attempts were made to brominate *trans*- π -camphanic acid by treating it with bromine and amorphous phosphorus, a method which, in the case of several acids derived from camphor, gives excellent results. In one experiment, carried out under the usual conditions, a large excess of bromine was used, and the product consisted of a greenish-black oil containing a large quantity of a pitch-like substance. In a second case, where a much smaller quantity of the halogen was added, the product was pale yellow, and insoluble in cold sodium carbonate solution; as, however, it could not be purified, it was not further examined.

Finely divided methylic π -bromocamphorate dissolves readily in concentrated aqueous ammonia at ordinary temperatures, and if the solution be kept for some time in a closed vessel, large, colourless plates are deposited; on allowing the mother liquors to evaporate spontaneously, more of the same compound separates from the solution in well-defined crystals, and, finally, ammonium bromide is obtained as a residue.

The amide, prepared in this way from purified methylic bromocamphorate, was washed with water, dried over sulphuric acid, and analysed.

0.1448 gave 0.3266 CO₂ and 0.0993 H₂O. C = 61.51; H = 7.62.

C₁₀H₁₅NO₃ requires C = 60.91; H = 7.61 per cent.

This analysis, and the presence of ammonium bromide in the mother liquors from the amide, show that the latter is derived from *trans*- π -camphanic acid. It melts at 107.5–108.5°, and is very readily soluble in cold chloroform or benzene, from which it separates in transparent, massive plates or prisms; it is fairly soluble in ether,

much less so in boiling light petroleum, and insoluble, or nearly so, in cold water, but readily soluble on heating to boiling. When heated with moderately dilute ammonia for a short time, it is converted into a substance which is freely soluble in cold water, possibly the amide of π -hydroxycamphoric acid. It distills readily under atmospheric pressure without carbonising to any great extent; the distillate, after recrystallisation, melts at $107-108^\circ$, so that, apparently, the amide does not undergo stereoisomeric change so readily as the corresponding acid.

The well-defined crystals of *trans*- π -camphanamide, which separated from the ammoniacal solution of the crude product (see above), were examined by Mr. Pope, whose report is now given.

"*trans*- π -Camphanamide crystallises in small, transparent, colourless octahedra of glassy lustre, belonging to the orthorhombic system (Fig. 2). The pinacoid $c\{001\}$ is small, and usually elongated in the direction of the b -axis; the pinacoid $a\{100\}$ is not often observed, and when present is very small and poorly developed. The two dome forms $q\{011\}$ and $r\{101\}$ give fairly good results on measurement, and constitute the dominant forms; the dome $r'\{201\}$ is very rarely observed, and its faces are very small and badly defined. The crystals possess one good cleavage, but, owing to their small size, the direction of cleavage could not be ascertained with certainty.

"The extinction in the face $c(001)$ is parallel to the traces of the other two pinacoids, and the acute bisectrix emerges perpendicularly to the face; the optic axial angle is fairly large and greater for blue than for red. The double refraction is weak and negative in sign, and the optic axial dispersion is slight and of the normal orthorhombic character.

"No opinion can be formed as to whether the crystals are hemihedral or not because no pyramid forms, but only pinacoids and domes, are present.

"Crystalline system. Orthorhombic.

$$a : b : c = 1.8287 : 1 : 1.4660.$$

"Forms present:

$$a\{100\}, c\{001\}, q\{011\}, r\{101\}, r'\{201\}.$$

FIG. 2.

"The following angular measurements were obtained :

Angle.	Number of measurements.	Limits.		Mean.	Calculated.
$cq = 001 : 011$	14	55°	15'—56° 9'	55° 42'	—
$qq = 011 : 01\bar{1}$	9	68	16—69 1	68 38	68° 36'
$qq = 011 : 0\bar{1}1$	4	111	3—111 39	111 19	111 24
$cr = 001 : 101$	17	38	21—39 4	38 43	—
$ar = 100 : 101$	15	50	43—51 57	51 16	51 17
$rr = 101 : 1\bar{0}1$	8	76	58—77 46	77 23	77 26
$rr = 101 : 10\bar{1}$	3	102	9—102 51	102 38	102 34
$ar' = 100 : 201$	4	31	18—32 27	31 55	31 57
$rr' = 101 : 201$	1	—	—	18 58	19 20

"On melting the amide and subsequently allowing the liquid to cool under a cover slip on a microscope slide, it solidifies readily, crystallising from centres in long, straight-sided flakes."

When either π -bromocamphoric acid or *trans*- π -camphanic acid is heated with excess of alkali in aqueous or alcoholic solution, and apparently, also, when either of these compounds is boiled with water for a long time it is converted into π -hydroxycamphoric acid. The latter is most conveniently prepared in large quantities by heating a solution of the bromo-acid (4 parts) in concentrated potassium hydroxide (5 parts) on the water bath until a portion no longer gives a precipitate of *trans*- π -camphanic acid on acidifying; it may be noted, however, that when the solution is highly concentrated, sulphuric acid sometimes produces a crystalline precipitate—probably a potassium hydrogen salt—which dissolves again on adding excess of the mineral acid. When hydrolysis is complete, the solution is cooled, mixed with excess of dilute sulphuric acid, and repeatedly extracted with ether; the combined ethereal extracts are then dried with anhydrous sodium sulphate, filtered, and evaporated.

The residue is a pale yellow oil weighing rather less than the bromo-acid originally taken; if placed over sulphuric acid, it becomes very viscous, but does not crystallise at all readily unless a crystal be added; if previously mixed with a little water, however, it usually solidifies to a mass of colourless crystals in the course of a few hours.

The first analysis was made with a sample of the crude oil which had been simply heated for a short time at 100° in order to drive off the ether; the second analysis refers to a sample of the crystalline acid, which had been washed with chloroform and ether and dried over sulphuric acid.

0.1359 gave 0.2700 CO_2 and 0.0903 H_2O . C = 54.2; H = 7.4.

0.1744 „ 0.3525 „ 0.1166 „ C = 55.1; H = 7.4.

$\text{C}_{10}\text{H}_{16}\text{O}_6$ requires C = 55.5; H = 7.4 per cent.

In preparing π -hydroxycamphoric acid in small quantities, it is more convenient to employ *trans*- π -camphanic acid; if this compound be boiled for a short time with moderately concentrated sulphuric acid, the solution, on keeping, deposits crystals of the hydroxy-acid.

π -Hydroxycamphoric acid separates from a mixture of chloroform and ether in transparent, rhomboïdal, almost rectangular plates, and in massive crystals of irregular appearance; it does not crystallise well from water, as it is so very readily soluble in this liquid, but it separates from hydrochloric acid and from diluted sulphuric acid, in which it is much less soluble, in groups of plates; it may also be recrystallised from a mixture of ether and ethylic acetate. It is very readily soluble in most of the ordinary organic solvents with the exception of chloroform and light petroleum. It melts at 130–131°, but traces of moisture depress its melting point very considerably.

The specific rotation was determined in alcoholic solution; 0.764 gram of the acid, dissolved in 12 c.c. of alcohol and examined at 20° in a 2-dm. tube, gave $\alpha_D = +3.57^\circ$; the specific rotation is, therefore, $[\alpha]_D = +28^\circ$ approximately.

The *barium* salt, prepared in the usual manner with the aid of barium hydroxide, is extremely soluble in water, and is deposited in crystalline crusts on evaporating its solution over sulphuric acid. A sample, which had been dried in the air on porous earthenware, was analysed.

0.4466 lost 0.0372 H_2O at 160°, and 0.4094 anhydrous salt gave 0.2712 BaSO_4 . $\text{H}_2\text{O} = 8.33$; Ba = 38.94.

$\text{C}_{10}\text{H}_{14}\text{O}_6\text{Ba}$ requires Ba = 39.03 per cent.

This salt was identical, as far as could be ascertained, with that prepared from *trans*- π -camphanic acid in the same way, and, like the latter, it seems to contain $1\frac{3}{4}$ mol. H_2O (theory, $\text{H}_2\text{O} = 8.54$ per cent.).

In a neutral solution of barium hydroxycamphorate, silver nitrate produces a colourless, copper acetate a greenish-blue, and ferric chloride a light brown, precipitate; all three salts seem to be amorphous. Mercuric and calcium chlorides do not cause any precipitation.

π -Hydroxycamphoric acid does not show any tendency to pass into a lactonic acid; under conditions which usually bring about lactone formation, it apparently undergoes no change, as, for example, when boiled with concentrated hydrochloric acid; this behaviour was, of course, to be expected, since *trans*- π -camphanic acid is converted into

the hydroxy-acid under these and similar circumstances. In other respects, also, π -hydroxycamphoric acid is a relatively stable substance; attempts to brominate it were unsuccessful.

The presence of a hydroxyl group in the acid just described is shown by its behaviour towards acetyl chloride, by which it is converted into an acetyl derivative; at the same time, however, the acid is converted into its anhydride. After boiling a solution of the hydroxy-compound in acetyl chloride for some hours, and then evaporating, there remains a thick syrup, which slowly crystallises. This product is easily purified by spreading it on porous earthenware, washing with a little cold water, and then recrystallising the dry substance from ether, or from a mixture of chloroform and light petroleum.

An analysis gave results bearing out the above statements.

0.1466 gave 0.3220 CO_2 and 0.0916 H_2O . C = 59.9; H = 6.9.

$\text{C}_{12}\text{H}_{16}\text{O}_5$ requires C = 60.0; H = 6.7 per cent.

The nature of this compound was also established by titration with boiling sodium hydroxide, under which conditions it was found to be resolved into acetic acid and π -hydroxycamphoric acid.

π -Acetoxycamphoric anhydride separates from ether in massive, transparent crystals, which melt sharply and completely at $86-87^\circ$; when the fused substance is caused to solidify in the warm bath by rubbing the capillary tube, it melts on heating again at $86-87^\circ$; if, however, it be made to crystallise, by dipping the capillary tube into cold water, it does not melt completely until the temperature rises to $89-90^\circ$. This behaviour shows that the substance is dimorphous, and the two forms can be obtained at will in the above manner; crystals melting at $89-90^\circ$ were also obtained from solution in some cases.

Well-defined crystals, deposited from dilute methylic alcohol, melt at $84-85^\circ$, but it is probable that their melting point is low, owing to slight hydrolysis having occurred.

π -Acetoxycamphoric anhydride is readily soluble in chloroform, benzene, and hot ether, but only sparingly in boiling light petroleum, and insoluble, or nearly so, in cold water; when crystals are placed in a solution of blue litmus, the colour does not change on keeping for some time at atmospheric temperatures, but, on boiling, the solution soon acquires an acid reaction.

The following is Mr. Pope's account of the crystals deposited from ethereal solution.

"The crystals consist of small, transparent, colourless, monosymmetric plates of a six-sided outline (Fig. 3). The dominant form is the basal pinacoid $c\{001\}$; this form, though large, is poorly developed, and gives multiple reflections. The pinacoid $a\{100\}$ is small, and only gives moderately good results on measurement; the form $p\{110\}$ is well developed, and gives good reflections. Since no form cutting the c - and another axis is ever observed, the axial ratio $c : b$ could not be determined.

"There is a perfect cleavage parallel to the face $a(100)$. The optic axial plane is perpendicular to the plane of symmetry, and, looking through the form $c\{001\}$, the acute optic axial angle may be seen lying in the real obtuse angle ac at the edge of the microscope field; the double refraction is negative in sign, and the optic axial dispersion is slight.

"The substance readily crystallises after melting on a microscope slide, solidifying in long, doubly-refracting flakes, radiating from centres. As the solid mass cools, the flakes are seen to crack perpendicularly to their directions of growth; one optic axis is usually to be found emerging through these flakes.

"Crystalline system. Monosymmetric.

$$a : b : c = 1.0825 : 1 : ?$$

$$\beta = 84^\circ 6'.$$

"Forms present:

$$a\{100\}, c\{001\}, p\{110\}.$$

"The following angular measurements were obtained:

Angle.	Number of measurements.	Limits.	Mean.	Calculated.
$ac = 100 : 001$	16	$83^\circ 10' - 84^\circ 59'$	$84^\circ 6'$	—
$ap = 100 : 110$	24	$46 \quad 8 - 48 \quad 1$	$47 \quad 7$	—
$pp = 110 : 110$	8	$84 \quad 36 - 86 \quad 4$	$85 \quad 23$	$85^\circ 46'$
$cp = 001 : 110$	12	$84 \quad 17 - 86 \quad 49$	$85 \quad 54$	$85 \quad 59''$

Distillation of π -Hydroxycamphoric acid.

When π -hydroxycamphoric acid is heated for some time at a temperature of about 150° , it becomes more sparingly soluble in water, and from the oily product a crystalline substance, melting at about 150° , can be isolated; this is probably the anhydride of the hydroxy-acid, but it was not investigated. On distillation under atmospheric pressure, the hydroxy-acid loses the elements of water and yields an oily distillate, which solidifies immediately on cooling,

no appreciable amount of carbonic anhydride being evolved during the operation, and but little carbonisation taking place.

The crystalline distillate, which is almost invariably coloured bright green in patches, is washed with a little cold dilute methylic alcohol to free it from traces of oil, allowed to dry, and then extracted repeatedly with cold chloroform, which dissolves a small quantity of a crystalline substance, leaving an almost colourless, granular powder. The portion insoluble in chloroform consists of the *cis*-camphanic acid described below, whereas the soluble portion is a neutral lacto-anhydride, which is evidently formed by condensation. These two products are identical with those obtained by the distillation of *trans*- π -camphanic acid (p. 934).

Lacto-anhydride of π -Camphanic acid.

This is deposited in crystals on evaporating the chloroform extract of the crude distillation product of π -hydroxycamphoric acid, or of *trans*- π -camphanic acid; it is easily obtained in a purified condition by recrystallising it first from boiling alcohol and then from a mixture of alcohol and chloroform. Analysis of a sample which had been dried at 100° gave the following results.

0.1559 gave 0.3597 CO₂ and 0.0967 H₂O. C = 62.92; H = 6.89.
 0.1439 „ 0.3322 „ 0.0903 „ C = 62.96; H = 6.97.
 C₂₀H₂₆O₇ = 2C₁₀H₁₆O₅ - 3H₂O requires C = 63.49; H = 6.88 p. c.

It crystallises from chloroform and other solvents in very slender, colourless needles, melting at 205—206°; it is very readily soluble in cold chloroform and in hot acetone, and moderately easily in boiling ethylic acetate and ethylic alcohol, but insoluble, or nearly so, in ether. It does not dissolve to any appreciable extent in boiling water, and it is insoluble in cold dilute sodium carbonate solution, although it dissolves on boiling. When heated with alcoholic potash for a short time, it yields the potassium salt of an acid, and, on acidifying the alkaline solution, after previously expelling the alcohol, this acid is precipitated as an oil. The acid did not crystallise, and, as it did not appear to be of much interest, it was not exhaustively examined; it seemed to be a very stable compound, as it appeared to be unchanged by boiling nitric acid, and its solution in sodium carbonate did not destroy the colour of potassium permanganate, except on prolonged boiling.

As the neutral substance just described is formed in small quantities, not only from the hydroxy-acid, but also by the distillation of *trans*- π -camphanic acid, and, as it is not identical either with the anhydride of the latter, or with the anhydride of *cis*- π -camphanic acid (p. 946),

it is probably a lacto-anhydride of the constitution indicated by the

The properties of the compound seem to agree with this view, and the fact that it decomposes to a very considerable extent on distillation is an indication of high molecular weight.

The principal object in view in preparing π -bromocamphoric acid was to convert it into an unsaturated acid by taking away the elements of hydrogen bromide, and the action of alkalis having led to the formation of *trans*- π -camphanic or π -hydroxycamphoric acid, it seemed possible that the desired end might be attained with the aid of quinoline. The experiments which were made for this purpose did not lead to the hoped-for result, but to the discovery of a *cis*- π -camphanic acid.

The action of quinoline on π -bromocamphoric acid was found to vary according to the temperature and duration of heating. When, for example, a solution of the acid in about twice its weight of dehydrated quinoline was boiled during about 40 minutes, and then allowed to cool, it set to a dark red, pasty mass, and, on adding alcohol and filtering, a red, micro-crystalline powder was obtained. This was insoluble, or nearly so, in most ordinary organic solvents, but it dissolved freely in acetic acid and in mineral acids, giving dark, wine-red solutions, from which it was precipitated on the addition of water; as it appeared to be some complex condensation product, it was not further examined.

When π -bromocamphoric acid was dissolved in about four times its weight of quinoline, dehydrated over potash, and the solution heated at about 170° , the action took a different course; when the operation was brought to an end after heating during about 15 minutes only, most of the bromo-acid seemed to be recovered unchanged, but after heating during about two hours this was not so. The thick, reddish-brown liquid, thus obtained, was dissolved in a little alcohol and the solution submitted to distillation in a current of steam in order to expel the quinoline; the red aqueous solution comprising the residue was then filtered from small quantities of dark brown, tarry matter, the latter extracted with boiling water, and the combined aqueous filtrate and extracts evaporated. During this process, crystals of *cis*- π -camphanic acid sometimes separated in long needles as the solution became concentrated, and, on further evaporation almost to dryness, a reddish, crystalline substance, doubtless the quinoline salt,

was deposited; excess of sodium carbonate was then added, the solution boiled for some time to expel the liberated quinoline, filtered from tarry matter, and, after cooling, acidified with sulphuric acid. The crude *cis*- π -camphanic acid, which was precipitated as an almost colourless powder, was then separated and purified by recrystallisation from alcohol.

A sample dried at 120° gave the following results on analysis.

0.1485 gave 0.3303 CO₂ and 0.1051 H₂O. C = 60.66; H = 7.86.

0.1668 „ 0.3698 „ 0.1072 „ C = 60.46; H = 7.14.

C₁₀H₁₄O₄ requires C = 60.60; H = 7.07 per cent.

The yield of this crystalline product was very poor, and, even when the conditions of the experiment were altered in various ways, the bromo-acid was principally converted into oily compounds; on extracting the acid filtrate from the *cis*- π -camphanic acid with ether, a thick, yellow oil was obtained in considerable quantities, but it was not carefully examined, as it probably consisted of π -hydroxycamphoric acid, which was more easily prepared in other ways.

The production of *cis*- π -camphanic acid was fortunately rendered a much simpler process by the discovery that it was formed during the distillation of *trans*- π -camphanic acid and of π -hydroxycamphoric acid; in both cases, as mentioned above, two compounds are formed, namely, *cis*- π -camphanic acid and the neutral lacto-anhydride already described; their separation, moreover, is very easily accomplished, owing to the insolubility of the former in cold chloroform.

The yellowish, granular powder which remains on treating the solid distillation product with chloroform (p. 942) consists almost entirely of *cis*- π -camphanic acid, which can be further purified by recrystallisation from alcohol; the portions finally deposited from the alcoholic mother liquors are coloured by some impurity which is difficult to remove by crystallisation, but which may be easily got rid of by boiling with concentrated nitric acid.

cis- π -Camphanic acid melts at about 226°, but begins to sublime at temperatures considerably below its melting point, being deposited on the cooler parts of the tube in long, transparent needles. It crystallises very readily, and in a great diversity of habits, many of which are very beautiful, as well as characteristic. From water, in which it is moderately soluble at 100°, it is deposited in beautiful, fern-like growths, and also in highly characteristic forms consisting of the three diagonals of a regular hexagon. It is comparatively readily soluble in boiling alcohol, but only very sparingly in the cold, and crystallises from this solvent either in forms similar to those obtained from the aqueous solution, or in beautiful, transparent plates having the outline of a regular hexagon; these crystals are

also sometimes obtained from aqueous solution, the rudimentary growths already referred to becoming filled in. When precipitated from its solution in sodium carbonate by the addition of a mineral acid, it is frequently obtained in the form of highly lustrous, truncated, hexagonal pyramids, whereas, when it crystallises slowly from such solutions, it often forms long, transparent prisms. It is readily soluble in boiling acetic acid, very sparingly in benzene, and practically insoluble in cold chloroform.

It will be seen from this account that *cis*- π -camphanic acid is very different from the isomeric *trans*-compound in ordinary physical properties, having a much higher melting point, and being far less readily soluble; it also differs from the *trans*-acid in being lævorotatory. A solution of 1.055 gram of *cis*- π -camphanic acid in ethylic alcohol, diluted to 25 c.c., and examined at 40° in a 2-dm. tube, gave $\alpha_D = -4.03^\circ$, from which $[\alpha]_D = -47.7^\circ$. Owing to the slight solubility of the acid in cold alcohol, the observations had to be made at a higher temperature than in the case of the isomeride.

The crystallographical and optical properties of this acid are described by Mr. Pope in the following paper.

cis- π -Camphanic acid has a comparatively feeble acidic character, and some of its salts readily undergo hydrolytic dissociation. As mentioned above, the acid is deposited from aqueous solutions of its quinoline salt which have been submitted to distillation in steam; when, also, the acid is dissolved in excess of ammonia and the solution allowed to evaporate at ordinary temperatures over sulphuric acid, or even in the air, a considerable quantity of the acid is deposited.

In spite of these facts, fairly sharp results were obtained on titrating with soda, using litmus as indicator; at ordinary temperatures, the substance behaves like a monocarboxylic acid, but when boiled with excess of sodium hydroxide it neutralises two molecular proportions of the alkali.

These results show that *cis*- π -camphanic acid is a lactonic monocarboxylic acid, which is decomposed by sodium hydroxide, giving a salt of *cis*- π -hydroxycamphoric acid; this hydroxy-compound, however, unlike the corresponding *trans*-acid, is immediately re-converted into the lactonic acid when liberated from its salts.

In order to confirm this conclusion by an analysis of the barium salt, the acid was dissolved in aqueous barium hydroxide, the boiling solution saturated with carbonic anhydride, and filtered; on evaporating the filtrate, it was found that the barium salt was unstable, the solution slowly becoming turbid, and depositing barium carbonate; on filtering again and concentrating further, a precipitate of barium carbonate was again formed, and, finally, a gum-like residue of the organic

barium salt remained. The latter was very readily soluble in water, and for this reason, and also because it was probably a mixture, it was not analysed. This curious decomposition is not due primarily to the action of atmospheric carbonic anhydride, as a current of this gas passed through a solution of the barium salt for some time does not produce a precipitate; it would seem, therefore, that the salt of the hydroxy-acid or of the *cis*- π -camphanic acid undergoes hydrolytic dissociation, the barium hydroxide being afterwards converted into carbonate on exposure to the air.

Methylic cis- π -Camphanate.

When *cis*- π -camphanic acid is dissolved in methylic alcohol and the solution treated with hydrogen chloride under the ordinary conditions without applying heat, etherification takes place very incompletely, and if, after the solution has become cold again and saturated with the gas it be placed aside in a closed vessel, the acid is slowly deposited in lustrous, truncated, hexagonal pyramids; on keeping at atmospheric temperature for some days, the acid does not re-dissolve, but if hydrogen chloride be passed into the hot solution for some time etherification proceeds fairly rapidly. The solution, on spontaneous evaporation, deposits the crystalline methylic salt, which is first treated with cold, dilute, sodium carbonate solution to free it from acid, and then dried in the air; it is best recrystallised from a mixture of ether and light petroleum.

A sample, on analysis, gave results agreeing with those required for the methylic salt of a lactonic monocarboxylic acid of the composition $C_9H_{13}O_2 \cdot COOMe$.

0.1429 gave 0.3271 CO_2 and 0.0978 H_2O . C = 62.43; H = 7.60.

$C_{11}H_{16}O_4$ requires C = 62.26; H = 7.55 per cent.

Methylic *cis*- π -camphanate melts at 74.5–75.5°; it is very readily soluble in alcohol, ether, chloroform, and most organic solvents even in the cold, but only very sparingly in cold light petroleum; it separates from a mixture of ether and light petroleum in transparent prisms and in fern-like crystals.

cis- π -Camphanic Anhydride.

cis- π -Camphanic acid is not readily acted on by acetyl chloride, and is recovered unchanged from a solution which has been heated for a considerable time; even when it is dissolved in a large excess of acetic anhydride and the solution boiled for about two hours, a portion of the acid undergoes no change. On distilling off most of the anhydride and then keeping the residue over sulphuric acid and potash, a yellowish, crystalline product is slowly deposited; this dis-

solves readily, but not completely, in cold chloroform, the insoluble portion being the unchanged acid, and on adding ether to the filtered solution the anhydride is precipitated in ill-defined plates. This preparation does not melt very sharply, owing to the presence of small quantities of the acid, but after repeated solution in cold benzene or chloroform and reprecipitation with dry ether, it seems to be homogeneous. A sample purified in this way and dried over sulphuric acid was analysed.

0.1443 gave 0.3333 CO_2 and 0.0882 H_2O . $\text{C} = 63.00$; $\text{H} = 6.79$.
 $\text{C}_{20}\text{H}_{26}\text{O}_7 = 2\text{C}_{10}\text{H}_{14}\text{O}_4 - \text{H}_2\text{O}$ requires $\text{C} = 63.49$; $\text{H} = 6.88$ per cent.

This result shows that the substance is an anhydride formed from 2 mols. of the acid, a conclusion which is confirmed by the fact that the anhydride is much less volatile than the acid; when heated in small quantities under atmospheric pressure, the greater portion chars, giving off most irritating vapours, whereas the acid itself may be distilled under these conditions without undergoing decomposition to any great extent.

cis- π -Camphanic anhydride melts at 164 – 165° , and crystallises from most anhydrous solvents in small, transparent plates or prisms; it separates from methylic alcohol in fern-like crystals, which have a lower melting point than 164° , doubtless owing to partial hydrolysis. It dissolves freely in chloroform and in benzene, but is almost, if not quite, insoluble in cold ether, water, and dilute sodium carbonate solution. It is hydrolysed slowly by warm water, and when heated with alcoholic sodium hydroxide for a few minutes it gives a solution from which mineral acids precipitate *cis*- π -camphanic acid.

The extraordinary stability of *cis*- π -camphanic acid is very clearly brought out in its behaviour towards potassium permanganate. When a solution of the acid (1 part) in dilute sodium carbonate is mixed with a dilute solution of potassium permanganate ($2\frac{1}{2}$ parts), and kept at atmospheric temperature, oxidation takes place extremely slowly, and the solution does not become colourless until after the lapse of about five weeks; even then a comparatively small proportion of the acid has undergone oxidation, since on evaporating the filtered alkaline solution and acidifying with hydrochloric acid a precipitate of *cis*- π -camphanic acid is produced, and the quantity thus recovered is at least 50 per cent. of the amount originally taken. When the acid filtrate from the *cis*-acid is evaporated to dryness, the residue extracted with methylic alcohol, and the extract evaporated, there remains a pale yellow oil which begins to deposit crystals on

the addition of a few drops of water; these crystals consist of a mixture of *cis*- π -camphanic acid and a new hydroxy-lactonic monocarboxylic acid of the composition $C_{10}H_{14}O_5$.

As oxidation proceeded so slowly, and was so incomplete at ordinary temperatures, experiments were made under other conditions, and it was found that the new acid could be more rapidly prepared by dissolving *cis*- π -camphanic acid (1 part) in a slight excess of dilute sodium carbonate solution, heating at $95-100^\circ$, and adding in the course of about nine hours an aqueous solution of potassium permanganate (5 parts). Even under these circumstances, about 20 per cent. of the *cis*- π -camphanic acid is recovered, and the yield of the hydroxy-acid is comparatively small, a considerable quantity of oily products being obtained. Further attempts to improve the method of preparation, or, rather, to obtain different products of oxidation, by first boiling the *cis*- π -camphanic acid with concentrated potash, in order to hydrolyse the lactonic ring, and then treating the alkaline solution with permanganate, were unsuccessful; apparently oxidation took place just as slowly, and the quantity of unchanged *cis*- π -camphanic acid which was finally recovered was about the same as before.

The new compound, obtained by these methods, was finally separated from *cis*- π -camphanic acid by treating the mixture with cold dilute alcohol, evaporating the filtered solution and recrystallising the residue from a mixture of moist acetone and ether.

Hydroxy-*cis*- π -camphanic acid was thus obtained in long transparent prisms, which were dried in the air for some time; they then contain 1 mol. of water of crystallisation.

0.2839 gram lost 0.0245 gram H_2O at 100° . $H_2O = 8.63$.

$C_{10}H_{14}O_5 + H_2O$ requires $H_2O = 7.76$ per cent.

A sample which had been dried at 100° until the weight was constant was analysed.

0.1461 gave 0.3005 CO_2 and 0.0870 H_2O . $C = 56.09$; $H = 6.62$.

$C_{10}H_{14}O_5$ requires $C = 56.07$; $H = 6.54$ per cent.

Hydroxy-*cis*- π -camphanic acid crystallises from water in long, transparent needles, which become opaque at 100° , and melt at $264-265^\circ$. It is very readily soluble in alcohol, acetone, hot ether, and boiling water, but it is much less readily soluble in boiling chloroform, and rather sparingly so in boiling benzene. It has an acid reaction to litmus, dissolves in sodium carbonate solution with effervescence, and has all the properties of a carboxylic acid. In a neutral solution of the ammonium salt, solutions of lead acetate, silver nitrate, magnesium sulphate, calcium chloride, and barium chloride do not produce a precipitate; a solution of copper sulphate also gives no immediate

precipitation in the cold, but, on boiling, a copper salt is quickly deposited in beautiful bluish-green, transparent prisms.

Hydroxy-*cis*- π -camphanic acid, as was to be expected from its method of preparation, is an extremely stable substance, and may be heated with concentrated nitric acid for hours without undergoing oxidation to any appreciable extent; on subsequently evaporating the solution, a homogeneous deposit of the hydroxy-acid is obtained. A solution of its sodium salt does not decolorise a solution of potassium permanganate except on prolonged boiling.

The presence of a hydroxyl group in hydroxy-*cis*- π -camphanic acid is shown by the formation of an acetyl derivative. When the anhydrous acid is boiled with excess of acetyl chloride for about two hours, and the solution finally evaporated over sulphuric acid and potash, there remains a yellowish syrup, which does not crystallise readily, but which, when mixed with a little ether, deposits a small quantity of a crystalline product; after separating the latter by filtration, and evaporating the ethereal solution, the acetyl derivative is again obtained as an oil, which slowly solidifies to a mass of crystals. Even after getting rid of oily impurity with the help of porous earthenware, this substance invariably separates as an oil when its solutions in various solvents are allowed to evaporate spontaneously; if, however, the oil be dissolved in a little ether, the solution mixed with a considerable quantity of light petroleum, and then heated on a water bath, long needles or prisms gradually separate from the petroleum solution above the layer of oil; these are then removed, a little ether added, and the heating continued, whereupon a second crop of crystals is obtained; by repeating these operations practically the whole of the original oil can be obtained in colourless crystals.

A sample which had been further purified and dried at 100° was analysed.

0.1506 gave 0.3110 CO₂ and 0.0863 H₂O. C = 56.32; H = 6.36.
C₁₀H₁₈O₆·CO·CH₃ = C₁₂H₁₆O₆ requires C = 56.25; H = 6.25 per cent.

w-Acetoxy-*cis*- π -camphanic acid crystallises from a mixture of light petroleum and ether in white, feathery needles or prisms, and from methylic alcohol in colourless, transparent crystals, which contain water or methylic alcohol; it is very readily soluble in cold ether, chloroform, benzene, and acetone, but only very sparingly in boiling light petroleum; crystals deposited from anhydrous solvents melt at

123—124°. It is moderately soluble in boiling water, from which it separates on cooling in long needles, which doubtless contain water of crystallisation, as they melt immediately when rapidly heated at 100°, but do not liquefy until 123—124°, if heated slowly from about 60°.

Crystals deposited from cold, dilute methylic alcohol were examined by Mr. Pope, with the following results.

"Acetoxy-*cis*- π -camphanic acid crystallises in small, colourless, transparent plates belonging to the monosymmetric system (Fig. 4). The

FIG. 4.

pinacoid $a\{100\}$ is the dominant form, and the form $c\{001\}$ is also usually large. The prisms $r\{101\}$ and $r_1\{\bar{1}01\}$ are generally small, and frequently absent; the form $p\{110\}$ is usually large and well developed. The dome $q\{011\}$ and the pyramid $o\{\bar{1}11\}$ are rarely present, and only approximate measurements can be obtained from their faces. The reflections given by the pinacoid $a\{100\}$ and the dome $p\{110\}$ are very good, but those from all the other forms are poor.

"The plane of symmetry is the optic axial plane, and one optic axis emerges through $a(100)$; the optic axial angle is fairly large, and the double refraction is positive and weak. The optic axial angle for blue, is greater than that for red, light. The crystals possess no apparent cleavage.

"Crystalline system. Monosymmetric.

$$a : b : c = 0.974 : 1 : 1.159.$$

$$\beta = 70^\circ 35'.$$

"Forms present:

$$a\{100\}, c\{001\}, r\{101\}, r_1\{\bar{1}01\}, q\{011\}, o\{\bar{1}11\}, p\{110\}.$$

"The following angular measurements were obtained.

Angle.	Number of measurements.	Limits.	Mean.	Calculated.
$ar = 100 : 101$	18	30° 20'—33° 7'	31° 47'	—
$rc = 101 : 001$	11	38 17—39 45	39 8	38° 49'
$cr_1 = 001 : \bar{1}01$	6	61 3—62 8	61 23	61 41
$r_1a = \bar{1}01 : \bar{1}00$	16	47 16—48 27	47 43	—
$ap = 100 : 110$	21	42 28—45 7	44 15	—
$pp = 110 : \bar{1}10$	9	90 25—93 56	91 30	91 30
$aq = 100 : 011$	3	75 41—78 24	77 26	77 3
$qo = 011 : \bar{1}11$	4	41 18—43 39	42 32	43 40
$ao = \bar{1}00 : \bar{1}11$	3	59 8—60 31	59 56	59 17

"After melting on a microscope slide the substance solidifies very slowly, the crystallisation requiring nearly an hour for completion. The resulting mass consists of long, straight, crystalline flakes, the faces of which are nearly perpendicular to the negative bisectrix of a large optic axial angle."

That *w*-acetoxy-*cis*- π -camphanic acid is a carboxylic acid is shown by its reaction to litmus, and by the fact that it dissolves readily in a cold dilute solution of sodium carbonate, expelling carbon dioxide. The *ammonium* salt is obtained in transparent plates on dissolving the acid in a slight excess of dilute ammonia, and allowing the solution to evaporate; it is readily soluble in methylic alcohol, and when treated with a mineral acid it gives a precipitate of the original acetyl derivative of the *cis*-acid. The *silver* salt is readily soluble in cold water, and is only deposited from concentrated solutions of the ammonium salt under the usual conditions; it appears to be amorphous. Solutions of lead acetate, magnesium sulphate, calcium chloride, and barium chloride do not produce a precipitate when mixed with a solution of the ammonium salt, but ferric chloride gives a light buff, amorphous precipitate; copper sulphate gives a bluish-green precipitate, which is readily soluble in cold water, but, on heating, an insoluble, apparently crystalline, copper salt is deposited.

The crystalline substance which is precipitated from the crude, oily product, on the addition of ether (see above), is very easily purified by recrystallisation from chloroform, from which it separates in compact prisms melting at 192–193°; it is much more sparingly soluble than *w*-acetoxy-*cis*- π -camphanic acid in most ordinary solvents, and hardly dissolves at all in boiling methylic alcohol or in benzene, although readily soluble in acetone. It is practically insoluble in boiling water and in a cold solution of sodium carbonate.

0.1020 gave 0.2174 CO₂ and 0.0564 H₂O. C = 58.13; H = 6.14.
 C₂₄H₃₀O₁₁(= 2C₁₂H₁₆O₆ – H₂O) requires C = 58.33; H = 6.07 p.c.
 C₂₀H₂₆O₈(= 2C₁₀H₁₄O₅ – H₂O) „ C = 58.5; H = 6.3 „

The neutral character of the compound, its method of formation, and the above analysis show that it may be the anhydride, either of *w*-hydroxy-*cis*- π -camphanic acid or of *w*-acetoxy-*cis*- π -camphanic acid; between these alternatives, however, a choice is difficult, inasmuch as when *w*-acetoxy-*cis*- π -camphanic acid is boiled with acetyl chloride, it is not converted into the compound in question.

trans-Camphotricarboxylic acid, C₇H₁₁(COOH)₃.

Although *cis*- π -camphanic acid is so remarkably stable towards oxidising agents in general, and especially towards nitric acid, the isomeric *trans*-acid is very easily oxidised by nitric acid, by which it is converted into a tricarboxylic acid of the composition C₁₀H₁₄O₆; in

the formation of this compound, the lactone ring in the *trans*-acid no doubt undergoes hydrolysis, and the $-\text{CH}_2\cdot\text{OH}$ group is then oxidised to the carboxyl group.

The preparation of *trans*-camphotricarboxylic acid is an easy matter under the following conditions. Purified *trans*- π -camphanic acid (6 parts) is covered with a mixture of nitric acid of sp. gr. 1.4 (23 parts) and water (15 parts), and a gentle heat applied; the crystals rapidly pass into solution, and as soon as the temperature has risen a little, oxidation commences, as is shown by the formation of ruddy fumes; at the same time the solution usually acquires a blue colour just like that of a moderately dilute solution of copper sulphate. After heating until ruddy fumes are only slowly evolved, which is the case in about an hour's time, the almost colourless solution is poured into a basin and concentrated by evaporation until crystallisation commences; it is then allowed to cool, and the crystals are separated by filtration and washed with a little water. The mother liquors and washings are combined and again evaporated to crystallisation, the crystals being separated as before; these processes are repeated until only a few drops of solution are left.

The acid which is thus obtained, both in the form of colourless, apparently anhydrous, prisms, and also in hydrated crystals, is homogeneous, and has a sharp melting point; when the various crops of crystals are placed together and dried at 100° , the preparation appears to be a mixture, as those deposited during the later stages—when most of the nitric acid has been expelled—become opaque, the others remaining transparent; nevertheless, they all consist of *trans*-camphotricarboxylic acid, and no other product is formed under the conditions stated above, at any rate in any appreciable quantity, the yield of the tricarboxylic acid being practically theoretical. In a quantitative experiment 6 grams of anhydrous *trans*- π -camphanic acid gave 6.2 grams of anhydrous *trans*-camphotricarboxylic acid, melting sharply at the correct temperature, and free from any estimable quantity of impurity. It is essential, however, that the nitric acid used for oxidising should not be too dilute, otherwise the reaction takes a different course, as described later, and the yield of crystalline *trans*-camphotricarboxylic acid is very poor.

Although the method just given was found to be the most suitable one for the preparation of *trans*-camphotricarboxylic acid, this compound may also be obtained by boiling *trans*- π -camphanic acid for a long time with dilute sulphuric acid and chromic acid; in this case also the tricarboxylic acid seems to be the sole product of oxidation, but as the presence of small quantities of other compounds might easily pass undetected, it is not possible to make as definite an assertion as when nitric acid is used as oxidising agent.

A much more important point, owing to its bearing on the nature of the change which occurs in the formation of the tricarboxylic acid, is the fact that this acid is produced by the oxidation of π -hydroxycamphoric acid; on warming the latter on the water bath with moderately concentrated nitric acid, ruddy fumes are rapidly formed, and after heating for about two hours the solution yields, on evaporating, a colourless, crystalline acid, identical with the compound obtained from *trans*- π -camphanic acid. When the nitric acid is sufficiently strong, *trans*-camphotricarboxylic acid seems to be the only product, but in one experiment a small quantity of an acid melting at about 218° was also isolated; the formation of the latter was probably due to the use of weak nitric acid, which in the case of *trans*- π -camphanic acid gives rise to different products (compare p. 960).

trans-Camphotricarboxylic acid crystallises from cold water, in which it is very readily soluble, in lustrous, transparent, six-sided plates; these crystals become opaque at 100° , and contain $\frac{1}{2}$ mol. H_2O .

0.8577 air-dried acid lost 0.0366 H_2O at 100° . $H_2O = 4.26$.

0.4630 " " 0.0184 H_2O at 100° . $H_2O = 3.97$.

$C_{10}H_{14}O_6 + \frac{1}{2}H_2O$ requires $H_2O = 3.76$ per cent.

A sample of the anhydrous acid, recrystallised from a mixture of methylic alcohol and ether, and dried at 100° , was analysed.

0.1500 gave 0.2860 CO_2 and 0.0829 H_2O . $C = 52.00$; $H = 6.14$.

$C_{10}H_{14}O_6$ requires $C = 52.17$; $H = 6.09$ per cent.

trans-Camphotricarboxylic acid seems to be more sparingly soluble in concentrated hydrochloric or nitric acid than in water, but the difference is not so great that it is deposited from a cold saturated aqueous solution on the addition of the mineral acid; the crystals deposited from a solution in concentrated nitric acid are long, transparent prisms, and seem to be anhydrous, as they do not become opaque at 100° . The anhydrous acid separates from a mixture of chloroform and ether, and from ether alone, in large, transparent plates, which rapidly become opaque on exposure to the air; it is very readily soluble in acetone and alcohol, and moderately easily in ethylic acetate, but nearly insoluble in boiling chloroform and benzene. It melts at 195 — 196° , effervescing considerably, but charring very little.

trans-Camphotricarboxylic acid is dextrorotatory in solution, like the π -hydroxycamphoric acid, corresponding with it in configuration; an alcoholic solution of 1.024 gram of the acid diluted to 25 c.c. and examined at 20° in a 2-dm. tube gave $\alpha_D = +3.05^{\circ}$ as the average of six concordant readings. Specific rotation, $[\alpha]_D = +37.2^{\circ}$.

The crystallographic character of this acid is described by Mr. Pope in the succeeding paper.

trans-Camphotricarboxylic acid, like *cis*- π -camphanic acid, is an extraordinarily stable substance. It may be heated at 100° with nitric acid of sp. gr. 1.5, or with weaker acid, for many hours, without being changed. A mixture of approximately equal volumes of concentrated sulphuric acid and nitric acid of sp. gr. 1.42 has very slight, if any, action, even on heating at 100° for some hours, and, on subsequently allowing the solution to cool, *trans*-camphotricarboxylic acid is deposited. It is only very slowly acted on by a boiling solution of chromic acid in dilute sulphuric acid; such a solution of the *trans*-acid, which had been heated during 60 hours, and which was still yellowish-brown, was repeatedly extracted with ether; on evaporating the dried extract, *trans*-camphotricarboxylic acid was deposited in crystals, and no other product could be detected; it is probable, therefore, that the small proportion of the acid which underwent oxidation was converted into acetic acid or carbonic anhydride. A solution of the sodium salt of the acid does not decolorise a very dilute solution of potassium permanganate except on keeping for a long time, and bromine at ordinary temperatures seems to be without action on the acid; on treatment with bromine and amorphous phosphorus at 100°, however, the *trans*-acid is readily attacked, as described later.

The *silver* salt was prepared and analysed in order to prove the presence of three carboxyl groups in the acid. This salt was precipitated from a solution of the ammonium salt, washed with water and alcohol successively, and dried at 100°.

0.2588 gave 0.1505 Ag. Ag = 58.15.

$C_{10}H_{11}O_6Ag_3$ requires Ag = 58.7 per cent.

Silver *trans*-camphotricarboxylate is only sparingly soluble in cold water, and turns pink on exposure to sunlight, but it does not change colour when heated at 100° in the dark. On titrating the tricarboxylic acid with a solution of sodium hydroxide, using litmus as indicator, the solution became neutral after adding almost exactly two-thirds of the quantity of alkali theoretically required for a tricarboxylic acid (namely, 12.7 c.c. instead of 18.4 c.c., and 20.2 c.c. instead of 31.4 c.c.); the change in colour, however, was not very sharp, and the exact point was difficult to determine. Using phenolphthaleïn as indicator, the results agreed fairly well with those required for a tricarboxylic acid, but in this case also the end reaction was not very sharp. This behaviour is similar to that of some of the substituted butanetetracarboxylic acids (Lean, *Trans.*, 1894, 67, 995).

A solution of *trans*-camphotricarboxylic acid in excess of ammonia acquires an acid reaction on evaporating it on the water bath. In a neutral or very faintly ammoniacal solution of the ammonium salt, copper acetate produces a light greenish-blue, lead acetate a colourless, and ferric chloride a light buff, amorphous precipitate; these three salts seem to be insoluble or practically insoluble in boiling water. Magnesium sulphate and cobalt nitrate do not give precipitates.

The behaviour of a faintly ammoniacal solution towards the chlorides of barium and of calcium is very characteristic, and serves as a fairly delicate test for small quantities of *trans*-camphotricarboxylic acid. In very concentrated solutions, barium chloride produces an apparently amorphous precipitate, which rapidly dissolves on adding a little water; in more dilute solutions, no precipitate is produced at ordinary temperatures, but, on warming gently, a thick, apparently crystalline, precipitate is formed, which disappears as the liquid cools again; this precipitation on heating, and re-solution on cooling, may be repeated; the salt is also precipitated from cold solutions on the addition of a little alcohol.

On adding calcium chloride to a faintly ammoniacal solution, a bulky, apparently amorphous, precipitate is thrown down; this substance, probably the normal salt, is readily soluble in acetic acid; on expelling the acetic acid by repeatedly boiling down after adding water, a compound is slowly deposited in well-defined prisms. This salt seems to be insoluble in boiling water and also in dilute acetic acid; it does not contain water of crystallisation, and appears to be the calcium hydrogen salt, analyses of a sample dried at 100° having given the following results.

0.2174 gave 0.1032 CaSO_4 . $\text{Ca} = 14.98$.

0.3318 „ 0.1663 CaSO_4 . $\text{Ca} = 15.04$.

$\text{C}_{10}\text{H}_{12}\text{O}_6\text{Ca}$ requires $\text{Ca} = 14.92$ per cent.

Many of the constitutional formulæ which have been proposed for camphoric acid, Bredt's among others, represent it as containing methyl groups, one of which is united to a carbon atom which in its turn is directly combined with a carboxyl group; *trans*-camphotricarboxylic acid, moreover, is doubtless derived from camphoric acid by indirectly converting a particular methyl group into carboxyl. Hence it was desirable to ascertain experimentally whether this particular methyl group which undergoes change is also that which is supposed to be united to the $-\overset{|}{\text{C}}-\text{COOH}$ complex; in other words, whether any two of the carboxyl groups in *trans*-camphotricarboxylic acid are directly combined with one and the same carbon atom.

The behaviour of *trans*-camphotricarboxylic acid when it is heated alone affords strong evidence that no two carboxyl groups are directly united to the same carbon atom, since carbonic anhydride is not evolved even at temperatures considerably above 260°. It might be argued, however, as Tiemann has done in support of his constitutional formula for camphoronic acid (*Ber.*, 1895, 28, 2163), that since the tricarboxylic acid is converted into its anhydride under the above conditions, this decomposition is prevented by the formation of

the relatively stable group $\begin{array}{c} \text{C}\cdot\text{CO} \\ \vdots \\ \text{COOH}\cdot\text{C}\cdot\text{CO} \end{array} \text{O}$. Although such an

argument is not very convincing, the behaviour of an aqueous solution of *trans*-camphotricarboxylic acid at high temperatures was also examined, the probability that a stable anhydride would be formed under these conditions being very remote.

For this purpose, a small quantity of the purified tricarboxylic acid was dissolved in a little water, and the solution heated in a sealed tube during several hours, the temperature, which was at first kept at about 200°, being ultimately raised to 260°. Before opening the tube, there was not sufficient internal pressure to burst the heated capillary, although the contents had carbonised a little, and, on evaporating the filtered aqueous solution, crystals of *trans*-camphotricarboxylic acid were deposited. It is true that the acid did not crystallise very readily until after it had been purified by digestion with a little concentrated nitric acid, but the large quantity which then separated in crystals showed that comparatively little had undergone change; the presence of the small quantity of foreign matter which retarded the crystallisation of the crude product was doubtless due to carbonisation; possibly also a small proportion of the acid had undergone stereoisomeric change.

Oxidation of trans-Camphotricarboxylic acid with Permanganate.—In spite of the ascertained stability of *trans*-camphotricarboxylic acid towards an alkaline solution of potassium permanganate, it seemed probable that some simple oxidation product might be obtained as the result of prolonged treatment at ordinary temperatures. A solution of the purified tricarboxylic acid (2·6 grams) in dilute sodium carbonate was therefore mixed with an aqueous solution of potassium permanganate (3·7 grams = 2 mols.) and kept at atmospheric temperature; at the expiration of more than six weeks, a considerable quantity of hydrated oxide had been deposited, but the solution had still a fairly deep pink colour. It was therefore warmed on the water bath during about six hours, at the end of which time the colour was discharged. After filtering, the clear alkaline solution was boiled down to a small bulk,

cooled, and excess of concentrated hydrochloric acid added; the crystalline precipitate which was gradually produced was separated, washed with a little dilute hydrochloric acid, and dried at 100°; it consisted of *trans*-camphotricarboxylic acid mixed with traces of alkali chlorides, and melted sharply at 194—195°. The quantity thus immediately recovered was 1·7 grams. The mother liquors were evaporated to dryness, and the crystalline residue, consisting for the most part of alkali chlorides, repeatedly extracted with warm ether; finally the residue was extracted with methylic alcohol until free from organic matter. The methylic alcohol extract gave, on evaporation, only a minute residue, which, moreover, was rich in inorganic chlorides, and which was not investigated. The ethereal extract, on spontaneous evaporation, yielded in the first place a small crop (0·2 gram) of *trans*-camphotricarboxylic acid, and then an oily residue which did not crystallise very readily; on adding a little concentrated hydrochloric acid, however, and allowing the mixture to stand after expelling the ether, a further quantity of the tricarboxylic acid was deposited, together with a considerable proportion of oxalic acid, which was identified by the usual tests. Other substances, as far as could be ascertained, were absent, and, considering the large proportion of the tricarboxylic acid which was recovered, there is little doubt that the relatively small quantity which was attacked under the above conditions had been completely oxidised to oxalic acid.

trans-Camphotricarboxylic Anhydride, $\text{COOH} \cdot \text{C}_7\text{H}_{11} < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{O}$.

trans-Camphotricarboxylic acid, like π -bromocamphoric acid, is very readily converted into its anhydride, this change taking place to a greater or less extent when the acid is heated at 200—210° for a short time. The anhydride is most conveniently prepared, however, by heating the anhydrous acid for about half an hour with acetyl chloride, in which it dissolves slowly; the solution is then evaporated and the residue recrystallised from a mixture of ether and chloroform.

0·1664 gave 0·3432 CO_2 and 0·0854 H_2O . C = 56·25; H = 5·63.

$\text{C}_{10}\text{H}_{12}\text{O}_5$ requires C = 56·60; H = 5·66 per cent.

trans-Camphotricarboxylic anhydride melts at 253—254°, but begins to sublime at a much lower temperature; it is readily soluble in boiling chloroform and ether, and moderately easily in boiling benzene, but insoluble, or nearly so, in light petroleum; it crystallises extremely well from a mixture of chloroform and ether, and, for the following account of the crystals thus obtained, the author is again indebted to Mr. Pope.

"*trans*-Camphotricarboxylic anhydride is obtained in colourless, transparent, monosymmetric crystals of 5 mm. or so in length, and of very variable habit (Fig. 5); they are, however, usually lengthened along the *b*-axis, and flattened perpendicularly to the *a*-axis. The pinacoid $a\{100\}$ is usually the dominant form, although sometimes

FIG. 5.

absent; it gives very good reflections; the pinacoid $c\{001\}$ and the prism form $r\{101\}$ are generally small, but give trustworthy results on measurement. The dome form $q\{011\}$ is sometimes the dominant form; it gives poor reflections, owing to its being considerably cor-

roded. The pyramid $o\{\bar{1}11\}$ is rarely observed, and only as a very narrow replacement on the edge aq ; the measurements obtained from it can only be regarded as approximate. The pinacoid $b\{010\}$ is usually present, but only as the half-form; it is very dull and corroded, and only gives poor reflections. The presence of but one face of the form $b\{010\}$ gives the crystals a hemimorphic habit, and further evidence of hemimorphism was therefore sought; no evidence of the development of pyro-electricity could be found by dusting the cooling crystals with the electrified mixture of powders by Kundt's process. Further, on etching the form $a\{100\}$ with water, very distinct etch-lines were obtained; they were, however, always parallel to the trace of the plane of symmetry on the face, so that the only evidence of hemimorphism consists in the constant occurrence of the half-form of $b\{010\}$.

"The plane of symmetry $b(010)$ is the optic axial plane. The pinacoid $a\{100\}$ is nearly perpendicular to a positive bisectrix, which is probably the obtuse one; an optic axis emerges through $a\{100\}$ in the angle ar . It was found difficult to grind sections for the optical examination, owing to the ready manner in which the crystal surface undergoes disintegration, causing the surface to become coated with a layer of fine particles showing aggregate polarisation. The crystals have a conchoidal fracture, but no pronounced cleavage, and can readily be hacked in any required direction; the fragments thus obtained, however, are unsuitable for optical examination because they mostly show aggregate polarisation.

"Crystalline system. Monosymmetric.

$$a : b : c = 1.0186 : 1 : 0.6255.$$

$$\beta = 63^{\circ} 28'.$$

"Forms present:

$$a\{100\}, b\{010\}, c\{001\}, r\{\bar{1}01\}, q\{011\}, o\{\bar{1}11\}.$$

"The following angular measurements were obtained :

Angle.	Number of measurements.	Limits.		Mean.	Calculated.
<i>ar</i> = 100 : 101	17	56° 16'—	56° 48'	56° 30'	—
<i>er</i> = 001 : 101	13	59 41—	60 20	60 2	60° 2'
<i>ac</i> = 100 : 001	18	63 9—	63 52	63 28	—
<i>qc</i> = 011 : 001	21	28 50—	29 35	29 14	—
<i>qb</i> = 011 : 010	19	60 16—	61 14	60 44	60 46
<i>qq</i> = 011 : 011	4	121 14—	121 58	121 27	121 32
<i>qq</i> = 011 : 011	6	58 18—	58 42	58 30	58 28
<i>aq</i> = 100 : 011	14	66 41—	67 24	67 5	67 3
<i>aq</i> = 100 : 011	7	112 45—	113 34	113 1	112 57
<i>rq</i> = 101 : 011	16	63 43—	64 24	64 7	64 9
<i>rq</i> = 101 : 011	4	115 35—	116 26	115 55	115 51
<i>ao</i> = 100 : 111	7	60 1—	61 8	60 39	60 42
<i>oq</i> = 111 : 011	5	51 49—	52 41	52 17	52 15
<i>ro</i> = 101 : 111	1	—	—	27 10	27 33
<i>oo</i> = 111 : 111	1	—	—	124 30	124 54

"On melting the anhydride on a microscope slide under a cover slip, it readily solidifies on cooling, giving a singly-refracting substance, which is consequently a cubic modification. The mass, on further cooling, changes suddenly into a uniaxial modification of negative double refraction; this form is seen to consist of large patches, which are filled with long striæ of twinned fragments, the corresponding directions in which lie at 90° and 61° (approx.) to each other. As this uniaxial modification is certainly crystallographically different from the biaxial monosymmetric form obtained by crystallisation from solution, camphotricarboxylic anhydride would seem to be trimorphous."

trans-Camphotricarboxylic anhydride dissolves at once in a cold dilute solution of sodium carbonate, the accompanying effervescence showing that the substance is still a carboxylic acid; when the finely powdered anhydride is shaken with cold water, it passes into solution extremely slowly, the water becoming distinctly acid to litmus. Even boiling water, in which it dissolves freely, hydrolyses it comparatively slowly, as, on cooling, it is deposited for the most part unchanged in long needles; when heated for a very short time with concentrated nitric acid, however, it seems to be completely converted into the tricarboxylic acid. The anhydride distils, when heated in small portions at a time under atmospheric pressure, charring only very slightly, and the distillate at once solidifies to a crystalline mass; the latter consists principally of the unchanged *trans*-anhydride, but it also contains a substance which crystallises in prisms melting at 220°, and which is doubtless the stereoisomeric anhydride described later (p. 970).

Oxidation of trans- π -Camphanic acid with very dilute Nitric acid.

According to the views already expressed, π -hydroxycamphoric acid contains the group $-\text{CH}_2\cdot\text{OH}$, which is characteristic of primary alcohols; when, therefore, this acid, or its lactone—*trans- π -camphanic acid*—undergoes oxidation, yielding *trans-camphotricarboxylic acid*, an aldehyde should be formed as an intermediate product of oxidation. In order, if possible, to obtain some evidence of the formation of this aldehyde, experiments were made on the incomplete oxidation of *trans- π -camphanic acid*, this compound being more easily purified than the hydroxy-acid.

When *trans- π -camphanic acid* is warmed on the water bath with about four times its weight of 5 per cent. nitric acid, it slowly dissolves, giving a deep green solution, which does not yield crystals of the original lactonic acid on evaporation. When a portion of this solution was neutralised with ammonia and an ammoniacal solution of silver nitrate added, a slight, but distinct, precipitate of silver was obtained after warming gently. Another portion of the solution, boiled with phenylhydrazine and a few drops of acetic acid, gave, on cooling, a crystalline deposit, which, after recrystallisation from dilute alcohol, was obtained in yellowish, fern-like forms; since *trans- π -camphanic acid*, π -hydroxycamphoric acid, and *trans-camphotricarboxylic acid* do not give a precipitate when treated with phenylhydrazine under these conditions, the above tests indicate the presence of an aldehyde in the solution of the partially oxidised π -hydroxycamphoric acid.

When, moreover, with the intention of completing oxidation and obtaining *trans-camphotricarboxylic acid*, a fairly large quantity of concentrated nitric acid was added to the warm solution, an extremely violent action occurred, such as might well be due to the oxidation of an aldehyde, and dense, ruddy fumes were evolved. The solution, after having been heated for about an hour longer, gave, on evaporation, a yellowish-green syrup, instead of a colourless, crystalline product free from oil, such as is obtained on oxidising the lactonic acid at the outset with fairly concentrated nitric acid in the manner already described (p. 952). Further experiments showed that when dilute nitric acid was used at the commencement of the oxidation process, *trans- π -camphanic acid* always gave a syrupy product, and, although, after keeping for some days, crystals of the tricarboxylic acid were deposited, the yield of the latter was invariably very small, being, on the average, only about 25 per cent. of the theoretical. The syrupy mother liquors, moreover, did not yield any tricarboxylic acid on prolonged warming with dilute or concentrated nitric acid.

In the hope of obtaining some definite oxidation product of *trans*- π -camphanic acid, other than the tricarboxylic acid, the uncrystallisable residues from various experiments were freed from water as much as possible by heating at 100° , and then boiled during about an hour with acetic anhydride; the dark brown liquid which remained after boiling off most of the anhydride was mixed with ether, the solution filtered from a small quantity of flocculent, carbonaceous matter, and placed aside. After some time crystals were deposited, and the addition of ether produced a further separation of the same substance; this product was easily purified by recrystallisation from hot chloroform, from which it separated in colourless prisms. It contained nitrogen, and gave the following results on analysis.

0.1365 gave 0.2691 CO_2 and 0.0651 H_2O . $\text{C} = 53.76$; $\text{H} = 5.20$.

$\text{C}_{10}\text{H}_{11}\text{O}_3\cdot\text{NO}_2$ requires $\text{C} = 53.3$; $\text{H} = 4.9$ per cent.

It crystallised from a mixture of ether and chloroform in transparent prisms, sometimes an inch in length; these crystals became opaque at about 130° , doubtless owing to a change in crystalline form, and began to effervesce and char at about 196° , slowly and completely decomposing if kept at this temperature; when heated quickly from about 180° , however, they decomposed from 196 to 206° . The substance was moderately soluble in cold ether, rather sparingly in cold methylic alcohol, and sparingly in boiling light petroleum. It seemed to be insoluble in cold, but was slightly soluble in boiling water, from which it was deposited, on cooling, in minute needles; it was also insoluble, or nearly so, in a cold dilute solution of sodium carbonate, but it rapidly dissolved in hot aqueous caustic alkalis.

The formation of this substance in the manner described above, its neutral character, and the analytical results, point to the conclusion that it is the anhydride of an acid of the composition $\text{C}_{10}\text{H}_{13}\text{O}_4\cdot\text{NO}_2$; the formation of such an acid from *trans*- π camphanic acid, however, is not easily accounted for, and as all attempts to throw some light on the nature of the substance failed, owing to lack of material, its composition cannot be regarded as established.

Isomeric Lactones derived from w-Hydroxycamphotricarboxylic acid.

It has been stated above that all attempts to obtain an oxidation product derived from *trans*-camphotricarboxylic acid in a simple manner, were unsuccessful, owing to the extraordinary stability of the acid; under these circumstances the most promising course to adopt seemed to be, to try and convert the tricarboxylic acid into a hydroxy-derivative, which would probably prove to be more readily oxidisable. For this purpose it was first necessary to brominate the acid; experiments made with this object showed that *trans*-campho-

tricarboxylic acid is not acted on when treated with bromine at ordinary temperatures under various conditions, but that its bromination can be readily accomplished in the following manner:—Purified *trans*-camphotricarboxylic acid (5 grams), dried at 100°, is intimately mixed with half its weight of dry amorphous phosphorus, the mixture placed in a Wurtz flask and dry bromine slowly added from a dropping funnel fitting into the flask; after about 4 c.c. of the halogen have been run in and the first violent action is at an end, the flask is heated on a water bath and the addition of bromine continued very slowly. In the course of about $1\frac{1}{2}$ hours, and when about 12 c.c. of bromine have been added, the evolution of hydrogen bromide seems to slacken, and bromine vapour escapes freely from the side-tube of the flask, but the end of the reaction is not easily ascertained. The contents of the vessel, namely a reddish-brown oil, which solidifies almost completely on cooling, are now transferred to an evaporating basin, and the excess of bromine is expelled by heating on a water bath.

The crude oily product is then cooled and slowly poured into a small quantity of cold water, with which it is afterwards well stirred; the clear aqueous solution, which contains the inorganic acids only, is then decanted and the residual oil warmed on the water bath with a small quantity of fresh water. During this process the product begins to crystallise, at the same time passing into solution, and if after a short period water is added in fairly large quantity, the whole heated to boiling and then filtered, a crystalline substance is deposited from the filtrate on cooling; the crystals are separated, the liquors again evaporated, filtered from a brown, flocculent substance, and allowed to cool; in this way a second crop of crystals is obtained, and by repeating these operations further quantities may be separated until very little liquid is left. The yield of crude air-dried product is about 75 per cent. of the *trans*-camphotricarboxylic acid employed; during the evaporation of the solutions, carbonisation takes place to a slight extent, doubtless owing to the presence of the hydrobromic acid, and the solutions invariably deposit brown flocks after renewed concentration.

The crude product consists usually of a mixture of two, sometimes of three substances; on treating it with boiling benzene a small proportion sometimes passes into solution, and on evaporating the filtered extract, colourless transparent crystals are deposited, which, when warmed, become opaque, and melt at about 178°. This compound is not always present, and, in any case it is obtained in very small quantities; as it was found to be converted by recrystallisation from water into the β -lactone described later on, it was not further examined.

The portion of the crude product which is insoluble in benzene, consists for the most part of a substance melting at about 220° , and on fractional crystallisation from a mixture of ether and methylic alcohol, this compound is finally deposited in colourless, ill-defined prisms. It was dried over sulphuric acid, and analysed.

0.1455 gave 0.2816 CO_2 and 0.0683 H_2O . $\text{C} = 52.78$; $\text{H} = 5.21$.

$\text{C}_{10}\text{H}_{12}\text{O}_6$ requires $\text{C} = 52.63$; $\text{H} = 5.26$ per cent.

The analysis shows that the compound contains two atoms of hydrogen less than *trans*-camphotricarboxylic acid; this fact, and the method of formation show that the substance is derived from a hydroxycamphotricarboxylic acid, $\text{C}_{10}\text{H}_{14}\text{O}_7$, by the loss of 1 mol. of water; for the reasons already stated (p. 922) it is regarded as a lactonic dicarboxylic acid, and is distinguished from the isomeride described below by using the prefix β .

The β -lactone of hydroxycamphotricarboxylic acid is sparingly soluble in cold, but readily in hot, water from which it separates on cooling, in long, flat, transparent, lustrous prisms; these crystals become opaque at about 200° when heated quickly from about 175° , and at about 210° they disintegrate and increase in bulk in a very noticeable manner, but remain colourless; the powder thus formed begins to turn greenish and melts at 220° , at the same time effervescing. From a mixture of benzene and ether, the lactone is deposited in transparent six-sided plates which are most likely orthorhombic and sphenoidally hemihedral; the larger face is perpendicular to a positive bisectrix, the optic axial plane being perpendicular to one side of the plate; the optic axes are outside the field. These crystals become opaque at about 205° , and swell up very much at 205 – 209° , giving a white powder; on further heating, the latter shows the behaviour just described.

This β -lactone is very readily soluble in cold ether and acetone, but only sparingly soluble or insoluble in chloroform and benzene. Its aqueous solution has an acid reaction to litmus, and dissolves calcium carbonate with effervescence; the salts of the acid were not examined owing to the uncertainty regarding their derivation. The substance, in fact, is slowly changed by boiling water, being converted into the isomeride described below, but even after prolonged treatment the change seems to be incomplete; when heated with ammonia or with aqueous potassium hydroxide for a few minutes, it yields a solution from which, after evaporating to a small volume, mineral acids precipitate the γ -lactone.

The alcoholic ethereal mother liquors from which the β -lactone has been deposited, contain a considerable quantity of an isomeride which can be isolated by further fractional crystallisation; this pro-

duct is doubtless formed from the β -lactone during the evaporation of the aqueous solution of the original product of bromination, since, as just stated, the β -lactone is slowly converted into the γ -isomeride when its solution in water is boiled. The most convenient way of obtaining the γ -compound free from the isomeride is by the action of potash on the latter; the alcoholic ethereal mother liquors referred to above are evaporated to dryness, the residue dissolved in a slight excess of potash, and the alkaline solution boiled for a short time; on subsequently mixing the cold concentrated solution with excess of hydrochloric acid, part of the product is deposited in crystals, together with potassium chloride, but a considerable quantity remains dissolved. The mixture is, therefore, evaporated to dryness, the residue extracted with methylic alcohol, the extract mixed with ether to precipitate traces of inorganic salt, and the filtered solution evaporated. The substance is finally recrystallised from a mixture of benzene and ether, or from concentrated hydrochloric acid; a sample obtained from the anhydrous solvents was dried at 100° and analysed.

0.1447 gave 0.2820 CO_2 and 0.0685 H_2O . C = 53.15; H = 5.26.

$\text{C}_{10}\text{H}_{12}\text{O}_6$ requires C = 52.63; H = 5.26 per cent.

The γ -lactone of hydroxycamphotricarboxylic acid separates from a mixture of ether and benzene in colourless, transparent, flattened needles, the sides of which curve to a point; sometimes, but rarely, their sides are parallel, the ends being replaced by dome faces. The crystals show straight extinction, and a positive bisectrix emerges normally to the flat face; the optic axes are outside the field. These crystals, heated fairly rapidly from about 195° , appear to begin to sublime at about 240° and turn grey or greenish at about 250° ; when the temperature rises to 265 – 270° , the substance chars and effervesces, but apparently without melting.

It resembles the isomeride in being readily soluble in ether and acetone, but it is practically insoluble in chloroform and benzene. Its behaviour towards water, however, is very different, inasmuch as it dissolves in this liquid so readily in the cold that it cannot well be recrystallised from it; on allowing the solution to evaporate spontaneously, a white powder, which consists of microscopic needles, is ultimately deposited. On adding concentrated hydrochloric acid to a cold saturated aqueous solution of the γ -lactone, it is at once precipitated in long transparent needles, its solubility in the mineral acid being very much less than in water; moderately concentrated hydrochloric acid is, in fact, one of the best solvents from which to recrystallise the lactone. If the hydrochloric acid solution, containing in suspension the needle-like crystals, be left exposed to

the air for some time so that the mineral acid may evaporate, the needles are gradually transformed into a granular powder; this behaviour might be taken to indicate that the lactone is converted into hydroxycamphotricarboxylic acid on dissolving it in water, the lactone being regenerated on the addition of hydrochloric acid; for various reasons, however, it does not seem probable that this change would take place so readily. The β -lactone described above is not precipitated from its cold saturated aqueous solution on the addition of concentrated hydrochloric acid.

The γ -lactone has all the properties of a carboxylic acid; its aqueous solution is acid to litmus, and decomposes metallic carbonates with effervescence. The *silver* salt, obtained as a white, gelatinous precipitate on adding silver nitrate to a feebly ammoniacal solution of the ammonium salt, was purified in the usual manner, dried at 100° , and analysed.

The analysis showed that the salt was derived from a lactonic dicarboxylic acid of the composition $\text{CO} \cdot \overline{\text{C}_7\text{H}_{10}\text{O}} (\text{COOH})_2$, the lactone ring in the original substance not being hydrolysed on treatment with cold dilute ammonia; the analysis, however, was unsatisfactory, as the salt darkened considerably during the drying.

The silver salt dissolved fairly readily in boiling water, without darkening, and was deposited again on cooling, the solution setting to a gelatinous mass.

In a neutral or feebly ammoniacal solution of the ammonium salt, lead acetate produces a colourless, gelatinous precipitate which is moderately easily soluble in boiling water; on cooling, the salt separates in long needles. Ferric chloride, under the same conditions, gives a light buff, apparently amorphous precipitate which does not dissolve on boiling. Copper sulphate produces no immediate precipitate in a cold solution, but on warming, a light blue, apparently amorphous salt is deposited. The calcium and magnesium salts are very readily soluble in cold water; the barium salt is also very readily soluble, and is only precipitated on the addition of barium chloride to very concentrated solutions, being then obtained as a granular powder.

This γ -lactone, like the tricarboxylic acid from which it is derived, is extremely difficult to oxidise. It may be heated at 100° with concentrated nitric acid for some hours, and then recovered unchanged on evaporating the solution. A solution of its sodium salt does not decolorise potassium permanganate at ordinary temperatures, even on keeping for some days, and, when the mixture is boiled, oxidation takes place very slowly. Owing to the enormous labour involved in the preparation of this substance from camphor,

and the unsatisfactory results of the attempts to oxidise it, experiments requiring the use of large quantities had necessarily to be abandoned.

It may be mentioned, however, that the lactone may be boiled with acetic anhydride during several hours without losing the elements of water; this fact seems to show that the particular carboxyl group which is engaged in the formation of the lactone ring is also that which takes part in the anhydride formation in the case of *trans*-camphotricarboxylic acid.

cis-Camphotricarboxylic acid, $C_7H_{11}(COOH)_3$.

The existence of the two isomeric π -camphanic acids has been accounted for on the assumption that the two compounds are *trans*- and *cis*-modifications derived from corresponding stereochemically isomeric π -hydroxycamphoric acids, of which one only, namely, the *trans*-form, can be isolated, owing to the ease with which the other passes into the corresponding lactone; assuming this explanation to be correct, it seemed *a priori* probable that, just as *trans*- π -camphanic acid and *trans*- π -hydroxycamphoric acid are converted into *trans*-camphotricarboxylic acid on oxidation, so *cis*- π -camphanic acid, on oxidation in a suitable manner, might yield a tricarboxylic acid corresponding with it in configuration. The great stability of *cis*- π -camphanic acid towards oxidising agents made it impossible to obtain the corresponding tricarboxylic acid in the manner suggested; nevertheless, this oxidation product may be obtained indirectly by causing the *trans*-tricarboxylic acid to undergo stereoisomeric change.

When *trans*-camphotricarboxylic acid (2 parts) is dissolved in ordinary concentrated sulphuric acid (5 parts), and the solution gradually heated to 150–160°, it begins to darken, and sulphur dioxide is evolved; after keeping the mixture at this temperature for about 15 minutes, it has changed to a black paste or froth, and the heating is discontinued. The product now contains *cis*-camphotricarboxylic anhydride and a small quantity of a porous, carbonaceous substance, possibly carbon; it may also contain *cis*-camphotricarboxylic acid, but more probably the latter is formed from its anhydride during the subsequent treatment; the original *trans*-tricarboxylic acid and its anhydride seem to be absent provided the heating has been sufficiently prolonged. The *cis*-acid and its anhydride are isolated as follows:—The black, pasty mass is slowly poured into a small quantity of cold water, cooling carefully, and the solution is then rapidly filtered. The residue consists of a mixture of the *cis*-anhydride and the carbonaceous matter; it is dried on porous earthenware, and then repeatedly extracted with boiling benzene; the hot filtered benzene extracts deposit colourless crystals of the *cis*-

anhydride on cooling. When thoroughly extracted with benzene, the remaining carbonaceous mass is treated two or three times with small quantities of ether, and there then remains what seem to be particles of carbon.

The ethereal extracts, on evaporation, give an almost colourless, very thick oil, which consists of *cis*-camphotricarboxylic acid; the small quantity thus isolated has doubtless been formed by hydrolysis of the anhydride during the treatment just described. A much larger quantity of the acid can be obtained from the original sulphuric acid filtrate, for which purpose the liquid is treated with barium chloride as long as a precipitate forms, and the filtered solution concentrated; when freed from traces of barium chloride or sulphuric acid and evaporated again it yields an oily residue which solidifies on prolonged heating on the water bath. This product, like that obtained from the ethereal extracts, consists of crude *cis*-camphotricarboxylic acid, and, as a rule, neither preparation crystallises at all readily; in fact, the partially purified acid can only be recrystallised under particular conditions. For this reason it is usually more advantageous to convert the whole of the acid into the anhydride, and, after purifying the latter, to re-convert it into the acid by hydrolysis with water.

The syrupy *cis*-acid is in any case most easily obtained in crystals by dissolving it in a little concentrated hydrochloric acid and then evaporating the solution on the water bath until a sufficient quantity has been deposited; curiously enough, crystallisation takes place much more readily at high than at ordinary temperatures when the acid is not pure, and even when the solutions have begun to deposit crystals at 90–100°, the impure acid subsequently separates as an oil or as a gelatinous film if the temperature be allowed to fall.

For analysis, a sample purified in this way was heated at 100° until almost constant.

0.1536 gave 0.2956 CO₂ and 0.0835 H₂O. C = 52.48; H = 6.04.

C₁₀H₁₄O₆ requires C = 52.17; H = 6.08 per cent.

cis-Camphotricarboxylic acid is deposited from aqueous solutions on spontaneous evaporation in massive, transparent prisms, similar crystals being also obtained from hot hydrochloric acid; these crystals evidently contain water of crystallisation and become opaque at 100°, but decrease in weight very slowly, and continue to do so even after having been heated during 20–30 hours; at the end of this time the acid has been partially converted into its anhydride some of which sublimes on to the sides of the vessel.

When the hydrated crystals are heated fairly quickly from about 80° they melt at about 145–150°, effervescing violently owing to the

escape of their water of crystallisation; on continuing to raise the temperature, the substance begins to solidify and melts again at about $219-220^{\circ}$, the melting point of the *cis*-anhydride. Dehydrated crystals show a different behaviour, and melt at about 167° , also effervescing and losing water, the anhydride being formed; the fused mass quickly solidifies again, and then melts at $219-220^{\circ}$ as before. All these data referring to the melting of the hydrated or anhydrous crystals of the acid are only approximate, as they depend entirely on the rate at which the temperature is raised; when, for example, the hydrated crystals are very slowly heated, they do not liquefy until the melting point of the anhydride is reached.

The anhydrous, like the hydrated, acid is extremely soluble in cold water, ether, and alcohol, but almost insoluble in boiling benzene and chloroform; like the γ -lactone of hydroxycamphotricarboxylic acid, it is precipitated from its cold saturated aqueous solutions on the addition of concentrated hydrochloric acid.

The silver salt was prepared by precipitation, using a faintly ammoniacal solution of the acid; after washing well with water the salt was dried at 100° and analysed.

0.2935 gave 0.1690 Ag. $\text{Ag} = 57.6$.

$\text{C}_{10}\text{H}_{11}\text{O}_6\text{Ag}$, requires $\text{Ag} = 58.7$ per cent.

Silver cis-camphotricarboxylate is a colourless, granular compound, only sparingly soluble in boiling water, from which it separates again on cooling, without darkening; it remains white when heated at 100° in the dark, and changes colour very slowly on exposure to diffused daylight. When heated moderately strongly, it decomposes rather suddenly, giving a considerable quantity of a crystalline product.

In a faintly ammoniacal solution of the ammonium salt, lead acetate produces a bulky, white, apparently amorphous precipitate, insoluble, or nearly so, in boiling water, but readily soluble in acetic acid; on expelling the acetic acid, the salt is deposited as a crystalline powder. Copper sulphate, under the same conditions, gives a pale blue, amorphous precipitate, which is also practically insoluble in hot water, but calcium chloride, barium chloride, and magnesium sulphate do not produce a precipitate. A sparingly soluble calcium hydrogen salt is not formed under conditions similar to those employed in preparing the acid salt of *trans*-camphotricarboxylic acid.

Attempts to oxidise *cis*-camphotricarboxylic acid were just as unsuccessful as in the case of the isomeride; when it is boiled with nitric acid of sp. gr. 1.42 it undergoes no change, and its solution in sodium carbonate does not decolorise potassium permanganate except on prolonged heating.

In addition to the method given above, *cis*-camphotricarboxylic acid may be obtained by fusing the *trans*-isomeride with potash at a fairly high temperature; the product, isolated by extracting with ether, may be directly recrystallised from hydrochloric acid, and appears to be quite free from the *trans*-tricarboxylic acid.

Crystals deposited from warm aqueous and hydrochloric acid solutions were submitted to Mr. Pope, who gives the following account of their properties.

"*cis*-Camphotricarboxylic acid crystallises in small, white, orthorhombic prisms (Fig. 6), of about half a millimetre in thickness, which have a laminated appearance, probably owing to rapid separation from the solution; the crystals are extremely fragile, and fall to pieces if not handled very gently. The crystals obtained by spontaneous evaporation of the solvent are large, colourless, transparent pyramids, crystallographically identical with the smaller ones mentioned above; they are, however, very unsuitable for goniometrical investigation, owing to the highly conchoidal nature of the faces.

"On the small crystals, the prism form $p\{110\}$ is the dominant one, and gives better results on measurement than any of the other forms, with the exception of the dome $r\{101\}$; the faces of the latter form are fairly large, and give fairly good reflections. The pinacoid $a\{100\}$ is usually small, but varies in size considerably and give poor reflections. The basal pinacoid $c\{001\}$ is but rarely observed, and reflects light very badly; the form $q\{011\}$ is always small, and gives poor reflections. As will be gathered from the appended table of measurements, the crystals are not very suitable for crystallographical examination, and the results are not very accurate; it was, however, thought well to investigate the crystals as far as possible, in order to compare their form with that assumed by the isomeric *trans*-camphotricarboxylic acid.

"The optic axial plane is the pinacoid $b(010)$, and the a -axis is the first mean line; the optic axial angle is fairly large and the double refraction is positive in sign.

"There are perfect cleavages parallel to $a\{100\}$ and to $p\{110\}$.

"Crystalline system. Orthorhombic.

$$a : b : c = 1.202 : 1 : 1.185.$$

"Forms present:

$$a\{100\}, c\{001\}, p\{110\}, r\{101\}, q\{011\}.$$

"The following angular measurements were obtained:

FIG. 6.

Angle.	Number of observations.	Limits.	Mean.	Calculated.
<i>ap</i> = 100 : 110	24	49° 21'—51° 10'	50° 15'	—
<i>pp</i> = 110 : 110	13	78 34—80 20	79 18	79° 30'
<i>ar</i> = 100 : 101	28	45 9—45 38	45 25	—
<i>rr</i> = 101 : 101	17	88 44—89 55	89 37	89 10
<i>rr</i> = 101 : 101	6	89 38—90 38	90 18	90 50
<i>cr</i> = 001 : 101	11	43 39—45 56	44 45	44 35
<i>pr</i> = 110 : 101	21	63 1—63 42	63 18	63 20
<i>rq</i> = 101 : 011	18	62 20—63 4	62 47	62 40
<i>qp</i> = 011 : 110	18	53 37—54 19	53 59	54 0 "

cis-Camphotricarboxylic Anhydride, $\text{COOH} \cdot \text{C}_7\text{H}_{11} < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{O}$.

cis-Camphotricarboxylic anhydride is formed, as already stated, when the *trans*-acid is heated at 150—160° with concentrated sulphuric acid, and it is deposited from the benzene extract of that portion of the product which is sparingly soluble in water. It may also be obtained by heating the *cis*-acid alone at about 180°, or by warming the acid with acetyl chloride for a short time. A sample which had been purified by crystallisation from ethereal benzene and then heated for a few minutes at 175°, to ensure the absence of any of the acid, was analysed.

0.1424 gave 0.2945 CO_2 and 0.0716 H_2O . C = 56.40; H = 5.58.

$\text{C}_{10}\text{H}_{12}\text{O}_5$ requires C = 56.60; H = 5.66 per cent.

cis-Camphotricarboxylic anhydride crystallises from ether in beautiful, transparent, six-sided plates, which slowly become opaque on exposure to the air, and rapidly effloresce at 50—60°, owing to the escape of ether of crystallisation; these crystals melt at 220—221° without decomposing. From benzene, the anhydride is deposited in long, transparent prisms, which also become opaque at ordinary temperatures, owing, doubtless, to the escape of benzene of crystallisation; their melting point is also 220—221°. The substance is very readily soluble in hot ether, acetone, and chloroform, but almost insoluble in boiling light petroleum; it is comparatively sparingly soluble in cold benzene, but dissolves readily on boiling. It dissolves slowly in cold water, but rapidly on warming; the solution has an acid reaction, and, on evaporation, gives a syrupy residue of the acid; the powdered substance is immediately dissolved by a cold dilute solution of sodium carbonate, carbon dioxide being evolved.

The anhydride is so readily reconverted into the acid that even when it is crystallised two or three times from ether, which has been dried over calcium chloride, the solutions give, on spontaneous evaporation, a considerable quantity of an oily deposit of the acid;

such residues, when simply heated at about 180° for a few minutes, are reconverted into the anhydride without charring.

When the *cis*-anhydride is heated at about 160° with concentrated sulphuric acid, it is gradually decomposed and carbonised, sulphur dioxide being evolved. When heated alone, in small quantities at a time, it distils apparently unchanged, and without charring to any appreciable extent.

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