LXXXVII.—*Derivatives of Camphoric Acid. Part II.*
Optically Inactive Derivatives.

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ALL the π -derivatives of inactive camphor which were studied by us some time ago (Trans., 1893, 63, 547; 1895, 67, 354, 371), namely, camphorsulphonic chloride, camphorsulphonic bromide, camphorsulphonamide, π -chlorocamphor, and π -bromocamphor, were carefully compared with the corresponding active compounds, the principal object being to ascertain whether the observed differences in properties between the several pairs of substances would throw any light on the phenomenon of racemism.

Since that time, a large number of optically active compounds, prepared from dextrorotatory π -bromocamphoric acid and less closely related to camphor, have been examined, both chemically and physically, in considerable detail (Trans., 1896, 69, 913—971), and the results of these observations were of such an interesting nature as to lead us to prepare the corresponding compounds of the inactive series, for the purpose of collecting further data relating to the character of externally compensated substances.

The experimental details of this work are recorded in the present paper, and may be briefly summarised as follows. By oxidising inac-

tive π -chlorocamphor and π -bromocamphor (Trans., 1895, 67, 371) with nitric acid, we have prepared inactive π -chlorocamphoric acid, $C_{10}H_{15}ClO_4$, and inactive π -bromocamphoric acid, $C_{10}H_{15}BrO_4$. The corresponding active acids have been previously described, the bromo-compound having been obtained by the oxidation of α - π -dibromocamphor (Trans., 1896, 69, 913), whilst the chloro-acid was prepared from α -bromocamphorsulphonic acid (Lapworth and Kipping, Trans., 1897, 71, 1) by a series of reactions which may be indicated as follows :

These four acids, two of which are optically active and two inactive, resemble one another very closely in all ordinary properties ; they are practically indistinguishable to the naked eye, and have not been obtained in individual crystals of any size, as they are invariably deposited from solvents either in very small crystals or in nodular, composite masses ; they all show very much the same behaviour towards solvents, and resemble one another closely in chemical properties, but they differ considerably in melting point, as is shown in the table given later.

The inactive chloro- and bromo-camphoric acids are readily converted into their anhydrides, and the two compounds thus obtained, although resembling the corresponding active compounds (Lapworth and Kipping, *loc. cit.*, and Trans., 1896, 69, 913), in most respects differ from them in not readily affording well-defined crystals of any size ; in the case of active π -bromocamphoric anhydride, for example, it is an easy matter to obtain large crystals, measurements of which are given later (p. 970), but we were unsuccessful in obtaining either of the inactive anhydrides in an equally suitable form. All four compounds are readily soluble in cold chloroform, whereas the acids are almost insoluble in this liquid, and they are all reconverted into the acids from which they are derived on treatment with concentrated nitric acid, as described in the case of *w*-bromocamphoric anhydride (Trans., 1896, 69, 61).

In the following table, the melting points* of these four acids and

* The following corrections applied to the melting points given in this paper show the values registered on a short standard thermometer with the thread almost entirely immersed. 110° (add 0.5°) ; 130° (add 1°) ; 150° (add 1.5°) ; 170° (add 3°) ; 200° (add 5°) ; 225 (add 6°) ; 250° (add 6.5).

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their anhydrides are given, but those of the former can only be taken as approximate, as, owing to anhydride formation, the observed melting point depends on the rate of heating and also varies with the size of the crystals.

	Active.	Inactive.
π -Chlorocamphoric acid	211—213°	194—195°
π -Chlorocamphoric anhydride	193—194	193—194
π -Bromocamphoric acid	216—217	201—203
π -Bromocamphoric anhydride	155—156	155—156

It may be pointed out that, whereas the inactive acids melt at a lower temperature than the corresponding active compounds, the inactive anhydrides have the same melting point as their active isomerides, and for this and other reasons may be regarded as pseudoracemic substances (compare following paper, p. 989). The further comparison of the properties of the above-mentioned somewhat poorly characterised inactive compounds with those of their active isomerides led to no very definite conclusions, and was not carried very far, as we hoped to obtain from them a series of inactive substances far more suitable for the purpose in view.

It has been already shown (Trans., 1896, 69, 929) that dextro-rotatory π -bromocamphoric acid is directly convertible into a lactonic monocarboxylic acid of the composition $C_{10}H_{14}O_4$, which, for reasons given at the time, was named *trans*- π -camphanic acid; further, that *trans*- π -camphanic acid, when distilled under atmospheric pressure, is converted into an isomeride, which is also a lactonic monocarboxylic acid, and which was called *cis*- π -camphanic acid; also that *trans*- π -camphanic acid is readily oxidised by nitric acid, giving a compound of the composition $C_{10}H_{14}O_6$, which received the name *trans*-camphotricarboxylic acid.

The following formulæ were then used to represent these three compounds, and, as recent work has only served to place Brecht's formula for camphor on a more secure foundation than before (compare preceding paper, p. 960), the three formulæ in question have also been more fully confirmed.

Now it was, of course, to be expected that three optically inactive substances, corresponding with these three active compounds, could be

prepared from inactive π -chloro- or π -bromo-camphoric acid by methods exactly similar to those previously employed, and experiment showed that this was the case.

Inactive trans- π -camphanic acid, prepared by treating π -chloro- or π -bromo-camphoric acid with sodium carbonate solution, is a well-defined, crystalline substance melting at 164—165°. We have not examined its chemical properties, except in two directions, as it may be taken for granted that they are identical with those of the active compound, but we have made a very careful comparison of the physical and crystallographic properties of the active and inactive isomerides.

The facts thus established show a very interesting relation between the two compounds, as will be seen from the following summary of the properties of the crystals obtained from various solvents, and by cooling the liquid substances :

ACTIVE trans- π -camphanic acid.	INACTIVE trans- π -camphanic acid.
Solvent—water.	Solvent—water.
Hydrated (1 mol. H ₂ O) monosymmetric prisms, $a:b:c=1.9110:1:1.4627$, $\beta=69^{\circ}5'$; melting point indefinite owing to presence of water of crystallisation.	Hydrated (1 mol. H ₂ O) monosymmetric prisms, $a:b:c=1.8105:1:1.4502$, $\beta=67^{\circ}41'$; indistinguishable from crystals of active acid except by goniometrical examination.
Solvent—ethylc acetate.	Solvent—ethylc acetate.
Hydrated (1 mol. H ₂ O) prisms, identical crystallographically with those from water.	Anhydrous, six-sided monosymmetric plates, $a:b:c=2.0157:1:1.19735$, $\beta=80^{\circ}5'$, which change in crystalline form at about 130°; m.p. 164—165°.
Solvent—benzene.	Solvent—benzene.
(a) Hydrated (1 mol. H ₂ O) orthorhombic needles, $a:b:c=0.9158:1:0.3551$; these crystals are deposited when solutions are exposed to ordinary moist air.	(a) Anhydrous rhomboidal plates, which differ only in habit from the six-sided plates mentioned above.
(b) Micro-crystalline, hygroscopic powder, probably anhydrous; obtained by crystallising over sulphuric acid.	
Solvent—chloroform.	Solvent—chloroform.
(a) Anhydrous orthorhombic prisms, $a:b:c=0.9584:1:0.7292$, which change in crystalline form at 100° and melt at 164—165°.	As from ethylc acetate and benzene.

Behaviour on cooling from the liquid state.

Changes in crystalline form twice; crystals first produced seem identical with those of the inactive acid which are first formed.

Changes in crystalline form three times.

Since these observations are discussed in the following paper, we will merely state here that the inactive *trans*- π -camphanic acid in the form of its anhydrous crystals must be regarded as a racemic compound, whereas the hydrated crystals of this substance consist of a non-homogeneous intercalation of the two antipodes and afford an example of what we call 'pseudoracemism.' It would seem that the hydrated substance cannot assume a type of structure compatible with its existence as a racemic compound, and consequently the nature of the solvent determines which of the two opposing tendencies, namely, to crystallise with water or to form a racemic compound, shall prevail.

Inactive *cis*- π -camphanic acid, prepared by distilling the inactive *trans*-isomeride, crystallises in large, transparent, hexagonal plates which are indistinguishable from those of the active acid, except in optical behaviour. Now, since it has been previously shown (Trans., 1896, 69, 971) that the crystals of the active acid are circularly polarising, it follows that if the crystals of the inactive substance are not those of a racemic compound they would also exhibit this interesting property; further, both right- and left-handed crystals must be deposited side by side.

Optical examination showed this to be the case, and we were thus able to separate the crystals of the dextro- from those of the lævo-rotatory acid, proving conclusively that the inactive *cis*- π -camphanic acid is a mere mixture of the two antipodes.

Inactive *trans*-camphotricarboxylic acid, $C_{10}H_{14}O_6$, which is easily obtained by oxidising inactive *trans*- π -camphanic acid, separates from cold water in lustrous, transparent, monosymmetric prisms, which differ from the crystals of the active acid deposited under the same conditions in being anhydrous, and consequently also in crystalline form. These facts show that inactive *trans*-camphotricarboxylic acid is a racemic compound. It melts at 224—225°, or about 30° higher than the corresponding active acid.

Inactive *trans*-camphotricarboxylic anhydride, $C_{10}H_{12}O_5$, seems to bear the same relation to the corresponding active compound as that existing between the hydrated monosymmetric crystals of the active and inactive *trans*- π -camphanic acids. It has the same melting point as the active anhydride, its melting point is not changed in intimate admixture with the latter, and the two substances have the same density; like the active compound (Trans., 1896, 69, 957), it forms monosymmetric crystals, and the two kinds, although quite distinct, show a remarkably close resemblance in crystalline form.

It is perhaps advisable to mention that the substances described in this paper have not been analysed; it seemed of little use to burn compounds, which had only been prepared with considerable trouble,

when their composition was already established by the analyses previously made in the case of the corresponding active compounds.

Optically Inactive π -Chlorocamphoric Acid, $C_{10}H_{15}ClO_4$.

The material used for the preparation of optically inactive π -chlorocamphoric acid consisted of samples of "inactive" camphorsulphonic chloride which had been prepared according to the method previously described (Trans., 1893, 63, 548), and then freed from excess of the dextrorotatory compound, so far as possible, first by repeated fractional crystallisation from ethylic acetate, and, afterwards, by picking out the crystals of the dextrorotatory substance. This material was heated at about 150° , and the product, which consisted of a mixture of optically inactive π -chlorocamphor with a considerable quantity of an oil of unknown nature, was purified by distilling it in steam. The π -chlorocamphor was then partially separated from the accompanying oil by fractional distillation, but, in order to avoid loss, this process was not carried very far, as the presence of the oil was found to be immaterial.

The oxidation of the π -chlorocamphor to optically inactive π -chlorocamphoric acid was effected by heating with a mixture of nitric acid of sp. gr. 1.4 (30 parts) and water (9 parts) just as described in the preparation of π -bromocamphoric acid (Trans., 1896, 69, 924). The oil of unknown nature was very readily attacked and dissolved, and at first the π -chlorocamphor sublimed into the condenser, but after heating during some hours the whole passed into solution. When the evolution of ruddy fumes abated, a considerable portion of the nitric acid was distilled off and the residue allowed to cool, whereupon crystals of impure π -chlorocamphoric acid were deposited; the solution was then decanted, mixed with the nitric acid which had been distilled off, and which contained some π -chlorocamphor, and boiled again during some hours. On subsequently evaporating to a small bulk, more π -chlorocamphoric acid was deposited, and the mother liquors, after further concentration, yielded a considerable quantity of oxalic acid, which had doubtless been formed by the oxidation of the oil contained in the π -chlorocamphor.

The crude π -chlorocamphoric acid, after being dried in the air and repeatedly washed with cold chloroform, was purified by recrystallisation from a mixture of ether and chloroform. An analysis was deemed superfluous, as, from its origin and properties, there could be no doubt that it had the composition $C_{10}H_{15}ClO_4$.

Optically inactive π -chlorocamphoric acid separates from a mixture of ether and chloroform in transparent, microscopic, oval crystals, and from concentrated nitric acid in transparent prisms or in flat rhom-

boidal plates; the crystals obtained from these and from other solvents are either too small for measurement or are aggregated together, forming indefinite, rosette-like masses. The acid melts fairly sharply at 194–195° when heated rapidly from about 150°, and does not darken appreciably, but on re-heating the solidified mass, the melting point is lower than before, doubtless owing to the presence of the anhydride; a finely-divided mixture of the optically inactive with the active chloro-acid (Lapworth and Kipping, *Trans.*, 1897, 71, 1) melts gradually between about 193° and 210°, but the result depends very much on the conditions of the experiment.

In all ordinary properties, optically inactive π -chlorocamphoric acid resembles the corresponding active acid very closely; it is readily soluble in cold methylic alcohol, acetone, acetic acid, and ether, but insoluble, or nearly so, in cold chloroform. It is only very sparingly soluble in boiling water, but dissolves freely in hot, concentrated nitric acid; its solution in the latter may be boiled for some time without any appreciable decomposition taking place, but in boiling aqueous solution the acid changes much more rapidly, and loses the elements of hydrogen chloride.

Optically inactive π -Chlorocamphoric Anhydride, $C_8H_{13}Cl \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} O$.

The acid just described, like its optical isomeride and the other acids of the π -series, is very readily converted into its anhydride by acetic chloride; on boiling a solution of the acid in this liquid for a short time and then evaporating, the anhydride remains as a crystalline mass, which is best purified by recrystallisation from a mixture of chloroform and ether. The crystals thus obtained consist of ill-defined nodular or fern-like masses quite different in appearance from the well-defined rhomboidal crystals of dextrorotatory π -bromocamphoric anhydride (see below), and from those of the optically active π -chlorocamphoric anhydride (Lapworth and Kipping, *loc. cit.*); crystallisation from other solvents failed to give measurable crystals.

Optically inactive π -chlorocamphoric anhydride melts at 193–194°, that is to say, at practically the same temperature as the acid from which it is derived; it is very readily soluble in cold chloroform, and dissolves freely in boiling ethylic acetate (small prisms on cooling), but is only sparingly soluble in boiling light petroleum and insoluble, or nearly so, in cold water and in a cold solution of sodium carbonate. It is appreciably soluble in boiling water, separating again on cooling in nodular crystals, and the aqueous solution does not acquire a distinctly acid reaction even after having been boiled; nevertheless, the anhydride may be converted into the acid without difficulty with the aid of concentrated nitric acid. It dissolves freely in the cold

acid (sp. gr. 1.4), and on heating the solution on the water bath the π -chloro-acid gradually separates either in fern-like crystals or in microscopic rhomboidal plates; this behaviour is similar to that of other anhydrides of halogen-substituted camphoric acids (compare Trans., 1896, 69, 61).

Optically Inactive π -Bromocamphoric Acid, $C_8H_{13}Br(COOH)_2$.

It was shown in an earlier paper (Trans., 1895, 67, 379) that, owing to the camphor-like nature of optically inactive π -chlorocamphor, it was almost impossible to decide whether the two optical antipodes united to form a true racemic compound or not; it appeared possible, therefore, that the inactive chlorocamphoric acid, prepared as described above, might contain a slight excess of one of the optically active modifications, which, although insufficient to be easily detected by optical examination, might yet effect to some extent the properties, not only of the acid itself, but also those of its derivatives. As it was essential that a possibility of this kind should be eliminated before studying the derivatives of the inactive acid, the corresponding π -bromocamphoric acid was prepared from the well-defined racemic π -bromocamphor previously described (*loc. cit.*); this bromo-acid, being known to be free from excess of either of the optical isomerides, was then used as a source from which to obtain pure optically inactive derivatives.

Optically inactive π -bromocamphoric acid is easily prepared by boiling racemic π -bromocamphor with moderately concentrated nitric acid during 6 to 8 hours; when the evolution of ruddy fumes has greatly diminished, the solution is diluted with a little water and kept for 24 hours; the acid, which is slowly deposited in colourless crystals, is dried in the air, washed with chloroform, and then recrystallised.

It separates from a mixture of ethylic acetate and chloroform in colourless, transparent, microscopic crystals, and in fern-like or nodular masses; it resembles the optically inactive chloro-acid very closely as regards general behaviour, and dissolves freely in cold ether, methylic alcohol, ethylic acetate, and acetone, but very sparingly in benzene; it is insoluble, or nearly so, in cold chloroform. It begins to sinter at about 197° and melts, effervescing vigorously, at about 203—204°, when rapidly heated from about 160°; the observed melting point, however, depends on the size of the crystals and on the rate of heating. A finely divided mixture of the inactive acid with dextrorotatory π -bromocamphoric acid (Trans., 1896, 69, 924) melts gradually from about 195 to 212°, the melting point of the active acid being about 216°. The other properties of the inactive acid need not be specially mentioned, as they are so similar to those of the other π -halogen derivatives of camphoric acid.

Optically Inactive π -Bromocamphoric Anhydride, $C_8H_{13}Br \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} O$.

Optically inactive π -bromocamphoric anhydride, prepared by boiling a solution of the acid in acetic chloride for a short time, crystallises from cold ether, in which it is moderately easily soluble, in small, but fairly well-defined prisms; it dissolves very freely in cold chloroform and ethylic acetate, but only very sparingly in cold light petroleum. It melts at $155\text{--}156^\circ$, that is to say, at the same temperature as the anhydride of the optically active bromo-acid, and its melting point is not lowered when it is intimately mixed with the active anhydride. It would seem, therefore, that the relation between the optically active and inactive compounds is similar to that which subsists in the case of the corresponding forms of *trans*-camphotricarboxylic anhydride; whereas, however, the crystals of the optically inactive π -brom-anhydride are usually small and unsuitable for measurement, those of the optically active compound are easily obtained of considerable size using either chloroform or ether as a solvent.

Active π -Bromocamphoric Anhydride.—The measurements of the crystals of the active anhydride had not been made at the time this compound was first described, and we therefore give them in this paper.

The crystals are large, of irregular shape, and extremely opaque owing to internal striation, so that their optical properties could not be ascertained.

Crystalline System :—Monosymmetric.

$$a : b : c = 1.0835 : 1 : 1.2340.$$

$$\beta = 91^\circ 0' 30''.$$

FIG. 1.

Forms present :— $a \{100\}$, $c \{001\}$, $r \{\bar{1}01\}$, $q \{011\}$, $p \{110\}$, $o \{\bar{1}11\}$.

The following angular measurements were made :

Angles.	Number of measurements.	Limits.	Mean.	Calculated.
<i>ac</i> 100:001	24	90° 0'—91° 47'	90° 59'	91° 0½'
<i>cr</i> 001:101	44	47 43—48 36	48 9	—
<i>ar</i> 100:101	28	40 16—41 20	40 57	40 50½
<i>cq</i> 001:011	37	50 24—51 36	50 58½	—
<i>qq</i> 011:011	35	77 46—78 57	78 16½	78 3
<i>ap</i> 100:110	21	46 54—47 59	47 15	47 17
<i>pp</i> 110:110	14	84 41—86 2	85 28	85 25
<i>ro</i> 101:111	17	38 17—39 33	38 59	38 54
<i>rp</i> 101:110	9	58 45—59 41	59 7	59 7
<i>pq</i> 110:011	39	55 3—56 25	55 43	—
<i>qr</i> 011:101	24	64 27—65 39	65 0½	65 9
<i>co</i> 001:111	8	58 1—59 4	58 37	58 43
<i>op</i> 111:110	19	30 5—30 57	30 39	30 35½
<i>pc</i> 110:001	12	90 11—91 15	90 53	90 41
<i>aq</i> 100:011	14	90 24—91 3	90 41	90 38

The predominant forms (Fig. 1) are usually *c* {001}, *a* {100}, *r* {101}, and *p* {110}, but the crystals are so variable in habit that *q* {011} and *o* {111}, which are frequently very small, sometimes become dominant; the faces of all forms give poor and indifferent reflections, so that a very large number of measurements was necessary. Considerable care was taken in order to obtain accurate results, in the hope that a morphotropic relationship might be established between the crystals of this substance and those of the isomeric *w*-bromocamphoric anhydride; attempts to discover such a relationship, however, were unsuccessful.

After having been melted, active π -bromocamphoric anhydride readily solidifies to a cubic modification; this, however, rapidly changes in crystalline form, and the film becomes converted into large individual flakes of a biaxial modification, in which one optic axis is sometimes perpendicular to the surface of the film, but the bisectrix never emerges perpendicularly.

It should be pointed out that active *w*-bromocamphoric anhydride is also dimorphous. After having been melted, it solidifies readily to a cubic modification, which, however, quickly changes into large individual flakes of a biaxial modification; these flakes are often perpendicular to an acute bisectrix of negative double refraction; the interference figure is a normal orthorhombic one.

When an aqueous solution of the sodium salt of inactive π -chlorocamphoric acid is boiled during a few minutes, sodium chloride is

formed, together with the sodium salt of optically inactive *trans*- π -camphanic acid; this simple decomposition is represented by the equation $C_{10}H_{13}ClO_4Na_2 = C_{10}H_{13}O_4Na + NaCl$.

As it has been previously shown that dextrorotatory *trans*- π -camphanic acid is a lactonic monocarboxylic acid derived from π -hydroxycamphoric acid, $OH \cdot C_8H_{13} \begin{smallmatrix} \nearrow COOH \\ \searrow COOH \end{smallmatrix}$, this must, of course, be equally true in the case of the inactive compound in question, and its constitution may therefore be expressed by the formula already given.

In preparing inactive *trans*- π -camphanic acid, the inactive π chlorocamphoric acid is suspended in warm water, and a solution of sodium carbonate is slowly run in until the whole of the acid is dissolved; after filtering, if necessary, from traces of oily impurity which are usually present in the crude chloro-acid, the solution is boiled during about 10 minutes, and then evaporated to a small volume; on adding a slight excess of dilute hydrochloric acid to the cold solution, the inactive *trans*- π -camphanic acid is precipitated in an oily or pasty condition, but it rapidly becomes hard and crystalline, and is then separated, washed, and recrystallised from dilute methylic alcohol.

As the first specimen which was obtained in this way appeared, on slight examination, to be identical with the dextrorotatory compound, it seemed not impossible that, during the various operations which occur in the conversion of camphorsulphonic chloride into *trans*- π -camphanic acid, the dextro-rotatory constituent of the only approximately inactive material had been partially fractionated out, and thus accumulated in considerable excess in the preparation in question; although an optical examination of the inactive acid failed to give any evidence of excess of either constituent, it seemed desirable to prepare another specimen from inactive π -bromocamphoric acid, which, for reasons already stated, cannot give other than optically inactive derivatives. This having been done, by a method exactly similar to that given above, and the two preparations having been found to be identical, we are justified in regarding the inactive acid now to be described as free from excess of either active component.

Inactive *trans*- π -camphanic acid resembles the dextrorotatory compound so closely in ordinary properties that at first it is not very easy to distinguish between them; as far as can be judged without actually making quantitative experiments, the solubility of the inactive acid in all ordinary solvents seems to be about the same as that of the dextrorotatory compound, and both acids melt at 164 — 165° ; moreover, a finely divided mixture of the two substances also melts at 164 — 165° .

On closer examination, however, considerable differences in behaviour are observed, as will be evident from the following comparative study of the two compounds.

*Comparison of Active and Inactive trans- π -Camphanic Acids.**Crystals from Aqueous Solutions.*

Active Acid.—This substance usually separates from cold water, in which it is only sparingly soluble, in large, fern-like aggregates, but by evaporating the solution slowly over sulphuric acid (compare E. Fischer and Beensch, *Ber.*, 1896, 29, 2929), well-defined, transparent prisms are deposited; these crystals contain $1\text{H}_2\text{O}$ (Trans., 1896, 69, 931) and become opaque when kept over sulphuric acid or when heated at 100° ; their behaviour on further heating has been previously described (*loc. cit.*). They consist of lustrous, flattened prisms measuring about 5 mm. in the direction of the a -axis, 1 mm. along the b -axis, and about 2 mm. along the axis c ; the faces of the form $c\{001\}$ are marked in parts by sharp-edged etch figures symmetrical to the plane of symmetry (010). There is a perfect cleavage parallel to $c\{001\}$ and an optic axis emerges nearly but not quite perpendicularly to this form; the dispersion is slight.

Goniometrical examination showed that these hydrated crystals are identical with those which were previously obtained (*loc. cit.*) by crystallisation from ethylic acetate, and we will therefore refer to the account there given of the comparative characters of the various forms, simply stating that a new form, namely $r'\{201\}$ has been observed to be frequently present upon the new crystals. The latter, however, are far better characterised than those formerly described, and therefore give measurements which lie between much narrower limits; for this reason, they were carefully examined, as it was necessary to establish the goniometric constants as accurately as possible in order to compare them with those of the inactive isomeride.

Crystalline system :—Monosymmetric.

$$a : b : c = 1.9110 : 1 : 1.4627.$$

$$\beta = 69^\circ 5'.$$

Forms present :— $a\{100\}$, $c\{001\}$, $q\{011\}$, $r\{\bar{1}01\}$ $r'\{201\}$.

The following angular measurements were obtained, the values previously given being stated in the last column :

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Angle.	Number of measurements.	Limits.	Mean.	Calculated.	
				New value.	Old values.
<i>cq</i> 001:011	26	53° 44'—53° 56'	53° 48'	—	53° 48'
<i>qq</i> 011:01 $\bar{1}$	18	72 12—72 43	72 24	72° 24'	72 24
<i>ac</i> 100:001	19	68 52—69 8	69 5	—	69 1
<i>cr</i> 001: $\bar{1}$ 01	14	44 22—44 47	44 32	—	44 33
<i>ar</i> $\bar{1}$ 00: $\bar{1}$ 01	11	66 6—66 49	66 22	66 23	66 26
<i>ar'</i> $\bar{1}$ 60: $\bar{2}$ 01	8	38 22—38 48	38 29	38 31	...
<i>rr'</i> $\bar{1}$ 01: $\bar{2}$ 01	7	27 24—27 56	27 49	27 52	...
<i>cr'</i> 001: $\bar{2}$ 01	3	72 24—72 31	72 27	72 25	...

Inactive Acid.—On allowing an aqueous solution of inactive *trans*- π -camphanic acid to evaporate spontaneously under as nearly as possible the same conditions as those employed in the case of the active acid, short, brittle, transparent prisms, which at first sight seem to have little in common with those of the latter, are deposited. These crystals become opaque when kept over sulphuric acid, and when heated at 100° they lose 1H₂O.

0.1543 lost 0.0131 H₂O at 100°. H₂O = 8.49 per cent.

C₁₀H₁₄O₄ + H₂O requires H₂O = 8.33 per cent.

When slowly heated from about 50°, they begin to become opaque at 90—95° and melt between 150° and 165°, according to the size of the crystals and the conditions of the experiment; when suddenly heated at about 125°, they liquefy, partly or entirely, in their water of crystallisation, then gradually become more or less solid again, and melt finally at 155—160°; this behaviour is similar to that of the hydrated crystals of the active acid.

These crystals are much more compact than those of the active acid, and usually differ less in linear dimensions along the three axial directions. The sizes of the various forms are in the same order as in the case of the active acid, although the differences in size are much less pronounced; the form *c*{001} is the predominant form, and this frequently exhibits etch figures very similar to those found on the crystals of the active substance, as in that case also the etchings are symmetrical to the plane of symmetry (010). Figures 2 and 3 represent the crystals of the active and inactive compounds respectively.

Crystalline system :—Monosymmetric.

$$a : b : c = 1.8105 : 1 : 1.4502.$$

$$\beta = 67^\circ 41'.$$

FIG. 2.

FIG. 3.

Forms present :— $a\{100\}$, $c\{001\}$, $q\{011\}$, $q'\{021\}$, $r\{\bar{1}01\}$, $r'\{\bar{2}01\}$.

Angle.	Number of measurements.	Limits.	Mean.	Calculated.
cq $001 : 011$	31	$52^\circ 49' - 53^\circ 34'$	$53^\circ 18'$	—
qq $011 : 01\bar{1}$	14	$73^\circ 1' - 73^\circ 58'$	$73^\circ 26'$	$73^\circ 24'$
ac $100 : 001$	29	$67^\circ 14' - 68^\circ 5'$	$67^\circ 41'$	—
cr $001 : \bar{1}01$	30	$46^\circ 29' - 47^\circ 2'$	$46^\circ 48'$	—
ar $\bar{1}00 : \bar{1}01$	27	$64^\circ 57' - 65^\circ 55'$	$65^\circ 80'$	$65^\circ 31'$
ar' $\bar{1}00 : \bar{2}01$	9	$36^\circ 48' - 37^\circ 31'$	$37^\circ 8'$	$37^\circ 7'$
rr' $\bar{1}01 : \bar{2}01$	11	$27^\circ 54' - 28^\circ 35'$	$28^\circ 10'$	$28^\circ 24'$
cr' $001 : \bar{2}01$	8	$74^\circ 50' - 75^\circ 38'$	$75^\circ 13'$	$75^\circ 12'$
qq' $011 : 021$	4	$16^\circ 1' - 16^\circ 19'$	$16^\circ 11'$	$16^\circ 16'$
$q'q'$ $021 : 02\bar{1}$	6	$40^\circ 21' - 41^\circ 7'$	$40^\circ 57'$	$40^\circ 53'$

One important difference between the crystals of the active and inactive acids may be noted, namely, that the faces of the former are plane and nearly always give but a single reflection, whereas those of the latter invariably show multiple images.

There is a good cleavage parallel to $c\{001\}$ and an optic axis emerges nearly normally to this form; the angle between the normal to $c\{001\}$ and this optic axial emergence seems, however, rather greater in the crystals of the inactive than in those of the active acid. The optic axial dispersion is slight, and the plane of symmetry is the optic axial plane.

A glance at the two series of angular measurements shows that the limits are not wide in either case, and a comparison brings to light the fact that, although the two sets of crystals are of the same type and

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extremely similar generally, yet the differences between them are quite distinct and cannot possibly be attributed to experimental error.

In the case of compounds such as these, which exhibit similarities of an isomorphous or morphotropic character, it is frequently found that the corresponding angles in one zone on the two crystals are more nearly equal than those in the other zones; this will be evident from the following table, which shows that there is closer similarity in the zone [100] than in the others:

	Angle.	Active acid.	Inactive acid.
<i>cq</i>	001 : 011	53° 48'	53° 18'
<i>qq</i>	011 : 01 $\bar{1}$	72 24	73 24
<i>ac</i>	100 : 001	69 5	67 41
<i>cr</i>	101 : $\bar{1}$ 01	44 32	46 48
<i>ar</i>	$\bar{1}$ 00 : $\bar{1}$ 01	66 23	65 31
<i>ar'</i>	$\bar{1}$ 00 : $\bar{2}$ 01	38 31	37 7
<i>cr'</i>	001 : $\bar{2}$ 01	72 24	75 12
<i>rr'</i>	$\bar{1}$ 01 : $\bar{2}$ 01	27 52	28 24

A comparison of the axial ratios and interaxial angles of the two substances brings to light the same fact.

Active acid. $a : b : c = 1.9110 : 1 : 1.4627$. $\beta = 69^\circ 5'$.

Inactive acid. $a : b : c = 1.8105 : 1 : 1.4502$. $\beta = 67.41$.

Crystals from Ethylic Acetate Solutions.

Active Acid.—It has already been mentioned that the hydrated crystals of the active acid which are deposited from water are identical with those obtained from cold ethylic acetate solutions, and in first describing the latter it was stated that they "become opaque at 100°, doubtless owing to the loss of included solvent or water" (Trans., 1896, 69, 931). An analysis showed that these crystals contain $1\text{H}_2\text{O}$, which is expelled at 100°.

0.2363 lost 0.0211 at 100°. $\text{H}_2\text{O} = 8.9$ per cent.

$\text{C}_{10}\text{H}_{14}\text{O}_4 + \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 8.3$ per cent.

They also lose their water when kept over sulphuric acid; when heated moderately quickly from about 50°, they become opaque at or below 105°, melt partially at about 110°, then solidify again, and melt finally at 164–165°.

Inactive Acid.—When inactive *trans*- π -camphanic acid crystallises slowly from ethylic acetate at ordinary temperatures, it is deposited in flat, transparent plates quite different in appearance from the crystals of the active acid obtained under similar conditions. These crystals also differ from those of the active acid in that they remain transparent when kept over sulphuric acid, or when heated during several hours in a water oven. When slowly heated in a capillary tube, they

undergo no visible change until the temperature rises to about $130-135^{\circ}$; they then become quite opaque, but without sintering, and melt on further heating at $164-165^{\circ}$. The fact that these crystals become opaque at $130-135^{\circ}$ is not due to loss of solvent or water of crystallisation, but to a change in crystalline form taking place; that they are anhydrous was proved firstly, by heating a weighed quantity at 100° , when no loss in weight occurred, and secondly, by dissolving a weighed quantity of the dehydrated substance in ethylic acetate and evaporating to dryness at ordinary temperatures, when no gain in weight occurred.

These anhydrous crystals of the inactive acid consist of six-sided, very lustrous, monosymmetric plates (Fig. 4); the pinacoid, $c\{001\}$, is the dominant form, and gives good results on measurement. The forms $a\{100\}$ and $r\{\bar{1}01\}$ are usually small, but give good reflections; the pyramid $o\{\bar{1}11\}$ is generally fairly well developed, but the form $p\{110\}$ is very seldom present.

Crystalline system :—Monosymmetric.

$$a : b : c = 2.0155 : 1 : 1.9733$$

$$\beta = 80^{\circ} 5'$$

FIG. 4.

Forms present :— $a\{100\}$, $c\{001\}$, $r\{\bar{1}01\}$, $o\{\bar{1}11\}$, $p\{110\}$.

The following angular measurements were obtained :

Angle.	Number of measurements.	Limits.	Mean.	Calculated.
ac $100:001$	24	$79^{\circ} 48' - 80^{\circ} 24'$	$80^{\circ} 5'$	—
ac $\bar{1}00:001$	6	$99^{\circ} 50' - 100^{\circ} 12'$	$99^{\circ} 58'$	$99^{\circ} 55'$
cr $001:\bar{1}01$	3	$49^{\circ} 1' - 49^{\circ} 38'$	$49^{\circ} 16'$	$49^{\circ} 14'$
ra $\bar{1}01:100$	5	$50^{\circ} 26' - 50^{\circ} 59'$	$50^{\circ} 45'$	$50^{\circ} 41'$
co $001:\bar{1}11$	13	$68^{\circ} 48' - 69^{\circ} 37'$	$69^{\circ} 10'$	$69^{\circ} 2'$
op $\bar{1}11:\bar{1}10$	7	$25^{\circ} 1' - 25^{\circ} 56'$	$25^{\circ} 29'$	$25^{\circ} 25'$
pc $110:001$	3	$85^{\circ} 9' - 85^{\circ} 41'$	$85^{\circ} 26'$	$85^{\circ} 33'$
oo $11\bar{1}:\bar{1}11$	21	$66^{\circ} 10' - 66^{\circ} 42'$	$66^{\circ} 27'$	—
oo $11\bar{1}:11\bar{1}$	17	$113^{\circ} 21' - 113^{\circ} 50'$	$113^{\circ} 33'$	$113^{\circ} 33'$
ao $\bar{1}00:\bar{1}11$	18	$68^{\circ} 59' - 70^{\circ} 18'$	$69^{\circ} 41'$	—
pa $110:100$	5	$62^{\circ} 58' - 63^{\circ} 37'$	$63^{\circ} 20'$	$63^{\circ} 16'$

There is a perfect cleavage parallel to $c\{001\}$; the optic axial plane is perpendicular to the plane of symmetry and the acute bisectrix emerges obliquely through $c\{001\}$. The optic axial angle is fairly large, and the double refraction positive in sign.

These anhydrous crystals are always well-developed, and never show the vicinal faces exhibited by the hydrated crystals of the acid; that they are quite different from the latter is obvious from the above description, and that they represent crystals of a racemic modification of *trans*- π -camphanic acid will be shown in the following paper.

Crystals from Benzene Solutions.

Active Acid.—Wishing to obtain anhydrous crystals of the active acid, in order to compare them with those of the inactive acid which have just been described, we next tried benzene as a solvent. The dehydrated active acid dissolves fairly easily in boiling benzene, and on allowing the cold solution to evaporate spontaneously in the air, small lustrous, transparent flattened needles slowly separate round the edges of the vessel, close to the surface of the liquid, whilst a few fern-like masses are deposited at the bottom of the vessel.

When these needles are slowly heated in a capillary tube, they remain transparent until the temperature rises to about 130° , and then gradually become opaque, melting at 164 – 165° ; when suddenly heated at about 160° , they do not show any signs of sintering. From this behaviour, which is practically identical with that of the anhydrous crystals of the inactive acid, it seemed probable that these needles were free from water of crystallisation; this, however, is not so, as when heated in a water oven they slowly become opaque, and lose in weight.

0.2921 air-dried substance lost 0.0243 at 100° . $\text{H}_2\text{O} = 8.3$.

$\text{C}_{10}\text{H}_{14}\text{O}_4 + \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 8.3$ per cent.

Nevertheless, goniometric examination showed that they are quite different from the crystals of the active acid which are deposited from water or ethylic acetate. They belong to the orthorhombic system, and are shown in Fig. 5.

The pinacoid $b\{010\}$ is the dominant form, and gives good images; the prism $p\{110\}$ is much smaller, but still gives good results on measurement. The dome $q\{011\}$ is small, and, owing to the great brittleness of the crystals, is not often obtained in measurable form; the measurements in which it is implicated may, however, be taken as fairly accurate. This dome form, however, is generally nearly wholly absent, because of the existence of a hollow cone which partly takes its place (Fig. 6). The crystals are elongated in the direction of the c -axis, and the forms $b\{010\}$ and $p\{110\}$ are striated in the direction of that axis.

Crystalline system :—Orthorhombic.

$$a : b : c = 0.9158 : 1 : 0.3551.$$

FIG. 5.

FIG. 6.

Forms present :— $b\{010\}$, $p\{110\}$, $q\{011\}$.

Angle.	Number of measurements.	Limits.	Mean.	Calculated.
bp $010 : 110$	18	$47^{\circ} 20' - 47^{\circ} 42'$	$47^{\circ} 31'$	—
pp $110 : \bar{1}10$	7	$84^{\circ} 46' - 85^{\circ} 4'$	$84^{\circ} 57'$	$84^{\circ} 58'$
bq $010 : 011$	16	$70^{\circ} 18' - 70^{\circ} 41'$	$70^{\circ} 27'$	—
qq $011 : 0\bar{1}1$	11	$38^{\circ} 56' - 39^{\circ} 24'$	$39^{\circ} 12'$	$39^{\circ} 6'$

The optical characters are those of normal orthorhombic crystals, although, owing to their small size and low double refraction, it could not be ascertained which of the three pinacoids is parallel to the optic axial plane; a bisectrix seems to emerge normally to $b\{010\}$.

The great tendency shown by active *trans*- π -camphanic acid to crystallise with $1H_2O$, forming two distinct hydrated crystalline modifications, is especially noteworthy, in view of the fact that the inactive isomeride is easily obtained in anhydrous crystals, and only combines with water when deposited from aqueous solvents. Even when the active acid is crystallised from benzene which has been carefully dehydrated, it still gives the hydrated orthorhombic crystals under the conditions stated above, the necessary moisture being obtained from the air; this explains why these crystals always form at or close to the surface of the benzene. When, however, the solution is so concentrated that crystallisation occurs on cooling, or when it is allowed to evaporate in a dry atmosphere, the acid is deposited either in large, fern-like, crystalline masses, or in the form of a microcrystalline powder.

These crystals appear to be anhydrous, as they do not lose in weight

when heated ; moreover, a sample of the crystalline powder which was exposed to the air at ordinary temperatures, gradually *gained* in weight during about two weeks, after which its weight became constant ; in the one quantitative experiment which was made, 0.2164 gram of substance gained 0.0152 gram H_2O , or about 7.02 per cent. At the same time, the substance slowly underwent a distinct change in appearance, the indefinite microcrystalline powder being transformed into small, opaque needles.

Although, therefore, it is evident that anhydrous crystals of the active acid are deposited from benzene under certain conditions, they are too small and ill-defined to be of any use for goniometric examination.

Inactive Acid.—When the inactive acid is crystallised from benzene at ordinary temperatures, it is deposited in well-defined, transparent, rhomboidal plates, which are identical crystallographically with the six-sided crystals obtained from ethylic acetate, although they differ from the latter in habit ; their behaviour when heated is consequently the same as that of the anhydrous crystals in question.

Crystals from Chloroform Solutions.

Active Acid.—Crystallisation from anhydrous benzene having failed to afford measurable anhydrous crystals of active *trans- π* -camphanic acid which could be compared with those of the inactive compound, we tried the use of other solvents, and finally succeeded with the aid of a mixture of chloroform and light petroleum. The dehydrated acid dissolves freely in cold chloroform, but is much less readily soluble in light petroleum, so that, on the addition of the latter to its solution in the former, it is precipitated as a crystalline powder ; this powder does not lose in weight when heated in a water oven during several hours.

On allowing a solution in a mixture of the above two solvents to evaporate at ordinary temperatures, various kinds of crystals are obtained, according to the conditions of the experiment. Sometimes long, flattened, ill-defined prisms, and large, transparent, extremely thin plates are deposited, chiefly at or near the surface of the liquid. Both these forms rapidly become opaque when heated in the water-oven, and are apparently hydrated crystals, identical with, or differing merely in habit from, the flattened hydrated needles obtained from benzene solution. In other cases, or accompanying the crystals just described, fairly large, highly lustrous, well-defined, transparent prisms, having almost the outline of cubes, are deposited at the bottom and on the sides of the vessel ; these prisms sometimes appear to become slightly opaque on exposure to the air, and soon do so when heated in the water oven, but without losing in weight. Many quantitative experiments which were made with preparations deposited

from mixtures of chloroform and light petroleum showed in some cases a loss in weight of 1 to 2 per cent. at 100° , whereas in others the loss was negligible; such preparations, therefore, consisted principally of anhydrous crystals, but also contained some hydrated ones. A sample consisting only of the cube-like prisms, each of which had been picked out separately, did not alter in weight when heated during 4 hours at 100° , although every crystal had become quite opaque, doubtless owing to a change in crystalline form.

These cube-like prisms (Fig. 7), which represent, therefore, anhydrous crystals of active *trans*- π -camphanic acid, are orthorhombic; the dominant form is usually $p\{110\}$, and gives good results on measurement, but the pinacoid $c\{001\}$ is also frequently of considerable size. The dome $r\{101\}$ is generally small, but lustrous; the pinacoid $b\{010\}$ is rarely observed, and when present is small. The tetrahedron $o\kappa\{111\}$ is very small, and whenever it is present no faces of the complementary tetrahedron are observed; for this reason we describe the crystals as sphenoidally hemihedral.

Crystalline system:—Orthorhombic. Sphenoidal Hemihedrism.

$$a : b : c = 0.9584 : 1 : 0.7292.$$

FIG. 7.

Forms present:— $b\{010\}$, $c\{001\}$, $p\{110\}$, $r\{101\}$, $o\kappa\{111\}$.

The following angular measurements were made:

Angle.	Number of measurements.	Limits.	Mean.	Calculated.
cr 001 : 101	24	$36^{\circ} 29' - 37^{\circ} 53'$	$37^{\circ} 16'$	—
rr 101 : 10 $\bar{1}$	11	$104^{\circ} 33' - 105^{\circ} 54'$	$105^{\circ} 19'$	$105^{\circ} 28'$
pp 110 : 1 $\bar{1}0$	36	$91^{\circ} 39' - 92^{\circ} 59'$	$92^{\circ} 26'$	—
pp 110 : 1 $\bar{1}\bar{0}$	31	$86^{\circ} 58' - 88^{\circ} 1'$	$87^{\circ} 31'$	$87^{\circ} 34'$
bp 010 : 110	20	$45^{\circ} 48' - 46^{\circ} 57'$	$46^{\circ} 16'$	$46^{\circ} 13'$
op 111 : 110	8	$43^{\circ} 1' - 44^{\circ} 8'$	$43^{\circ} 37'$	$43^{\circ} 30'$
oc 111 : 001	9	$45^{\circ} 26' - 47^{\circ} 0'$	$46^{\circ} 21'$	$46^{\circ} 30'$
or 111 : 101	12	$29^{\circ} 43' - 30^{\circ} 47'$	$30^{\circ} 14'$	$30^{\circ} 8'$

The crystals possess a perfect cleavage parallel to $c\{001\}$, and the axis- c is apparently the obtuse bisectrix.

A certain morphotropic resemblance would seem to exist between the orthorhombic hydrated crystals of *trans*- π -camphanic acid and the anhydrous crystals just described; this is shown by a comparison of the axial ratios of the two substances when written in the following form:

Hydrated crystals:— $a : b : c/2 = 0.9158 : 1 : 0.3551$

Anhydrous „ $a : b : c = 0.9584 : 1 : 0.3646$

Referring the crystals to these axial ratios, corresponding angles in the principal zone $[100]$ would be very nearly equal, and corresponding angles lying in the other two co-ordinate planes would not differ greatly; this case presents certain similarities to that of camphoric acid and its anhydride (Trans., 1896, 69, 1696).

Before concluding this account of the various crystalline forms of the two *trans*- π -camphanic acids, it may be mentioned that the behaviour of various samples of crystals of the active acid, deposited from a mixture of chloroform and light petroleum, is in some respects indicative of the existence of two anhydrous crystalline modifications; when, for example, the proportion of light petroleum present is comparatively small, the acid separates in long, massive, highly transparent, well-defined prisms, which although similar so far as the eye can judge, show a different behaviour when they are heated in a water-oven; under these conditions, about half the crystals gradually become opaque in the course of an hour or two, but without losing in weight to any appreciable extent, whereas the rest remain quite transparent, even after heating during 10—12 hours. In other cases, apparently when the proportion of light petroleum is large, the acid is deposited in crystals having quite a different appearance, namely, in small, ill-defined, transparent but slightly clouded prisms, all of which retain their lustre even after prolonged heating in the water oven.

It would seem, therefore, that the active acid may be obtained from such solutions in two anhydrous crystalline modifications, one of which, namely, the orthorhombic form described above, is unstable at 90—100° whilst the other undergoes no change in crystalline form at this temperature.

Behaviour during Cooling from the Liquid State.

On melting a little of either of the two *trans*- π -camphanic acids on a microscopic slide under a cover-slip, and then allowing the liquid to solidify, a crystalline film is obtained suitable for microscopic examination; the behaviour of the two acids under these conditions is, at first, extremely similar, as they both solidify readily, giving broad individual

crystalline patches which extinguish uniformly; these patches are strongly marked with straight lines, usually lying at an angle of about 60° to each other, and are uniaxial or slightly biaxial with positive double refraction. The appearances and characteristics of the two films when examined in polarised light are so similar as to be indistinguishable, thus affording strong evidence that at, or near, the melting point, the two acids are crystallographically of identical structure; the fact that they have the same melting point is thus explained.

Both acids are polymorphous, and the crystalline films when preserved at ordinary temperatures change slowly but in different ways.

The *inactive* acid is slowly transformed into a modification which grows from centres in radiate masses showing aggregate polarisation; this form is biaxial and shows negative double refraction. After several days, however, this form in turn undergoes gradual conversion into a third crystalline modification; this consists of an extremely confused mass, which shows aggregate polarisation to such an extent that its crystallographic properties could not be ascertained.

The first obtained crystalline modification of the *active* acid seems to undergo only one change at ordinary temperatures, being gradually converted into a form which shows aggregate polarisation and which, consequently, could not be further characterised.

Judging from the whole behaviour of the films of these two substances, it would seem that, although the crystalline forms are apparently identical at, or near, the melting point, they subsequently become dissimilar; this can only be due to the formation of a racemic compound in the case of the externally compensated substance, and as already demonstrated, the anhydrous acid is readily obtained as a racemic compound by crystallisation at the ordinary temperature. It has also been mentioned that the anhydrous crystals both of the active acid and of the racemic compound become opaque when heated owing to a change in crystalline form; this fact affords further evidence in support of the conclusion that the two substances are of identical crystalline structure at, or near, the common melting point.

Owing to the fact that both active and inactive acids are appreciably soluble in all the solvents at our disposal, we were unable to determine the densities of the crystals.

Dextrorotatory *trans- π -camphanic acid* is partly converted into a stereochemical isomeride when it is distilled under ordinary atmospheric pressure, small quantities of a neutral substance of the composition $\text{C}_{20}\text{H}_{26}\text{O}_7$, probably a lactoanhydride, being also formed (Trans., 1896, 69, 934). As was to be expected, the inactive *trans- π -camphanic acid*

just described undergoes a similar intramolecular change on distillation and yields two products, namely, inactive *cis*- π -camphanic acid, and a substance which doubtless corresponds with the lactoanhydride obtained from the dextrorotatory acid.

The preparation and separation of these two inactive substances are carried out exactly as described for the preparation of laevorotatory *cis*- π -camphanic acid from π -hydroxycamphoric acid, and need not be repeated.

Inactive *cis*- π -camphanic acid resembles the corresponding active compound so closely that it is impossible to distinguish one from the other except by optical examination; the two compounds melt at the same temperature (at about 226°) when heated separately or when intimately mixed, and all the varied crystalline habits of the active acid are met with again on crystallising the inactive substance from various liquids; even slight differences in behaviour such as have been mentioned in the comparative description of the *trans*- π -camphanic acids are never observed.

Such a close agreement in properties almost forced us to the conclusion that the two optically active modifications of *cis*- π -camphanic acid do not combine to form a racemic compound, but crystallise separately, side by side, when deposited from solution.

This conclusion was verified by experiment. When the inactive *cis*- π -camphanic acid is very slowly crystallised from a cold mixture of methylic alcohol and chloroform, it is deposited in large, flat, hexagonal plates, similar to those which have been already described in the case of the laevorotatory acid (Trans., 1896, 69, 971). A number of these crystals from various crops were examined in polarised light, right- and left-handed circularly polarising quartz plates being used as before, and it was thus proved that some of the crystals were dextro-, others laevo-rotatory. Large crops of crystals were usually found to contain an approximately equal number of crystals of each kind, but other samples, which had been removed from the solution when only 10—20 separate crystals had been deposited, frequently consisted of a much larger number of one or other modification; this fact is, of course, easily accounted for, as there would probably be a tendency for the first crystal to promote the deposition of others of the same kind until the solution became more or less supersaturated towards crystals of the opposite modification.

The inactive lactoanhydride referred to above separated from methylic alcohol in well-defined, but very small, transparent crystals, apparently quite different from the long needles of the corresponding active compound; owing to the small quantity at our disposal, we were unable to examine this substance very fully, and although it seemed to be a racemic compound, we did not arrive at a definite conclusion.

Optically Inactive trans-Camphotricarboxylic Acid, $C_{10}H_{14}O_6$.

Inactive *trans*-camphotricarboxylic acid can be easily obtained from inactive *trans*- π -camphanic acid by dissolving the latter in a small quantity of concentrated nitric acid, and heating the solution on the water-bath; after a short time, the tricarboxylic acid begins to separate in lustrous, transparent, fern-like crystals, free from any appreciable quantity of foreign matter except nitric acid, which they seem to retain in small quantities. Inactive *trans*-camphotricarboxylic acid is readily soluble in cold water, but less soluble in concentrated nitric acid; it also dissolves freely in alcohol and acetone, but is comparatively sparingly soluble in ethylic acetate and in ether, and is precipitated by the last named from its solutions in methylic alcohol; it is insoluble, or nearly so, in chloroform.

It usually separates from cold water in white, opaque aggregates, composed of transparent prisms, but when crystallisation takes place very slowly these prisms are obtained as separate individuals of considerable size; unlike the crystals of the active acid (*Trans.*, 1896, 69, 951), they are anhydrous and do not become opaque or lose in weight at 100° . When quickly heated from about 80° in a capillary tube, they remain transparent until the temperature rises to 180° ; at about this temperature, it can be clearly seen, in the case of the larger crystals, that some change occurs, as the prisms either become opaque, or disintegrate with such violence that portions are sometimes projected a considerable distance up the tube; on continued heating, the substance seems to begin to sinter at about 210° and then melts at $224\text{--}225^\circ$ effervescing vigorously and charring slightly.

The transparent prisms just referred to seem to be an unstable, crystalline form of the acid, as they often become opaque when warmed in contact with the supernatant saturated solution. Similar crystals are obtained when the acid slowly separates from a dilute solution in acetic acid.

Since active *trans*-camphotricarboxylic acid crystallises in lustrous hydrated pseudo-hexagonal orthorhombic plates which have very interesting properties (*Trans.*, 1896, 69, 978), the crystallographic examination of the inactive acid was especially desirable, and was made with crystals obtained from aqueous solutions; although further evidence of the racemic character of the compound was thus adduced, the results, unfortunately, were not of any particular interest in other ways.

The crystals consist of large, monosymmetric prisms (Fig. 8), which, although highly lustrous, are not very well suited for goniometric examination; they are usually of rhomboidal shape, the forms $c\{001\}$ and $p\{110\}$ being the dominant forms. The pyramid $o\{111\}$ is always very small but brilliant.

Crystalline system :—Monosymmetric.

$$a : b : c = 0.8264 : 1 : 0.5764.$$

$$\beta = 61^\circ 17'.$$

FIG. 8.

Forms present :— $c\{001\}$, $p\{110\}$, and $o\{\bar{1}11\}$.

The following angular measurements were made :

Angle.	Number of measurements.	Limits.	Mean.	Calculated.
op $11\bar{1} : 110$	12	$62^\circ 13' - 63^\circ 37'$	$62^\circ 48'$	$63^\circ 3'$
cp $001 : 110$	18	$66^\circ 47' - 67^\circ 27'$	$67^\circ 6'$	—
co $001 : \bar{1}11$	15	$49^\circ 10' - 50^\circ 30'$	$49^\circ 51'$	—
pp $110 : \bar{1}\bar{1}0$	17	$71^\circ 21' - 72^\circ 36'$	$71^\circ 52'$	—
$\bar{p}p$ $110 : \bar{1}10$	14	$107^\circ 36' - 108^\circ 53'$	$108^\circ 11'$	$108^\circ 8'$

The extinction through $p\{110\}$ makes 26° with the edge $110 : \bar{1}10$ and 47° with the edge $110 : 001$; the optic axial plane is the plane of symmetry and an optic axis emerges through $c\{001\}$ in the real obtuse angle β .

Optically Inactive trans-Camphotricarboxylic Anhydride, $C_{10}H_{12}O_5$.

Inactive *trans*-camphotricarboxylic acid dissolves very slowly in warm acetic chloride and on evaporating the solution after having boiled during about 20 minutes, the anhydride is slowly deposited in crystals; it is easily purified by recrystallisation from a mixture of ether and chloroform.

Inactive *trans*-camphotricarboxylic anhydride melts at $253-254^\circ$ without darkening, and sublimes at even lower temperatures; its melting point is the same as that of the corresponding active compound

(Trans., 1896, 69, 957), and a mixture of the two anhydrides also melts at 253—254°. It dissolves freely in cold chloroform, methylic alcohol, and boiling ether, but is only moderately or sparingly soluble in boiling benzene and insoluble or nearly so in boiling light petroleum; it is only slightly soluble in cold water, to which it imparts an acid reaction, but it dissolves readily in cold dilute sodium carbonate, causing effervescence.

The crystals deposited from a mixture of ether and chloroform are lustrous, transparent, monosymmetric plates (Fig. 9), much smaller than the crystals of the active acid obtained under similar conditions, and which have been previously measured (Trans., 1896, 69, 958); the pinacoid, $a\{100\}$, is usually dominant, but the crystals are very variable in habit and the form $q\{011\}$ is sometimes dominant. The two forms $a\{100\}$ and $q\{011\}$, are frequently the only ones present, and the crystals are then of rhombohedral habit. The faces are all poorly developed, give multiple images, and do not fall properly into zones, so that the agreement between the calculated and observed values is not very close; they thus contrast strongly with the crystals of the active anhydride. The form $p\{120\}$ is very seldom observed.

Crystalline system:—Monosymmetric.

$$a : b : c = 0.6053 : 1 : 0.6374.$$

$$\beta = 62^\circ 12'.$$

FIG. 9.

Forms present:— $a\{100\}$, $c\{001\}$, $r\{\bar{1}01\}$, $q\{011\}$, and $p\{120\}$.

Angle.	Number of measurements.	Limits.	Mean.	Calculated.
ar 100 : $\bar{1}0\bar{1}$	24	56° 2' — 56° 58'	56° 27'	—
cr 001 : $\bar{1}01$	23	60 20 — 62 12	61 27	61° 21'
ac 100 : 001	26	61 32 — 63 4	62 12	—
aq 100 : 011	9	64 22 — 66 54	65 44	66 2
aq $\bar{1}00$: 011	14	113 9 — 115 38	114 32	113 58
cq 001 : 011	21	28 44 — 29 58	29 25	—
qq 011 : $0\bar{1}\bar{1}$	8	58 46 — 59 24	59 12	58 50
qq 011 : $0\bar{1}1$	17	120 24 — 122 0	121 4	121 10
ap 100 : 120	8	46 10 — 48 5	47 5	46 58
pp 120 : $\bar{1}20$	7	84 16 — 86 59	85 33	86 4

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The optical properties of the crystals of the inactive anhydride, in so far as they can be determined microscopically, are identical with those of the crystals of the active compound; in both cases, it is doubtful whether the optic axial plane is the plane of symmetry or perpendicular thereto, but one or both optic axes emerge through $a\{100\}$ in the angle ar . The crystals are very brittle and too small to allow of sections being cut.

The very close crystallographic similarity between the active and inactive anhydrides is evident from a comparison of their principal angles and their axial data.

	Inactive.	Active.
ac 100:001	$62^{\circ} 12'$	$63^{\circ} 28'$
cr 001: $\bar{1}01$	61 21	60 2
ar 100:10 $\bar{1}$	56 27	56 30
aq 100:011	66 2	67 3
cq 001:011	29 25	29 14

Inactive. $a:b:c = 0.6053:1:0.6374$. $\beta = 62^{\circ} 12'$.

Active. $a:b:c = 0.6007:1:0.6255$. $\beta = 63^{\circ} 28'$.

On melting the inactive substance on a microscopic slide under a cover-slip, and then allowing it to solidify, it is found to be trimorphous, and the behaviour of the crystalline film thus obtained is indistinguishable from that of the active acid; the description given of the latter (Trans., 1896, 69, 959) therefore holds for both.

The densities of the inactive and active anhydrides were determined by Retger's method, the crystals being floated in a solution of mercuric potassium iodide; the results obtained are as follows, and are obviously identical within the limits of experimental error.

Inactive anhydride sp. gr. $18^{\circ}/16^{\circ} = 1.3890$

Active „ „ „ = 1.3894

We conclude from the above observations that the crystals of inactive *trans*-camphotricarboxylic anhydride obtained in the manner described are those of a pseudoracemic substance (compare following paper).

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