XLIII.— π -Halogen Derivatives of Camphor.

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THE sulphonic chlorides and bromides of camphor, α -chlorocamphor, and α -bromocamphor, which we have described in former papers (Trans., 1893, **63**, 548, and this vol., p. 354), when heated alone at temperatures below 180° , are decomposed into sulphur dioxide and simple halogen derivatives of camphor; this change may be represented by the equation

in which X represents H, Cl, or Br, and Y is Cl or Br.

The compounds prepared in this way are seven or eight in number, namely, two monochlorocamphors (dextrorotatory and racemic or inactive), two monobromocamphors (dextrorotatory and racemic), one dichlorocamphor (dextrorotatory), one dibromocamphor (dextrorotatory), and one, probably two, dextrorotatory chlorobromocamphors.

As these substances are not identical with the corresponding halogen derivatives of camphor which are already known, we propose to distinguish them, at any rate provisionally, by using the letter π (recalling their pyrogenic formation) to denote that halogen atom (Y) which, originally, is contained in the sulphonic group; in the case of the new di-halogen derivatives, therefore, the one halogen atom is distinguished by π , the other (X) by α , the sulphonic derivatives themselves having been prepared from the ordinary halogen compounds which are usually classed as α -derivatives.

For the sake of clearness, we give, in the first place, a list of those chloro-, bromo-, and chlorobromo-derivatives of camphor, containing one or two atoms of halogen, which have been prepared up to the present time.

The table (p. 372) includes, we believe, all the simple chloro- and bromo-derivatives of camphor, containing one or two atoms of these halogens, which have been described; it is possible—even probable—however, that of all the above mono-halogen compounds, only the α -, i -, and π -derivatives have any real existence, and we hope in the near future to curtail this formidable list by proving this to be the case.

The preparation of the π -halogen derivatives described in this paper is, as a rule, an extremely simple operation, as it is only necessary to heat the sulphonic chloride or bromide for a short time at a temperature ranging from 140° to 180° until the evolution of sulphur dioxide is practically at an end; in some cases, a portion

	Prepared by	M. p.	Rotatory power.
Monochlorocamphor, $C_{10}H_{15}ClO$	{ Wheeler, <i>Annalen</i> , 146 , 81.....	95°	—
α -	{ Cazeneuve, <i>Compt. rend.</i> , 109 , 229 ...	124—125°	$[\alpha]_D = +40^\circ$
β -	Cazeneuve, <i>Bull. Soc. Chim.</i> , 38 , 9 ...	96°	$[\alpha]_D = +90^\circ$ †
π -	" " 39 , 116 ..	100°	$[\alpha]_D = +90^\circ$
π -	Kipping and Pope, this paper.....	139—139.3°*	$[\alpha]_D = +99.9^\circ$
Monobromocamphor, $C_{10}H_{15}BrO$	" " ".....	138—138.3°	Inactive.
α -	Cazeneuve, <i>Compt. rend.</i> , 109 , 444	144—145°	$[\alpha]_D = +40^\circ$
β -	Maisch, <i>Jahresb.</i> , 1873 , 499.	76°	$[\alpha]_D = +132—139^\circ$
ι -	Marsh, <i>Trans.</i> , 57 , 82.	61°	$[\alpha]_D = +29.4^\circ$
π -	Haller, <i>Compt. rend.</i> , 105 , 66	51°	Inactive.
π -	Kipping and Pope, this paper.....	93.4°	$[\alpha]_D = +116^\circ$
α -Dichlorocamphor, $C_{10}H_{11}Cl_2O$	" " ".....	92.7°	Inactive.
β -	Cazeneuve, <i>Bull. Soc. Chim.</i> , 37 , 454. ..	96°	$[\alpha]_D = +57.3^\circ$
$\alpha\pi$ -	" " ".....	77°	$[\alpha]_D = +60.6^\circ$
α -Chlorobromocamphor, $C_{10}H_{14}ClBrO$	Kipping and Pope, this paper.....	118—118.5°	$[\alpha]_D = +86.7^\circ$
β -	Cazeneuve, <i>Bull. Soc. Chim.</i> , 44 , 116. ...	98°	$[\alpha]_D = +78^\circ$
$\alpha\pi$ -	" " ".....	51.5°	$[\alpha]_D = +51^\circ$
$\pi\alpha$ -	Kipping and Pope, this paper.....	138—138.5°	$[\alpha]_D = +85.2^\circ$
α -Dibromocamphor, $C_{10}H_{14}Br_2O$	" " ".....	132—133°?	$[\alpha]_D = +107.5^\circ$?
β -	Kachler and Spitzer, <i>Monatsh.</i> , 3 , 205. .	61°	—
$\alpha\pi$ -	" " ".....	115°	—
"	Kipping and Pope, this paper.....	152—153°	$[\alpha]_D = +98.8^\circ$

* The melting points given by us are not corrected.

† We take this opportunity of correcting the erroneous assertion that the two monochlorocamphors described by Cazeneuve are polymorphous modifications of one substance. Lehmann (*Molekularphysik*, **1**, 664) cites the conversion of β - into α -chlorocamphor on heating with alcoholic potash as an instance of irreversible change; Azruni (*Physik. Chemie d. Krystalle*, 1893, 57), in noting this statement, interprets it as meaning that α - and β -chlorocamphor are monotropic modifications—an obviously erroneous reading.

of the product sublimes during the process, and is deposited in crystals on the cooler parts of the vessel, the rest being easily obtained in a pure condition by recrystallisation or by distillation in steam. In a few instances, however, notably in the preparation of dextrorotatory π -chlorocamphor and in the decomposition of bromocamphorsulphonic chloride, a large quantity of carbonaceous matter is formed as the result of secondary actions, and the product is not easily isolated. In the case of optically inactive π -monochlorocamphor, the action takes an unusual course, inasmuch as a large proportion of the product consists of a pleasant-smelling oil from which the crystalline π -chloro-compound may be separated by fractional distillation. Finally, it is interesting to note that the sulphonic bromides undergo decomposition at a lower temperature than the corresponding sulphonic chlorides, and give virtually a theoretical yield of the π -halogen derivatives, whereas, in the decomposition of the sulphonic chlorides, the yield is comparatively small owing, apparently, to the occurrence of secondary changes.

As regards physical properties the π -halogen derivatives are, on the whole, very similar to the corresponding compounds already known. The π -monohalogen derivatives dissolve freely in all ordinary organic solvents, from which, with the exception of inactive π -monochlorocamphor, they are deposited in small needles or prisms; the π -dihalogen derivatives, on the other hand, are less readily soluble, and are easily obtained in large well-defined orthorhombic prisms. All the π -halogen derivatives sublime readily, usually at temperatures below their melting points, and they are all volatile in steam.

In spite of the fact that the number of mono- and di-halogen derivatives of camphor now known amounts to at least 16, and the great probability that all these compounds are related to one another in an extremely simple manner, there does not seem to be any regularity in the melting points of the halogen derivatives themselves, or any connection between the melting points of the π -derivatives and those of the sulphonic compounds from which they are produced. Dextrorotatory π -monochlorocamphor, for example, melts at $139-139.3^\circ$, and the corresponding bromo-compound at 93.4° , a difference of 46° ; in the case of the ordinary α -monohalogen derivatives, however, the difference in melting point is only 20° ; again, $\alpha\pi$ -dichloro- and $\alpha\pi$ -dibromo-camphor melt at $117.5-118.5^\circ$ and $152.5-153^\circ$ respectively, whereas in the case of the corresponding α -dihalogen compounds the dibromo-derivative melts at a lower temperature than the dichloro-derivative. A similar want of regularity is observed on comparing the melting points of the π -derivatives with those of the sulphonic compounds from which they are derived; but

here, unfortunately, some of the data are rendered untrustworthy by the fact that the sulphonic bromides decompose at, or below, their melting points.

A very remarkable phenomenon is observed in the case of racemic and dextrorotatory π -monobromocamphor; these two compounds melt at practically the same temperature, namely, at 92.7° and 93.4° respectively, and the melting point of the one is not appreciably affected by the presence of the other; consequently all mixtures of the two substances have practically the same melting point, namely, $92.7-93.4^{\circ}$. A similar behaviour is met with in the case of inactive and dextrorotatory π -monochlorocamphor; the difference in melting point is only about 1° , and all mixtures of the two substances melt at $138-139^{\circ}$.

As is well known, the determination of a melting point in the ordinary manner is not a very accurate process, and even with one and the same apparatus and one and the same substance, the observed melting point varies slightly according to the way in which the operation is conducted; hence, in the case of compounds which melt at so nearly the same temperature as the two π -monochlorocamphors and the two corresponding bromo-compounds, it is almost impossible to observe any difference in melting points unless the two substances are directly compared. The results of experiments made in this manner at first indicated that the isomerides in question had exactly the same melting point (Proc., 1895, 39), as they liquefied simultaneously when the capillary tubes were heated together in one bath; these observations, however, proved to be not quite correct, probably owing to the fact that the active isomerides were not absolutely pure and liquefied slightly below their true melting points. When carefully purified samples of the two π -monochlorocamphors and of the two π -monobromocamphors, the melting points of which were constant, were examined, it was found that the optically inactive compound invariably melted before its active isomeride; the difference, however, was very small and did not exceed 1° in either case.

All these observations with the π -monohalogen compounds were made with a standard thermometer graduated to 0.2° , and in every case the temperature was raised extremely slowly. The active π -monobromo-compound melted absolutely sharply, and the active π -monochloro-derivative liquefied completely within a range of about 0.3° ; the inactive compounds, however, especially the chloro-derivative, did not melt quite sharply even after about 20 recrystallisations, and the two mixtures which were examined showed a similar behaviour; it seems hardly possible that this slight sintering in the case of the inactive substances, could have been due to the presence

of traces of the active compounds, since the addition of large quantities of the latter produced no appreciable effect; we are, therefore, inclined to adopt the view that the somewhat indefinite melting points of these inactive compounds is due to a change in crystalline form or is a specific property of the substances.

Unfortunately, owing to our inability to obtain the inactive π -chlorocamphor in a form suitable for crystallographic examination, we are unable to state positively that it is a true racemic compound: we consider it to be so, however, for the following reasons:—Optically inactive π -monobromocamphor, as is shown by crystallographic examination, is a true racemic modification, that is to say, it is a definite crystalline compound, and not a mere mixture of the two optical antipodes; since, therefore, the relation between optically inactive π -monochlorocamphor and its optical isomeride is, on the whole, very similar to that between racemic π -monobromocamphor and its optical isomeride, and the two optically inactive substances are so nearly related in composition and constitution, it is probable, judging from analogy, that the optically inactive chloro-compound is also a racemic modification.

Leaving the π -monochloro-derivatives out of consideration, there still remains the case of the π -monobromo-compounds, which we believe to be the first on record in which two substances, differing in crystalline form, have no effect on each other when melted together; in this respect they show the behaviour of isomorphous substances, a fact which is all the more remarkable when it is borne in mind to how great an extent the melting point of a substance is usually lowered by admixture with a stereochemical isomeride; it would be of interest, therefore, to ascertain whether this behaviour is shown by other organic compounds which are related to one another in the same way as these two derivatives of camphor.

The possible importance of cases of polymorphism amongst substances possessing optical activity in solution, in connection with the question of circular polarisation, has been recently pointed out by Jungfleisch and Léger (*Compt. rend.*, 1895, **120**, 325), and, in the course of this investigation, opportunities have occurred for studying substances of this nature. Several of the π -monohalogen derivatives of camphor are polymorphous, and the crystalline forms of the different physical modifications have been examined to some extent; we have, however, by no means exhausted the investigation of these highly interesting substances, and the facts recorded in this paper are merely those which were brought out during the ordinary examination of the new compounds. In one instance, namely in that of dextrorotatory π -monobromocamphor, two of the forms in which it exists are directly obtainable by crystallisation under different con-

ditions, the one melting at about 60° , the other at 93.4° ; the change of the less into the more stable modification at ordinary temperatures may be accomplished without the aid of heat, in a very simple manner, and as the change is accompanied by a marked alteration in form, clearly visible to the naked eye, the operation is a very suitable one for lecture demonstration.

In the majority of cases, only one of the modifications appears to be sufficiently stable at ordinary temperatures to allow of its preparation by crystallisation under the usual conditions; it is possible, however, that the experiments which are now in progress may show that other modifications may be obtained and kept, as in the case of dextrorotatory π -monobromocamphor.

As is well known, when a substance exists in polymorphous forms, the modification stable at the highest temperature is usually that possessing greatest geometrical symmetry; in this respect the π -monohalogen derivatives form no exception to the general rule, the modifications in question belonging to the cubic system, which has nine planes of symmetry, whilst those stable at ordinary temperatures are either tetragonal or orthorhombic with five and three planes of symmetry respectively.

The $\alpha\pi$ -dihalogen derivatives which we describe are evidently substances of analogous constitution, judging both from their methods of formation and from their crystallographic properties; they form a very well-defined, isomorphous series, the angular dimensions and the axial ratios of the various members being very nearly the same.

The specific rotations of all the new optically active π -halogen compounds have been determined, and the values are considerably higher than those for the previously known isomerides; the experimental data thus obtained, and those collected during the study of the sulphonic chlorides and bromides, together with the recorded values for the known halogen derivatives, are sufficiently numerous to afford material for a careful consideration of the relation between chemical composition and specific rotatory power; this matter has already received our attention, but, in view of its importance, we reserve its discussion for a future paper.

The main object of our work in this particular field, namely to throw some light on the still problematic constitution of camphor, is advanced but little by the facts recorded below; hitherto we have been led to neglect the purely chemical side of the question by the constant occurrence, in the substances prepared, of interesting physical properties, well worthy of a much more exhaustive study than we have yet been able to bestow.

Attention may, however, be drawn to the more important chemical facts which have been established, one being that on sulphonating

camphor, the sulphonic group does not displace the particular hydrogen atom which is eliminated on converting camphor into the ordinary α -monohalogen derivatives; this follows, of course, from the non-identity of the π - and the α -halogen compounds, and also from the fact that on reducing bromocamphorsulphonic acid with zinc dust and ammonia, it is converted into a sulphonic acid, the sulphonic chloride of which yields a π -monochlorocamphor, identical with that obtained from the camphorsulphonic acid prepared by direct sulphonation of camphor. It has also been found that the π -halogen atom, which is introduced with the aid of the sulphonic group, is eliminated, on reduction, much less readily than the α -halogen atom, inasmuch as $\alpha\pi$ -dichlorocamphor is converted into π -monochlorocamphor on treatment with nascent hydrogen.

The further investigation of these new halogen derivatives, and of the sulphonic compounds from which they are derived, is in progress, and the results which have already been obtained (Proc., 1895, 33), give promise of others even more interesting as the work advances.

Dextrorotatory π -Monochlorocamphor, $C_{10}H_{15}ClO$.

Pure dextrorotatory camphorsulphonic chloride (m. p. $137\cdot5^\circ$), prepared by the method already described (this vol., p. 358), is heated in quantities of about 2 grams at a time, in a loosely corked test-tube dipping into a metal bath, the temperature of which is indicated by a thermometer placed in the test-tube; decomposition commences at about 160 — 170° , and a brisk effervescence sets in at about 175° , but at the same time the liquid darkens considerably, and traces of hydrogen chloride seem to be evolved; after heating for about 10 minutes, the temperature having been slowly raised to about 190° , the evolution of gas practically ceases. The product, a thick, tarry mass, is then subjected to distillation in steam, whereupon an almost colourless, pleasant-smelling oil passes over, a large quantity of pitchy matter remaining in the distilling flask. The oil soon becomes pasty, and after a few days solidifies to a crystalline mass, which is separated and spread on porous earthenware to free it from adhering oil; the crude dextrorotatory π -monochlorocamphor thus obtained is finally purified by crystallisation from dilute alcohol, or from light petroleum.

0.1432 gave 0.3400 CO_2 and 0.1053 H_2O . $C = 64\cdot75$; $H = 8\cdot17$.

Theory. $C = 64\cdot37$; $H = 8\cdot04$ per cent.

The yield of π -monochlorocamphor by the above method is comparatively small, amounting only to about 15 per cent. of the theoretical, the main product consisting of a pitch-like mass, which did not invite investigation.

Dextrorotatory π -monochlorocamphor melts at 139—139.3° and sublimes in needles, even at temperatures below its melting point; it is volatile in steam, and distils under ordinary atmospheric pressure when heated in small quantities at a time, only slight decomposition taking place. It is practically odourless at ordinary temperatures, but when heated it evolves vapours which have a faint, camphor-like smell, and at the same time a slight odour of turpentine. Although it is not so readily soluble as inactive π -monochlorocamphor (see below), it nevertheless dissolves very freely in all ordinary organic solvents, even in cold light petroleum, and for this reason could not be obtained from its solutions in well-defined crystals; it is usually deposited from dilute alcohol in long, flat needles, and from petroleum in small, acicular crystals, but from a mixture of petroleum and ethylic acetate it is sometimes obtained in long, transparent, flattened prisms, terminating in ragged ends. The best-defined crystals, however, were obtained from the porous earthenware which had been used in the purification of the crude product. On exposing the clean side of the ware to a very gentle heat for some weeks, the compound slowly sublimed on to the outside in well-defined prisms. These crystals were about 1 mm. in length and 0.1 mm. in diameter, and were simply hollow prismatic shells; the extinctions in the prism zone were straight, but no trace of an interference figure could be discerned through them. On measuring the angles in the prism zone, several were found to be 45°, thus indicating that the crystals were tetragonal.

On melting a little of the substance on a microscope slide under a cover slip, and allowing it to cool, the solidified mass, whilst still warm, is seen to be perfectly isotropic; as it cools still further, however, cracks are seen to gradually run across it, and the crystalline plates become feebly anisotropic. The double refraction increases to such an extent that, on rotating the nicols, the plate may be seen to consist of a number of individuals which do not all extinguish at the same time; the birefringence is, however, still very weak. Suddenly, as the temperature continues to fall, the crystalline form of the substance commences to change at one corner of the plate, and a new growth runs rapidly across; the new crystals thus obtained possess fairly strong double refraction, and apparently belong to the tetragonal system, as the interference figure of a uniaxial crystal can be seen through some of the individuals of which the plate is composed. The examination of the interference figure is complicated by the fact that the optic axis always appeared at the edge of the microscopic field, and could not be got central. The cross in the centre of the figure appears to open slightly as the nicols are rotated; this, however, is very slight, and may be attri-

buted to the same cause as that which makes many tetragonal substances appear biaxial, with a small axial angle. On reheating the cooled preparation, the same series of changes occurs, but in the reverse order; this substance therefore affords a case of enantiotropy.

The above observations show that dextrorotatory π -monochlorocamphor is dimorphous, crystallising in the cubic system at high, and in another system, apparently the tetragonal, at ordinary, temperatures; the polymorphism is, however, not so well marked as in the case of the active π -monobromocamphor described below, inasmuch as the change of one modification into the other proceeds less regularly, and does not give such large and easily distinguished crystalline individuals.

The specific rotation of dextrorotatory π -monochlorocamphor is $[\alpha]_D = +99.88^\circ$; a solution of 0.5882 gram in chloroform, made up to 25 c.c., and examined in a 2 decimetre tube, having given a rotation of $\alpha_D = +4^\circ 42'$ as the mean of eight concordant observations.

Inactive π -Monochlorocamphor.

Since the two optically active modifications of camphorsulphonic chloride do not form a very definite racemic compound, and since, moreover, the sulphonic chloride obtained from the product of the sulphonation of camphor contains a larger proportion of the dextro- than of the lævo-rotatory isomeride, it was necessary to carefully recrystallise a large quantity of the sulphonic chloride, in order to separate as far as possible the excess of the dextrorotatory substance from the samples to be employed in the preparation of inactive π -monochlorocamphor; otherwise, should the inactive π -chlorocamphor be as readily soluble as the active isomeride just described, its separation from the latter would not be easily accomplished. For this reason, a considerable quantity of the crude sulphonic chloride was repeatedly recrystallised from cold ethylic acetate, and any tetrahedra which were deposited were separated mechanically. Having thus obtained a preparation which had doubtless a comparatively small rotatory power, the substance was heated in loosely corked test-tubes in quantities of about 2 grams at a time; its behaviour was very similar to that of the active sulphonic chloride, except that effervescence seemed to set in at a rather lower temperature, and only a trace of, if any, hydrogen chloride was evolved; after heating for about 15 minutes, slowly raising the temperature to about 190° , effervescence ceased, and the thick, dark, oily residue was subjected to steam distillation.

The pale yellow oil which collected in the receiver had a very pleasant, sweet odour, quite unlike that of camphor; as it did not

solidify, it was extracted with ether and fractionally distilled under a pressure of 100 mm. It began to boil at about 160° , and the thermometer then rose continuously to about 185° , by which time the whole had passed over; the two fractions in which the distillate had been collected, at once deposited a considerable quantity of a crystalline substance which looked like camphor, and which was separated by filtration; further quantities of this solid were isolated by fractionating the oily mother liquors under atmospheric pressure, and then cooling the several fractions ($220-240^{\circ}$, $240-255^{\circ}$, $255-270^{\circ}$) in a freezing mixture, when that of highest boiling point solidified almost completely.

The crystalline product was now freed from oil with the aid of porous earthenware, recrystallised from dilute alcohol, and dried over sulphuric acid. Analysis showed it to be a monochlorocamphor.

0.1619 gave 0.3794 CO_2 and 0.1205 H_2O . $\text{C} = 63.91$; $\text{H} = 8.27$.

0.1438 „ 0.3383 „ „ 0.1096 „ $\text{C} = 64.16$; $\text{H} = 8.47$.

0.2754 „ 0.2155 AgCl . $\text{Cl} = 19.35$.

Theory: $\text{C} = 64.37$; $\text{H} = 8.04$; $\text{Cl} = 19.00$ per cent.

A sample was then examined in the polarimeter, in order to ascertain what excess, if any, of the dextrorotatory chlorocamphor was present, as it was probable that the sulphonic chloride which had been used in its preparation was feebly dextrorotatory; a solution of 0.9602 gram in chloroform, diluted to 25 c.c., and examined in a 2 decimetre tube, gave $\alpha_D = +0^{\circ} 23'$, from whence $[\alpha]_D = +4.99^{\circ}$.

The excess of the dextrorotatory compound was therefore about 5 per cent. The sample was then fractionally recrystallised from dilute alcohol, the middle fraction collected, and again recrystallised; the middle fraction from this second operation was employed for an examination of the properties of the substance.

Although it is impossible to say with certainty that the substance prepared in this way is a definite racemic compound, owing to its somewhat ill-defined properties, we believe that this conclusion accords best with our observations. The optically inactive π -monochlorocamphor melts at $138-138.3^{\circ}$, but sinters slightly at about 136° , even after repeated recrystallisation; it is readily soluble in all ordinary organic solvents, and, like the dextro-modification, it sublimes readily, is volatile in steam, and distils without decomposition under atmospheric pressure; its vapours have a camphor-like odour, but the substance itself has only a very faint, sweet smell at ordinary temperatures. It usually crystallises from cold dilute alcohol in fern-like forms, similar in appearance to flowers of camphor, and quite different from the long, flattened prisms of the active modification;

if, however, these fern-like crystals are left in contact with the mother liquors, they are sometimes slowly converted into compact, opaque, crystalline masses (A), which on microscopic examination are seen to consist of slender needles having straight extinction. If, on the other hand, these fern-like crystals are left on porous earthenware for some weeks, part changes into highly lustrous, well-defined crystals, which are seen embedded in the remaining camphor-like mass. These lustrous crystals are compact pyramids, quite distinct in shape from the thin needles mentioned above. It may be noted, too, that in one case a sample of the compact opaque crystals (A), which were kept for some weeks in a dessicator, underwent a complete change in outward appearance, minute needles having grown from the central compact mass, from which they projected in all directions. The melting point of all these forms was the same, namely, 138—138·3°.

As in the case of the optically active modification, some of the best defined crystals of inactive π -monochlorocamphor were obtained from the porous earthenware on which the crude product had been spread; these consisted of slender prisms showing straight extinction, and, like the other forms, melted at 138—138·3°.

The behaviour of inactive π -monochlorocamphor, on heating, is remarkable; as stated above, all the samples obtained by crystallisation or by the spontaneous change of such samples melt not quite sharply at 138—138·3°, and, on quickly cooling the melting point tube, by taking it out of the sulphuric acid, the solidified substance fuses again at the same temperature; if, however, the tube be allowed to remain in the sulphuric acid while the latter cools slowly to the ordinary temperature, the substance sometimes does not solidify until the temperature falls to about 20°, and, on again heating, it melts at 25—28°. Inactive π -monochlorocamphor is therefore dimorphous, the two forms differing in melting point by about 110°. So large a difference in melting point between two such modifications is, we believe, unique, as the various polymorphs of one substance usually melt within a few degrees of each other, and only in very few cases does the difference in melting point exceed 20°.

This peculiar behaviour towards heat would seem to stamp optically inactive π -monochlorocamphor as physically distinct from its active isomeride, and, for this and other reasons already mentioned, the conclusion that the inactive substance is a true racemic compound would seem to be a legitimate one.

Owing to the incomplete separation of the solid inactive π -monochlorocamphor from the oil by which it was accompanied, a comparatively small yield is obtained, although the quantity of the crude oily mixture which distilled in steam amounted to rather more than

50 per cent. of the weight of sulphonic chloride taken; the rest was converted into carbonaceous matter. The formation of an oil in such large quantities in this case is certainly an interesting fact, since no similar product was obtained in the decomposition of optically active camphorsulphonic chloride. An analysis of the oil has not yet been made, as, with the quantity at our disposal, it could not be completely separated from the chlorocamphor by distillation; it was found, however, to be readily oxidised by potassium permanganate in cold acetic acid solution, and also by nitric acid. When it was heated with dilute nitric acid in a reflux apparatus, a large quantity of chlorocamphor collected on the cooler parts of the condenser, and the oil gradually passed into solution; from this solution, a considerable quantity of a crystalline acid, which was sparingly soluble in boiling water, was isolated, and oxalic acid and an oily product were also obtained; these oxidation products will be further examined.

Dextrorotatory π -Monobromocamphor, $C_{10}H_{15}BrO$.

On heating dextrorotatory camphorsulphonic bromide (this vol., p. 364) in a beaker placed in a metal bath and covered with a clock-glass, decomposition sets in just as the crystals begin to melt, and, on raising the temperature to about 155° , a very vigorous evolution of sulphur dioxide commences; when treating quantities of about 4 grams at a time, the conversion into π -monobromocamphor is complete in about 5–7 minutes. No fumes of hydrogen bromide are observed during the operation, and the product is only slightly coloured; it is unnecessary, therefore, to distil in steam, as the compound is easily purified by recrystallisation.

An analysis of the pure preparation showed it to be a monobromocamphor.

0.1503 gave 0.2874 CO_2 and 0.0937 H_2O . $C = 52.15$; $H = 6.93$.

Theory: $C = 51.95$; $H = 6.5$ per cent.

The yield in this case is practically theoretical, no carbonaceous matter or secondary products being formed; this fact is all the more striking when it is borne in mind that, in the decomposition of the corresponding sulphonic chloride, the yield of dextro- π -monochlorocamphor is comparatively small.

For the determination of the rotatory power of the substance, a solution of 1.5301 grams in chloroform, diluted to 25 c.c., was examined at 15° in a 2 decimetre tube; the average of nine concordant observations gave $\alpha_D = +14^{\circ} 12'$, whence the specific rotation $[\alpha]_D = +116.01^{\circ}$.

Optically active π -monobromocamphor is volatile in steam and sublimes readily; it dissolves freely in all ordinary organic solvents,

and is best recrystallised from light petroleum or dilute alcohol, from both of which it separates in the cold in long, colourless needles; the melting point of the crystals obtained in this way is usually 93.4° , but the compound is di- or poly-morphous, and shows the following interesting behaviour.

On allowing its solution in warm dilute alcohol to crystallise rapidly, but without agitation, moss-like needles are sometimes deposited; if these crystals be taken out of the solution and spread on porous earthenware, they melt at about $60-63^{\circ}$, but frequently change spontaneously into the modification melting at 93.4° , without any change in form visible to the naked eye; as a rule, however, without any very obvious alteration in the conditions of the experiment, the crystals directly deposited from the alcoholic solution melt at 93.4° . In one experiment, in which a warm solution had been put to crystallise slowly during the night, these two modifications were deposited side by side, the smaller needles from the upper layers melting at 93.4° , whereas a few larger ones, which were deposited at the bottom of the beaker, melted at about 63° . Although this extraordinary behaviour was only noted on one occasion, there is no doubt as to its correctness; it might, of course, be explained by assuming that all the crystals really consisted of the modification melting at $60-63^{\circ}$, but that the larger ones did not change into the form melting at 93.4° so readily as the smaller ones, and consequently remained unaltered during the operations attending their removal from the solution and introduction into the melting-point tube. This assumption, however, in our opinion, is not warranted, because the two kinds of crystals differed so much in appearance that they were thought to be different substances, and for this reason only were they melted separately; it must be concluded, therefore, that, at first, crystallisation took place at a temperature at which the modification melting at $60-63^{\circ}$ is stable, but that, as the solution cooled, the conditions became favourable to the deposition of the form melting at 93.4° , the two crystalline varieties thus separating at different temperatures. This view is, we think, much more probable than that crystallisation occurred at the temperature of equilibrium between the two modifications, and is supported by the fact that the two kinds of crystals were not, to our knowledge, touching each other, but, from the loosely aggregated character of the crystalline mass (which resembled that assumed by metadinitrobenzene crystallising from its dilute solution in weak alcohol), might well have been quite apart, in which case, of course, the modification stable at the lower temperature would have been unable to induce the change of the less stable form.

When dextrorotatory π -monobromocamphor is melted and then

rapidly cooled from about 95° , by taking the tube out of the hot bath, the substance immediately solidifies, giving the modification melting at 93.4° ; if, however, the tube containing the liquefied substance be allowed to remain in the bath until the temperature falls to about 50° , and is then taken out, the liquid solidifies on further cooling, giving the modification melting at about 60° ; the melting point, however, is not very sharp, owing, doubtless, to partial change into the other form taking place.

The existence of two crystalline forms, and the change of one into the other, may be very easily demonstrated in the following manner. The substance is dissolved in such a quantity of warm dilute alcohol that crystallisation takes place readily on cooling a little; the test-tube containing the warm, clear solution is then rapidly cooled under the tap, stirring vigorously all the time; in this way, the modification of lower melting point is deposited as a granular powder, consisting of fern-like crystals; if, now, a fragment of the modification melting at 93.4° be dropped into the solution and the mixture stirred, the granular powder immediately changes into a bulky, moss-like mass of needles, totally different in appearance from the granular powder. This change sometimes occurs spontaneously, when the test-tube containing the liquid and crystals is allowed to stand at ordinary temperatures for a few hours.

On pouring some of the contents of the test-tube on to a microscope slide before the change of the granular powder has been brought about, and then watching the crystals under a low power, the transformation is exceedingly interesting; on placing a crystal of the modification melting at 93.4° in contact with the edge of the liquid, the fern-like crystals rapidly change into small prisms; long needles then at once begin to form and gradually grow longer and longer, and, as they approach the prisms, the latter disappear, their place being taken a second or two later by a mass of the long needles. This would seem to indicate that the substance is trimorphous, and further evidence in favour of this view is adduced below. The curious disappearance of the prismatic crystals as the needles approach them is probably due to their solubility being greater than that of the needles; a similar phenomenon has been observed by Lehmann in the case of two of the modifications of ammonium nitrate.

On fusing a few milligrams of active π -monobromocamphor on a microscope slide under a cover slip, and then allowing it to cool, solidification to a cubic modification occurs while the slide is still hot; this modification crystallises in long needles with projecting branches on either side, and is completely isotropic. It may be conveniently observed orthoscopically under a $\frac{1}{2}$ -inch objective with the nicols

crossed so as not quite to extinguish the light. After the preparation has cooled to nearly the ordinary temperature, a change in crystalline form is observed to start at one corner of the field and pass slowly across; the new modification is seen to consist of large numbers of small patches possessing fairly strong double refraction, so that the field is illuminated by interference colours of high orders. The crystals are uniaxial, the principal axis of many of the patches being perpendicular to the surface of the slide, and the double refraction is positive. The line of progress of this modification across the plate is followed very rapidly by another, the crystalline form apparently changing a second time; the new crystals thus

FIG. 1.

obtained have the same outline as the patches of the first uniaxial modification, and the principal axis of the latter remains the principal axis of the new form which also has positive double refraction. The only apparent difference between these two uniaxial forms is that the magnitude of their double refraction is slightly different; the two forms may, therefore, ultimately be found to be structurally identical but possessing refractive indices which change considerably with the temperature. A rough representation of these various modifications undergoing change is given in the appended sketch (Fig. 1).

These changes may be conveniently observed macroscopically as they occur on the slide: the cubic modification is first seen to form and to sweep slowly across the slide converting the liquid into a transparent film; after a few seconds, part of the outside of the film becomes white and much less transparent, and this change also slowly extends across the plate; a millimetre or so behind this the second change in crystalline form occurs, and is seen to pass over the plate, rendering it even more white and opaque.

The uniaxial modification of active π -monobromocamphor which finally results from this series of changes is identical in form with that deposited from cold petroleum solutions. The latter consists of long, flattened, transparent prisms possessing a vitreous lustre; the

FIG. 2.

faces are bright when the crystals are first removed from the solution, but on exposure to the air for a few hours, lose greatly in brilliancy. There is a great deal of internal striation parallel to the c -axis; as a rule, the crystals only exhibit faces in the prism zone, the ends being ragged, but sometimes they show several faces of the form $o\{111\}$ at one end; the faces are not very plane, and give bad images. On cutting a fragment perpendicular to the c -axis, a piece is obtained through which the interference figure of a uniaxial crystal can be seen; the

double refraction is positive in sign and fairly strong.

Crystalline System: Tetragonal.

$$a : c = 1 : 0.4377.$$

Forms observed—

$$\begin{array}{lll} a & \dots\dots\dots & \{100\} \dots\dots\dots \infty P\infty, \\ o & \dots\dots\dots & \{111\} \dots\dots\dots P. \end{array}$$

The following angular measurements were obtained.

Angle.	No. of observations.	Limits.	Mean.	Calc.
$ao = 100 : 111$	14	$67^{\circ} 31' - 68^{\circ} 47'$	$68^{\circ} 9'$	—
$oo = 111 : \bar{1}\bar{1}\bar{1}$	6	$43^{\circ} 0' - 44^{\circ} 11'$	$43^{\circ} 34'$	$43^{\circ} 42'$

These being tetragonal crystals of a simple kind, two sets of indices are possible, the alternative set being $a\{110\}$ and $o\{101\}$; using these indices, the axial ratio is $a : c = 1 : 0.6190$. No trace of hemihedrism could be detected in the crystals, the faces of the form $o\{111\}$ never being reduced in number so as to accord with a tetragonal hemihedrism, although usually only two or three of them are present on the crystals.

On rapidly heating these transparent crystals by plunging the melting-point tube containing them into sulphuric acid at or above 60° , they immediately become opaque and then transparent again, but without breaking up; they do not melt, however, until the temperature rises to 93.4° .

Racemic π -Monobromocamphor, $C_{10}H_{15}BrO$.

The camphorsulphonic bromide which was required for the preparation of optically inactive π -monobromocamphor was obtained by the method described in the preceding paper (this vol., p. 359), and, for reasons already mentioned, samples containing as small an excess as possible of the dextro-modification were employed; such samples were prepared by repeatedly recrystallising portions of 4 or 5 grams and separating any of the characteristic tetrahedra of the active modification which were deposited. The approximately inactive substance, in quantities of about 2 grams at a time, was then heated at 145 — 155° in a beaker placed in a metal bath and covered with a clock glass; its behaviour was very similar to that of the active sulphonic bromide, sulphur dioxide was evolved with great rapidity, and very little charring occurred; after heating for about five minutes, the residue, which solidified on cooling, was purified by recrystallisation from dilute alcohol with addition of animal charcoal, and then from a mixture of ether and petroleum.

Analysis gave results agreeing with those required for a bromo-camphor.

0.1691 gave 0.3226 CO_2 and 0.1014 H_2O . $C = 52.03$; $H = 6.66$.

$C_{10}H_{15}BrO$ requires $C = 51.95$; $H = 6.5$ per cent.

The yield of crude but practically pure inactive π -monobromocamphor obtained in this way is very nearly theoretical, and no secondary actions of any importance occur.

An optical examination of a preparation which had been crystallised two or three times showed it to be practically free from dextro-rotatory π -monobromocamphor, inasmuch as a chloroform solution of 2.7600 grams diluted to 25 c.c. gave in a 2 decimetre tube $\alpha_D = +16'$, corresponding with $[\alpha]_D = +1.20^{\circ}$; the quantity of the dextro-rotatory modification was therefore only about 1 per cent.

Inactive π -monobromocamphor resembles the other π -monohalogen compounds in ordinary properties; it sublimes readily, is volatile in steam, and distils without decomposition under atmospheric pressure if heated in small quantities at a time. Although it dissolves freely in all ordinary organic solvents, it is certainly less soluble in boiling light petroleum than the corresponding active modification, and apparently also in other solvents; it also crystallises more readily

and in a greater diversity of habits than the active isomeride, the crystals, moreover, being more massive. It separates from a mixture of light petroleum and ether, for example, in well-defined transparent prisms (see below), and from ether alone in very massive pyramids which easily attain 1 cm. in thickness. As ordinarily obtained from solution, it melts at 92.7° , but, like the active isomeride, it is undoubtedly dimorphous; when the liquefied substance is allowed to cool, it soon solidifies to a transparent, crystalline mass, which gradually becomes opaque as the temperature falls to about 40° ; on heating again, the reverse change is observed, but the transparent crystals do not melt until the temperature rises to 92.7° . The exact temperature at which the change from the opaque to the transparent crystals occurred could not be ascertained, as the change appeared to be gradual.

When the melted substance solidifies under a cover slip on a microscopic slide, a well-defined, cubic modification is produced; this changes, however, as the temperature falls, in just the same way as in the case of the corresponding active π -bromocamphor, and a strongly anisotropic modification is produced. After this conversion, the film is seen to consist of a large number of small patches of a biaxial substance of large axial angle, the interference figure closely resembling that of the crystals obtained from petroleum solution.

The latter are massive, transparent prisms, which, when first taken from the solution, are highly lustrous, although their ends always terminate in very dull curved surfaces; more than one zone, namely that containing the four prism faces was never present, so that the crystalline system is unknown. The prism angle was found to be $69^{\circ} 30'$, as the mean of about 20 measurements. There is a fairly good cleavage parallel to one of the prism faces, and through a thin cleavage plate a biaxial interference figure can be seen; the two optic axes cannot be got into the field commanded by a $\frac{1}{12}$ -inch oil immersion objective, so that this prism face is probably normal to the obtuse bisectrix; the extinction through the prism faces is straight.

Active π -monobromocamphor belongs to the tetragonal system, and is consequently uniaxial, whilst its inactive isomeride crystallises in a biaxial system, probably the orthorhombic; there can, therefore, be no doubt that the latter is a true racemic modification, and the same would seem, by analogy of behaviour, to hold for the inactive π -monochlorocamphor. A series of melting-point determinations of mixtures of racemic and dextrorotatory π -monobromocamphor showed that the presence of one substance does not depress the melting point of the other, and indeed does not seem to effect it at all, inasmuch as all the mixtures melted at 92.5 — 93.5° ; after the fused mixtures had

solidified they melted, on re-heating, at the same temperature as before. This behaviour is much the same as would be expected of two isomorphous substances having almost the same melting point, as the curve plotted between the melting points and compositions of mixtures of isomorphous compounds is a straight line joining the melting points of the two constituents.

Melting-point determinations of mixtures of dextrorotatory and inactive π -monochlorocamphor showed that in this case also all the mixtures have the same point of fusion, namely 138—139°.

The parallel between the two pairs of substances is, therefore, very complete, and confirms us in our belief that the inactive π -monochlorocamphor is a true racemic compound.

$\alpha\pi$ -Dichlorocamphor, $C_{10}H_{14}Cl_2O$.

The decomposition of chlorocamphorsulphonic chloride, unlike that of the other sulphonic chlorides which have been examined, is a very simple process, unaccompanied by any secondary actions; in preparing this dichlorocamphor, therefore, it is only necessary to heat the sulphonic chloride for about 15 minutes at 160—180°, and then recrystallise the residue from ethylic acetate or alcohol, with addition of a little animal charcoal; the yield is almost theoretical.

Analysis of the pure compound gave the following results.

0.1480 gave 0.2945 CO_2 and 0.0888 H_2O . C = 54.27; H = 6.66.

0.1907 „ 0.2476 AgCl (by the lime method). Cl = 32.12.

0.2220 „ 0.2863 AgCl „ „ Cl = 31.90.

$C_{10}H_{14}Cl_2O$ requires C = 54.34; H = 6.34; Cl = 32.03 per cent.

$\alpha\pi$ -Dichlorocamphor crystallises from hot dilute alcohol and acetic acid in very long, slender needles, melting at 118—118.5°; it is very readily soluble in cold benzene and cold chloroform, but only sparingly in light petroleum, its solubility in all ordinary solvents being much less than that of the π -monohalogen derivatives described above. It has no smell, but when heated it gives off vapours which are very irritating, and the odour of which is quite unlike that of camphor; it sublimes readily, is volatile in steam, and may be distilled under atmospheric pressure if only small quantities be taken, although it decomposes on continued heating.

For the determination of the specific rotation, a chloroform solution containing 1.0376 grams was diluted to 25 c.c., and examined in a 2 decimeter tube at 12°; the rotation $\alpha_D = +7^\circ 12'$ whence $[\alpha]_D = +86.74^\circ$.

$\alpha\pi$ -Dichlorocamphor is readily reduced when its alcoholic solution is treated with sodium amalgam, and if, after action has proceeded for some time, the solution be diluted and then cooled, colourless,

slender needles will be deposited; this product, after recrystallisation from alcohol, melts at $139-139.3^{\circ}$, and is identical with the optically active π -monochlorocamphor obtained by the decomposition of dextrorotatory camphorsulphonic chloride.

On further treatment with sodium amalgam under the above-mentioned conditions, the optically active monochloro-compound seems to undergo no change, or, at any rate, reduction takes place very slowly. Of the two halogen atoms in $\alpha\pi$ -dichlorocamphor, therefore, the one which is originally introduced by chlorination is readily eliminated, whereas the π -chlorine atom, which comes from the SO_2Cl -group, and which is united with a different carbon atom, is more firmly held.

The crystals of $\alpha\pi$ -dichlorocamphor deposited by spontaneous evaporation of its cold ethylic acetate solution are somewhat elongated, flattened prisms, which attain a length of several centimetres (Fig. 3). They belong to the orthorhombic system, and show no indication of hemihedrism, although the substance is

optically active in solution; this, however, is not surprising since no pyramid forms—the only ones affected by an enantiomorphous hemihedrism—are present. The forms in the prism zone are always much striated in the direction of the c -axis, the direction in which the crystals are elongated; the pinacoid $b\{010\}$ is usually the

dominant form, but the habit varies considerably with the conditions of growth. The prism forms $n\{130\}$ and $m\{110\}$ are the next largest developed, and give only medium reflections; the dome forms $l\{011\}$ and $r\{101\}$ are usually small, and give good results on measurement, whilst the pinacoid c is rather larger and not so good in character. The crystals have a dull, vitreous lustre, and, if grown quickly, are filled with internal striæ; those which develop slowly, however, are quite transparent and much more lustrous. The c -axis is parallel to the first mean line. The optic axial angle for sodium light was measured in glycerol through a section ground parallel to $c\{001\}$.

No. of observations.	Limits.	Mean angle in glycerol.	Calculated angle in air.
6	$41^{\circ} 29' - 41^{\circ} 32'$	$41^{\circ} 30'$	$62^{\circ} 18'$

The dispersion is very small, and the double refraction is positive in sign and weak.

Crystalline System: Orthorhombic.

$$a : b : c = 0.6933 : 1 : 0.3297.$$

Forms present—

<i>a</i>		{100}		$\infty \bar{P}\infty$,
<i>b</i>		{010}		$\infty \bar{P}\infty$,
<i>c</i>		{001}		0P,
<i>m</i>		{110}		∞P ,
<i>n</i>		{130}		$\infty \bar{P}3$,
<i>l</i>		{011}		$\bar{P}\infty$,
<i>r</i>		{101}		$\bar{P}\infty$.

The following angular measurements were obtained.

Angles.	No. of observations.	Limits.	Mean.	Calc.
<i>nb</i> = 130 : 010	14	25° 37' — 25° 49'	25° 43'	25° 41'
<i>nn</i> = 130 : 130	16	51 10 — 51 34	51 26	51 21
<i>mn</i> = 110 : 130	17	29 22 — 29 47	29 33	29 35
<i>am</i> = 100 : 110	7	34 35 — 34 49	34 41	34 44
<i>mm</i> = 110 : 110	9	69 18 — 69 33	69 25	69 28
<i>bm</i> = 010 : 110	21	55 3 — 55 39	55 16	—
<i>bl</i> = 010 : 011	15	71 32 — 71 56	71 47	71 45
<i>ll</i> = 011 . 011	5	143 24 — 143 41	143 32	143 30
<i>ll</i> = 011 : 011	6	36 20 — 36 52	36 29	36 30
<i>cl</i> = 001 : 011	4	18 1 — 18 25	18 11	18 15
<i>ar</i> = 100 : 101	12	64 17 — 64 40	64 28	64 34
<i>cr</i> = 001 : 101	24	25 11 — 25 47	25 26	—
<i>rr</i> = 101 : 101	8	50 31 — 51 2	50 47	50 52

 $\alpha\pi$ -Dibromocamphor, $C_{10}H_{14}Br_2O$.

Bromocamphorsulphonic bromide, like the other sulphonic bromides, decomposes very rapidly when heated at about 165°, and its conversion into $\alpha\pi$ -dibromocamphor is readily accomplished in the usual manner; although only traces of hydrogen bromide are evolved, a small quantity of carbonaceous matter is produced during the operation, and the product is usually of a brown colour; as it does not volatilise in steam very rapidly, the $\alpha\pi$ -derivative is most conveniently purified by a preliminary recrystallisation from hot acetic acid, a little nitric acid being added to destroy the coloured impurities; it is then obtained almost colourless, and may be further purified by crystallisation from dilute alcohol or acetone. The yield is practically theoretical.

Analysis gave the following results.

0.1804 gave 0.2538 CO₂ and 0.0801 H₂O. C = 38.4; H = 4.9.

0.2310 „ 0.2802 AgBr; Br = 51.57.

C₁₀H₁₄Br₂O requires C = 38.7; H = 4.5; Br = 51.61 per cent.

$\alpha\pi$ -Dibromocamphor crystallises from hot dilute alcohol, acetone, or acetic acid in long, silky needles, but from cold ethylic acetate or chloroform in short, compact, transparent prisms; it is less readily soluble than the above-described dichloro-compound in the ordinary organic solvents. It melts at $152\text{--}153^\circ$, sublimes readily, and slowly volatilises in steam; when quickly heated under atmospheric pressure, a large proportion distils unchanged, but the distillate is of a dark colour.

The specific rotatory power of a chloroform solution containing 0.9800 gram in 25 c.c. was determined in a 2 decimetre tube at 13° ; the mean of eight concordant readings gave $\alpha_D = +7^\circ 45'$ whence $[\alpha]_D = +98.85^\circ$.

The cold ethylic acetate solution, on spontaneous evaporation, deposits highly lustrous, stout prisms, which can readily be grown of a centimetre or so in length. If the crystals are deposited slowly from the cold solution, they are usually very transparent and show no trace of internal striæ; if they separate rapidly they are found to be considerably elongated in the direction of the c -axis, and are quite opaque, owing to the development of a fibrous internal structure.

FIG. 4.

The crystals belong to the orthorhombic system, although, owing to the absence of pyramid faces, it is impossible to say whether they are hemihedral or not. The prism forms $m\{110\}$ and $n\{130\}$ are usually the largest present, whilst the pinacoids $a\{100\}$ and $b\{010\}$, which are so conspicuous on crystals of the corresponding dichloro-derivative, are usually small and frequently absent; the

dome forms $r\{101\}$ and $l\{011\}$ are generally large and well-developed. All the forms give very fair reflections on the goniometer, although the crystals are rarely so suitable for measurement as those of $\alpha\pi$ -dichlorocamphor.

Crystalline System: Orthorhombic.

$$a : b : c = 0.6860 : 1 : 0.3323.$$

Forms present:—

a		$\{100\}$		$\infty \bar{P}\infty$
b		$\{010\}$		$\infty \bar{P}3$
c		$\{001\}$		$0P$
m		$\{110\}$		∞P
n		$\{130\}$		$\infty \bar{P}3$
l		$\{011\}$		$\bar{P}\infty$
r		$\{101\}$		$\bar{P}\infty$

The following angular measurements were obtained:—

Angles.	No. of observations.	Limits.	Mean.	Calculated.
$nb = 130 : 010$	12	$25^\circ 51' - 26^\circ 4'$	$25^\circ 57'$	$25^\circ 55'$
$nn = 130 : \bar{1}30$	5	$51 39 - 51 58$	$51 47$	$51 50$
$mn = 110 : 130$	15	$29 26 - 29 45$	$29 36$	$29 38$
$an = 100 : 130$	3	$64 0 - 64 12$	$64 7$	$64 5$
$mm = 110 : \bar{1}\bar{1}0$	13	$68 40 - 69 7$	$68 53$	$68 52$
$am = 100 : 110$	5	$34 18 - 34 31$	$34 24$	$34 26$
$bm = 010 : 110$	23	$55 27 - 55 39$	$55 33$	—
$bl = 010 : 011$	18	$71 34 - 71 41$	$71 37$	—
$ll = 011 : 0\bar{1}\bar{1}$	9	$36 40 - 36 53$	$36 46$	$36 46$
$cl = 001 : 011$	3	$18 16 - 18 32$	$18 19$	$18 23$
$ar = 100 : 101$	5	$64 1 - 64 18$	$64 12$	$64 9$
$cr = 001 : 101$	8	$25 40 - 26 3$	$25 53$	$25 51$
$rr = 101 : \bar{1}01$	2	$51 34 - 51 56$	$51 45$	$51 42$

$\alpha\pi$ -Chlorobromocamphor, $C_{10}H_{14}ClBrO$.

The preparation of this substance needs little description; on heating pure α -chlorocamphorsulphonic bromide in quantities of about 5 grams at a time at about 150° rapid effervescence sets in, and $\alpha\pi$ -chlorobromocamphor sublimes in large quantities, being deposited on the cooler parts of the beaker in beautiful fern-like crystals; after about five minutes heating the operation is at an end.

The product is easily purified by recrystallisation from hot alcohol and ethylic acetate successively, and the yield is practically a theoretical one, 5 grams of the sulphonic bromide giving 3.8 grams of $\alpha\pi$ -chlorobromocamphor. Two specimens obtained in different preparations gave satisfactory results on analysis.

0.1662 gave 0.2756 CO_2 and 0.0823 H_2O . $C = 45.22$; $H = 5.5$.

0.1675 „ 0.2764 „ 0.0792 „ $C = 45.00$; $H = 5.25$.

Theory: $C_{10}H_{14}ClBrO$ requires $C = 45.2$; $H = 5.27$ per cent.

$\alpha\pi$ -Chlorobromocamphor crystallises from hot alcohol or acetic acid in long, flattened needles, and from cold ethylic acetate in beautiful, transparent prisms (Fig. 5); it resembles the dichloro- and dibromo-derivatives in its behaviour with most of the ordinary solvents, and is a very well characterised substance in all respects. It melts at $138-138.5^\circ$, almost the mean of the melting points of the dibromo- and

FIG. 5.

dichloro-compounds, and its melting point does not change on recrystallisation from acetic acid or other solvents.

A chloroform solution containing 1.6790 grams in 25 c.c. gave a rotation $\alpha_D = +11^\circ 27'$ in a decimetre tube at 14° as the average of 10 observations; the specific rotation is therefore $[\alpha]_D = +85.24^\circ$.

The crystals deposited by spontaneous evaporation of the ethylic acetate solution closely resemble those of $\alpha\pi$ -dibromocamphor both in habit and appearance, and differ from them only by possessing somewhat less lustre.

Crystalline System: Orthorhombic.

$$a : b : c = 0.6884 : 1 : 0.3301.$$

Forms present:—

<i>a</i>		{100}		$\infty \bar{P}\infty$
<i>b</i>		{010}		$\infty \bar{P}\infty$
<i>c</i>		{001}		0P
<i>m</i>		{110}		∞P
<i>n</i>		{130}		$\infty P3$
<i>l</i>		{011}		$\bar{P}\infty$
<i>r</i>		{101}		$\bar{P}\infty$

The following angular measurements were obtained.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
<i>nb</i> = 130 : 010	16	25° 39'—25° 57'	25° 47'	25° 50'
<i>un</i> = 130 : 130	5	51 31—51 49	51 38	51 40
<i>mn</i> = 110 : 130	18	29 20—29 58	29 35	29 37
<i>an</i> = 100 : 130	7	64 0—64 28	64 12	64 10
<i>am</i> = 100 : 110	12	34 23—34 39	34 30	34 33
<i>bm</i> = 010 : 110	15	55 16—55 30	55 25	55 27
<i>bl</i> = 010 : 011	26	71 31—71 56	71 44	—
<i>ll</i> = 011 : 011	11	36 24—36 37	36 30	36 32
<i>cl</i> = 001 : 011	17	18 1—18 39	18 16	18 16
<i>ar</i> = 100 : 101	28	64 14—64 35	64 23	—
<i>er</i> = 001 : 101	12	25 19—26 1	25 42	25 37
<i>rr</i> = 101 : 101	9	51 2—51 29	51 14	51 14

$\alpha\pi$ -Bromochlorocamphor, $C_{10}H_{14}BrClO$.

The great difference between the sulphonic chlorides and the sulphonic bromides as regards their decomposition has already been alluded to, but the best example of this difference is afforded by a comparison of the behaviour of α -bromocamphorsulphonic chloride with that of α -chlorocamphorsulphonic bromide; whereas the latter undergoes decomposition very readily at about 150° , and gives an almost theoretical yield of $\alpha\pi$ -chlorobromocamphor, its isomeride does

not begin to decompose until the temperature has risen to about 170° , and the action which then occurs is apparently very complex, considerable quantities of hydrogen chloride or bromide being evolved together with sulphur dioxide and hydrogen sulphide, and a large proportion of carbonaceous matter being formed.

When the tarry mass obtained by heating the sulphonic chloride at about 180 — 190° for some time is subjected to distillation in steam, comparatively small quantities of a yellow oil, and, later on, a crystalline solid, pass over; after a time the oil solidifies, and the whole may then be separated by filtration. On repeatedly recrystallising this product from hot dilute alcohol and light petroleum, it was finally obtained in long, colourless needles, which melted, apparently quite sharply, at 142 — 143° , and which were so similar in appearance to the crystals of $\alpha\pi$ -chlorobromocamphor that it was impossible to distinguish between them by ordinary methods. The analysis, however, did not give the calculated results, the percentage of carbon varying from 41.9 to 42.2 , and that of hydrogen from 4.9 to 5.0 , whereas a bromochlorocamphor contains 45.2 and 5.27 per cent. respectively; for this reason, we refrained from asserting in our first note (Proc., No. 124, 130) that this product was a bromochlorocamphor. Further investigation having shown that the substance was in reality a mixture, and all attempts to separate its constituents having failed, the decomposition of α -bromocamphorsulphonic chloride under various conditions was carefully studied. By varying the temperature at which the decomposition was carried out and the duration of the heating, products of very variable character were obtained; some of these, in fact, on repeated fractional crystallisation from alcohol, ethylic acetate, and other solvents, yielded fractions melting at temperatures ranging from about 120 — 150° (the most soluble portions melting almost sharply at 120° , the least soluble at 147 — 149°), but in no case could a definite product be isolated. The decomposition of the sulphonic chloride was then carried out under other conditions; in some experiments, iron filings were added, as their presence seemed to accelerate the decomposition, or the heating was carried out under greatly reduced pressure; in others, the sulphonic chloride was heated in boiling nitrobenzene solution. The products from these, as from previous experiments, crystallised readily in long needles, but were not homogeneous, and failed to yield a definite compound when subjected to repeated fractional crystallisation or fractional distillation in steam.

As it had been observed that the evolution of hydrogen chloride or bromide during the decomposition of the sulphonic chloride, and the darkening of the oil, were least noticeable during the first stages of the decomposition, a large quantity of the sulphonic chloride was

carefully heated, in portions of about 2 grams at a time, the operation being continued only until the substance began to darken; the product, which contained a large quantity of unaltered sulphonic chloride, was now subjected to steam distillation, and the crystalline substance which collected in the distillate gently warmed with dilute alcoholic potash, to decompose any sulphonic chloride which had passed over. Two experiments, made in this way, gave a substance which crystallised from ethylic acetate in beautiful, transparent prisms, and which, in both cases, melted sharply at $132-133^{\circ}$; as all the mother liquors also gave crystals melting at $132-133^{\circ}$, it appeared probable that these products consisted of pure $\alpha\pi$ -bromochlorocamphor. Analyses gave the following results.

$$\left. \begin{array}{l} \text{C} = 44.3; \text{H} = 5.84 \\ \text{C} = 44.4; \text{H} = 5.86 \end{array} \right\} \text{Theory: C} = 45.3; \text{H} = 5.3 \text{ per cent.}$$

As the analyses did not agree very satisfactorily with the calculated results, a further investigation of the substance was made, the results of which showed it to be a mixture; although on recrystallisation from alcohol four times, its melting point did not change, four crystallisations from acetic acid yielded a small fraction melting, not quite sharply, at $136-137^{\circ}$. This product, therefore, although certainly much less impure than that obtained in other ways, still contained a certain quantity of some compound from which experience had shown it could not be easily separated. For this reason, further attempts to prepare a pure $\alpha\pi$ -bromochlorocamphor, isomeric with the compound already described, were not made.

The rotatory power of the impure compound in question was, however, determined, in order to make a rough comparison with that of the isomeride: 1.4658 grams dissolved in chloroform, and made up to 25 c.c., gave a rotation of $\alpha_D = +12^{\circ} 36\frac{1}{2}'$ in a 2 decimetre tube at 13° , whence the specific rotation $[\alpha]_D = +107.52^{\circ}$.

The specific rotation is therefore $+107^{\circ}$, whereas that of the isomeride is $+85^{\circ}$; this great difference can hardly be due to the impurity present in the one bromochlorocamphor, and affords evidence of the non-identity of the two compounds. The nature of the substance which is present in the $\alpha\pi$ -bromochloro-compound is unknown, but, as far as can be ascertained, it is the $\alpha\pi$ -dibromocamphor melting at $152-153^{\circ}$; this is probable, from the fact that the melting point of some of the fractions rises to $147-149^{\circ}$, from the results of numerous combustions and halogen determinations, and from the great difficulty experienced in separating the impurity by fractional crystallisation; the two substances are isomorphous, and hence they crystallise together, giving crystals which appear to be those of a definite substance. The crystals obtained from various preparations,

though having different melting points, give excellent results on goniometrical examination, no multiple images being obtained, as would be expected from ordinary impure substances.

Some of the crystals of the product melting at $132\text{--}133^\circ$, obtained from ethylic acetate solution, were examined, and found to belong to the orthorhombic system, and to exhibit the same forms as the preceding $\alpha\pi$ -di-derivatives. The faces of the various forms are developed to about the same comparative sizes as those of the crystals of $\alpha\pi$ -dibromocamphor, which they greatly resemble in appearance.

Crystalline System: Orthorhombic.

$$a : b : c = 0.6861 : 1 : 0.3317.$$

Forms present:—

<i>a</i>		{100}		$\infty\bar{P}\infty$
<i>b</i>		{010}		$\infty\bar{P}\infty$
<i>c</i>		{001}		0P
<i>m</i>		{110}		∞P
<i>n</i>		{130}		$\infty\bar{P}3$
<i>l</i>		{011}		$\bar{P}\infty$
<i>r</i>		{101}		$\bar{P}\infty$

The following angular measurements were obtained.

Angles.	No. of observations.	Limits.	Mean.	Calculated.
<i>nb</i> = $130 : 010$	12	$25^\circ 41' \text{--} 26^\circ 8'$	$25^\circ 54'$	$25^\circ 55'$
<i>nn</i> = $130 : \bar{1}30$	7	$51 43 \text{--} 51 57$	$51 50$	$51 49$
<i>mn</i> = $110 : 130$	14	$29 20 \text{--} 29 48$	$29 30$	$29 28$
<i>an</i> = $100 : 130$	4	$64 1 \text{--} 64 18$	$64 7$	$64 5$
<i>mm</i> = $110 : \bar{1}\bar{1}0$	3	$55 24 \text{--} 55 41$	$55 34$	$55 32$
<i>am</i> = $100 : 110$	18	$34 19 \text{--} 34 45$	$34 27$	$34 27$
<i>bm</i> = $010 : 110$	5	$55 12 \text{--} 55 39$	$55 26$	$55 23$
<i>bl</i> = $010 : 011$	29	$71 24 \text{--} 71 56$	$71 39$	—
<i>ll</i> = $011 : 0\bar{1}1$	16	$36 24 \text{--} 37 1$	$36 40$	$36 42$
<i>cl</i> = $001 : 011$	9	$18 0 \text{--} 18 41$	$18 19$	$18 21$
<i>ar</i> = $100 : 101$	24	$63 58 \text{--} 64 29$	$64 12$	—
<i>cr</i> = $001 : 101$	12	$25 31 \text{--} 26 7$	$25 46$	$25 48$

The proportion of impurity present in this sample of $\alpha\pi$ -chlorobromocamphor, judging from the analytical results, is small, and, as stated above, it is, in all probability, the isomorphous $\alpha\pi$ -dibromocamphor; from the close approximation of the axial ratios of $\alpha\pi$ -chlorobromocamphor and of the corresponding dibromo-derivative, it is evident that such an impurity could affect the axial ratios of the substance but slightly, since the axial ratios of an isomorphous mixture lie between those of its constituents, and are proportional to the amounts of each present. We therefore consider that the goniometric measurements made on this slightly impure sample of

$\alpha\pi$ -bromochlorocamphor give very nearly the true axial ratios of the substance.

It is evident that the four new $\alpha\pi$ -dihalogen derivatives form a very well-defined isomorphous series, the axial ratios of the various members of which approximate very closely to each other, as shown in the following table.

Substance.	$a : b : c.$	$a : c : b.$
$\alpha\pi$ -dichloro-	0.6933 : 1 : 0.3297	2.1029 : 1 : 3.0331
$\alpha\pi$ -chlorobromo-..	0.6884 : 1 : 0.3301	2.0856 : 1 : 3.0296
$\alpha\pi$ -bromochloro-..	0.6861 : 1 : 0.3317	2.0684 : 1 : 3.0149
$\alpha\pi$ -dibromo-	0.6860 : 1 : 0.3323	2.0642 : 1 : 3.0090

The variation in dimensions in passing from one member of the series to another, is shown in the best possible manner by the following table of the principal angles lying in the three planes of symmetry.

Substance.	Angles.		
	$am = 100 : 110.$	$bl = 010 : 011.$	$ar = 100 : 101.$
$\alpha\pi$ -dichloro-	34° 44'	71° 45'	64° 34'
$\alpha\pi$ -chlorobromo- . .	34 33	71 44	64 23
$\alpha\pi$ -bromochloro- . .	34 27	71 39	64 12
$\alpha\pi$ -dibromo-	34 26	71 37	64 9

These two tables show that the axial ratios and principal angles of $\alpha\pi$ -chlorobromocamphor approximate very much more closely to those of $\alpha\pi$ -dichlorocamphor than do those of $\alpha\pi$ -bromochlorocamphor. It would seem, further, from a comparison of the dimensions of the two chlorobromo-compounds with those of the dibromo- and dichloro-derivatives, that the axial ratios are determined by the halogen atom occupying the α -position to a greater extent than by that which occupies the π -position.

The changes in values of the ratios a/b and c/b during the passage from one member of the series to another are in reverse directions but, within the limits of experimental error, of the same magnitude, so that the quantity $\frac{a}{b} \times \frac{c}{b}$ is approximately constant. It is evident

that the $\alpha\pi$ -dihalogen derivatives differ in this respect from the previously measured dihalogen derivatives of camphor, for, as we pointed out in an earlier paper (Trans., 1893, 63, 597), in the isomorphous series formed by these compounds, the comparative lengths of one pair of axes (a/b) are almost constant, whilst those of the other pair (c/b) change considerably during the passage from one member of the series to another.

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