

XL.—*Studies of the Terpenes and Allied Compounds. The Sulphonic Derivatives of Camphor. Part I.*

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THE experiments recorded in this paper were undertaken with the object of obtaining camphorsulphonic acid, a substance which many chemists hitherto have vainly sought to prepare, and also with the object of ascertaining the nature of the changes involved in the formation of acetylorthoxylene by the interaction of camphor and sulphuric acid (compare Armstrong and Kipping, this vol., p. 75).

The fact that camphor is almost entirely converted into "camphren" on treatment with ordinary sulphuric acid, and cannot, therefore, under these conditions, yield anything but a very small quantity of a sulphonic derivative, even if sulphonation occurs at all, led us to study its behaviour towards anhydrosulphuric acid and chlorosulphonic acid; in both cases sulphonation takes place readily, camphorsulphonic acid and other compounds being formed.

The camphorsulphonic chloride prepared from the acid obtained by either of these methods is a mixture of optical isomerides, but as the dextrorotatory modification is present in rather the larger proportion, we have been able to isolate and examine it.

The optically inactive, or feebly active, mixture of sulphonic chlorides shows a very remarkable behaviour; it is deposited from solution in well-defined crystals, which, though apparently homogeneous, are simply mixtures of the two active compounds in variable proportions, and are partially resolved into enantiomorphous forms on recrystallisation.

Camphorsulphonic acid, its amide, and a variety of its salts have been prepared, and attention is drawn to the remarkable crystallographic character of some of these compounds, more especially in the case of the active substances.

Bromocamphor is readily converted into a sulphonic acid on treatment with anhydrosulphuric acid or with chlorosulphonic acid; chlorocamphor has, hitherto, only been sulphonated with the latter. The sulphonic derivatives of both these substances are optically active, and are remarkable for the extraordinary facility with which they crystallise; the sulphonic chlorides, the amides, the acids, and a number of salts are described, the optical and crystallographic characters of many of the compounds being given.

Marsh and Cousins (Trans., 1891, 59, 966) have described sulphonic derivatives of bromocamphor and chlorocamphor, obtained by

means of chlorosulphonic acid, but as most of their preparations were impure, their account of the properties of these substances is very misleading; their work is frequently referred to later.

Cazeneuve (*Compt. rend.*, **110**, 719), who has studied the action of sulphuric acid on chlorocamphor, has obtained results of considerable interest, but as they have no immediate bearing on our own work, we will not discuss them in the present paper.

Speaking generally, the sulphonic derivatives of camphor are compounds of exceptional beauty, and, judging from the results thus far obtained, their further study will probably lead to conclusions of considerable importance.

### *Sulphonic Derivatives of Camphor.*

*Sulphonation of camphor with anhydrosulphuric acid.*—When dry powdered camphor is treated at ordinary temperatures with about twice its weight of anhydrosulphuric acid containing about 15 per cent. of anhydride, a very energetic action, accompanied by a considerable rise in temperature, sets in, and the solution rapidly darkens, sulphur dioxide being evolved in large quantities; after about 20 seconds, sulphonation is nearly complete—that is to say, very little camphor is precipitated on pouring the solution into water; if the action be allowed to proceed, it gradually becomes more and more vigorous, the mixture froths over, and practically the whole of the camphor is converted into carbonaceous matter. When acid containing less than about 15 per cent. of anhydride is employed, the camphor at once passes into solution, but is only partially converted into products soluble in water, even on keeping for some time; when, on the other hand, the anhydro-acid is too concentrated, the action is so violent that it cannot be kept under control.

These observations led to the adoption of the following method of sulphonating camphor:—Dry, powdered camphor, in quantities of about 50 grams, is placed in a large beaker, and 15 per cent. anhydrosulphuric acid, about 100 grams, poured over it; after action has proceeded for about 20 seconds, the dark brown solution is poured on to powdered ice, and these operations are repeated with fresh quantities of camphor, until about 1000 grams have been treated. The yellow or brown aqueous solution—which has the characteristic smell of “camphren,” owing to the presence of small quantities of this oil—having been filtered to separate unchanged camphor, is boiled to expel sulphur dioxide, and neutralised with chalk or milk of lime; in the latter case carbon dioxide is afterwards passed into the boiling liquid, until the excess of calcium hydroxide is precipitated. The sulphate and carbonate of calcium are then separated by filtration

through calico, and the filtrate boiled down to a small bulk, the calcium sulphate which crystallises out being removed from time to time. Water having been added, the calcium salt is converted into sodium salt by treating with sodium carbonate, and the filtered solution evaporated to dryness. The resulting brown, viscid product is heated in an air-bath at about  $120^{\circ}$ ; at first it melts to a thick paste and froths very much, owing to the escape of water vapour, but ultimately it is converted into a friable, light brown mass, which is quickly powdered in a warm mortar, and, being very hygroscopic, kept in a desiccator or in a stoppered bottle.

The quantity of crude anhydrous sodium salt obtained in this way from 1 kilo. of camphor is usually rather more than 600 grams; we have not yet made any attempt to ascertain the proportion of pure sodium camphorsulphonate present in the product, but have employed it without purification for the preparation of camphorsulphonic chloride.

*Treatment of sodium salt with phosphorus pentachloride.*—In preparing camphorsulphonic chloride, a quantity of about 100 grams of the anhydrous sodium salt is placed in a mortar and triturated with a small quantity of phosphorus pentachloride, a little phosphorus oxychloride being added, if necessary, to start or hasten the action; a very slight evolution of hydrogen chloride occurs if the salt has been carefully dried, but the mixture becomes distinctly warm and soon turns pasty; the addition of small quantities of pentachloride is then continued, until the total quantity employed amounts to about 100 grams ( $1\frac{1}{2}$  mol. props.); after about half an hour, the semi-fluid mass is slowly poured on to, and stirred up with, powdered ice. The sulphonic chloride, which separates in the form of dirty-grey, sticky clots, is extracted by repeatedly shaking the mixture with ether, a process which is sometimes rendered very tedious by the formation of an emulsion, from which the ether separates with difficulty. The ethereal solution, after being washed several times with small quantities of water until free from phosphorus oxychloride, is carefully dried with calcium chloride and the ether evaporated. The dark brown, oily residue is heated at  $100^{\circ}$  for some time to expel ether, and is afterwards placed in a desiccator over sulphuric acid and potash; in the course of a few days, the crude sulphonic chloride partially solidifies, the crystalline cake which forms containing a considerable proportion of oily substances. The yield of crude product is very variable, but is usually 60—80 per cent. of the sodium salt employed; when the crude dried calcium salt of the sulphonic acid is treated with phosphorus pentachloride, the yield of sulphonic chloride is very small, apparently because the salt is only partially acted on.

*Camphorsulphonic Chloride*,  $C_{10}H_{15}O \cdot SO_2Cl$ .

When spread on biscuit ware, the crude, dark brown, pasty sulphonic chloride slowly changes into a hard, brown mass, from which crystalline substances can be obtained without difficulty with the aid of solvents. This treatment, however, occupies a long time, and involves very considerable loss, the oil carrying with it a large proportion of the crystalline products, which thus escape investigation. Under these circumstances we adopted the following method of purification, which has the advantages of being very rapid and simple.

The crude sulphonic chloride, obtained by evaporating the ethereal solution, is placed in a flask together with about 50 c.c. of light petroleum boiling at 35—40°: the flask is then connected to a reflux condenser, and warmed on the water-bath for about 15 minutes, frequently shaking. The light petroleum, which does not mix with the oily sulphonic chloride, is then decanted or filtered into a beaker, and the oil in the flask again extracted in a similar manner. After repeating these operations two or three times, light petroleum of a higher boiling point (about 70—80°) is employed, the four or five extracts with this solvent being kept separate from those previously obtained, and, to a certain extent, from one another, according to their character. The extraction is then continued with petroleum boiling at 80—90°, and finally with some of the solvent boiling at 90—100°, until a black, tarry mass, insoluble, or only very sparingly soluble, in light petroleum, remains in the flask; this residue appears still to retain one or more crystalline substances which can be extracted with the aid of boiling benzene; the remaining tar contains small quantities of substances soluble in water, probably sulphonic acids, produced by the hydrolysis of the sulphonic chlorides by traces of water.

The first petroleum extracts have a brown or yellow colour, but the last are almost colourless; the first three or four contain a large quantity of yellow oil, which, on cooling, is quickly deposited, together with a small quantity of pale yellow crystals; the next series of extracts deposit yellowish crystals and a little oil; the later extracts deposit crystals only, and it is convenient, in order to avoid the use of too large a quantity of solvent, to use the mother liquors from these crystals in continuing the extraction.

By proceeding in this manner, and collecting the various extracts in the same or in different vessels, according to the character of the crystals which are deposited, it is possible, after a little experience, to effect a rough separation of the several constituents of the mixture in a very short time; the petroleum mother liquors from the crystals, and from the oil, yield further quantities of these products on

evaporation at ordinary temperature, and, as before, the character of the deposits is very different.

It is unnecessary to enter here into the details of the treatment by which it is possible to isolate pure camphorsulphonic chloride from the crystalline deposits thus obtained, because until the other constituents of the mixture have been isolated and characterised, we shall not arrive at the simplest method; it may, however, be stated that the camphorsulphonic chloride, being more sparingly soluble in light petroleum than the other crystalline products, is present in the largest proportion in the last extracts of the crude oil; when the crystalline deposits from these solutions are collected, again extracted with light petroleum, and the process repeated until the deposited crystals are colourless, an apparently homogeneous substance is obtained in lustrous crystals.

Analyses of samples purified in this way, and then dried at 80°, gave the following results.

0·1665 gave 0·2914 CO<sub>2</sub> and 0·0915 H<sub>2</sub>O. C = 47·73; H = 6·10.  
 0·1534 „ 0·0870 AgCl and 0·1401 BaSO<sub>4</sub>. Cl = 14·00; S = 12·54.  
 C<sub>10</sub>H<sub>15</sub>O·SO<sub>2</sub>Cl requires C = 47·92; H = 5·99; Cl = 14·14; S = 12·78 per cent.

The combustion was made with lead chromate, a silver spiral being placed in the front of the tube; the chlorine and sulphur were estimated by Carius' method, the sulphuric acid being precipitated with barium nitrate after separating the silver chloride.

The further investigation of this substance is described later (p. 554).

#### *Sulphonation of Camphor with Chlorosulphonic acid.*

As the preparation of pure camphorsulphonic chloride from the sulphonic acid produced by the action of anhydrosulphuric acid on camphor was at first a matter of very considerable difficulty, owing to the complex nature of the crude product, the behaviour of camphor with chlorosulphonic acid was examined.

Marsh and Cousins (Trans., 1891, 59, 967) have stated that camphor does not yield a sulphonic acid on treatment with chlorosulphonic acid in chloroform solution; although our experiments have shown that camphor is readily acted on under these conditions, hydrogen chloride being evolved, we have not yet examined the nature of this action more fully, as it was found that camphorsulphonic acid could be produced without difficulty by the action of chlorosulphonic acid on camphor in the absence of a solvent or diluent.

The following is the method employed:—Dry powdered camphor,

in quantities of about 100 grams, is placed in a large flask, and treated with about 70 grams of chlorosulphonic acid; the camphor quickly passes into solution, the mixture becoming warm, but no violent action occurs, as in the case of anhydrosulphuric acid, only a slight evolution of hydrogen chloride being observed. The flask is now fitted with a cork, through which a calcium chloride tube passes, and gently heated on the water-bath; a rapid evolution of hydrogen chloride sets in, and the solution darkens a little. After heating for about 20 minutes, and frequently shaking, the mixture is cooled; a further quantity of about 80 grams of chlorosulphonic acid is then added, and the solution again heated on the water-bath until the evolution of gas slackens very considerably, and a portion of the solution poured into water gives a comparatively very slight precipitate of camphor, which is usually the case after about half an hour. In this process of sulphonation, very little carbonisation occurs, and sulphur dioxide, if formed at all, is produced only in very small quantities.

The brownish syrupy solution is allowed to cool, carefully poured into water, the precipitated camphor (about 6 grams) separated by filtration, and the filtrate treated with barium carbonate and barium hydroxide successively until slightly alkaline; after passing carbon dioxide into the boiling mixture to precipitate the excess of barium hydroxide, an operation which is to be recommended, because the coloured impurities are in this way to a great extent got rid of, the solution is filtered, and the filtrate treated with sodium carbonate as long as a precipitate is produced.

The almost colourless solution of the sodium salts is evaporated to dryness on the water-bath, the residue dried at about  $120^{\circ}$ , ground to a fine powder, and repeatedly extracted with 96 per cent. alcohol, in which the sodium camphorsulphonate readily dissolves, leaving a residue of sodium chloride; finally the alcoholic extract is evaporated and the residue dried at  $110-120^{\circ}$ .

The crude sodium camphorsulphonate, obtained in this way, is employed without further purification for the preparation of the sulphonic chloride; the yield is usually about 115 grams from 100 grams of camphor.

The treatment with pentachloride having been carried out in the manner previously described, and the product isolated by extracting with ether, crude camphorsulphonic chloride is obtained as a yellow oil which partially solidifies to a crystalline mass in the course of a few days; under ordinary conditions the yield amounts to about 40 per cent. of the sodium salt employed.

*Camphorsulphonic Chloride, C<sub>10</sub>H<sub>16</sub>O·SO<sub>2</sub>Cl.*

The crude product appears to be very much the same as that prepared from camphor with the aid of anhydrosulphuric acid; it is, however, usually lighter in colour, and apparently a larger proportion solidifies. We have not yet examined it very fully, but have succeeded in isolating camphorsulphonic chloride from it by extracting the crude oil with boiling light petroleum exactly as described above (p. 551). The crystalline deposits from the light petroleum solutions consist of at least two substances, but, as before, the camphorsulphonic chloride being the more sparingly soluble, is present in the largest proportion in the deposits from the last extracts; after repeated recrystallisation from light petroleum, a colourless substance, which seems to be homogeneous, is obtained.

Analyses of this product showed that it had the same composition as the sulphonic chloride previously prepared.

0.1650 gave 0.2889 CO<sub>2</sub> and 0.0931 H<sub>2</sub>O; C = 47.75; H = 6.27.  
0.2265 „ 0.1287 AgCl and 0.2180 BaSO<sub>4</sub>. Cl = 14.03; S = 13.21.  
C<sub>10</sub>H<sub>16</sub>O·SO<sub>2</sub>Cl requires C = 47.92; H = 5.99; Cl = 14.14; S = 12.78 per cent.

*Isolation of Dextrorotatory Camphorsulphonic Chloride.*

The second method of preparation, described above, not having been attempted until some time after the commencement of our experiments, our investigations were at first limited to the study of the sulphonic chloride obtained from the product of the interaction of camphor and anhydrosulphuric acid. Various preparations from this source, all of which had been extracted from the crude product with boiling light petroleum, and then purified by repeated crystallisation from the same solvent, were examined, and appeared to be identical; they all showed the same behaviour when heated, and, on examination under the microscope, seemed to be homogeneous; samples which were analysed gave results agreeing closely with those required by a compound of the composition C<sub>10</sub>H<sub>16</sub>O·SO<sub>2</sub>Cl.

One fact, however, seemed at first to indicate the presence of impurity in the preparations, namely, their behaviour when heated; portions which had been repeatedly crystallised from boiling petroleum fused partially at about 107°, but did not completely liquefy until the temperature rose to about 108.5°, or even higher; after solidification they melted, on reheating, sharply at 105.5–106.5°. As well-defined crystals obtained with the aid of other solvents showed a similar behaviour, melting at a higher temperature, and less sharply, when heated for the first time than they did afterwards, we concluded that

we were dealing with a case of dimorphism, and no longer doubted the purity of our preparations.

Under these circumstances we proceeded to study some of the derivatives of the sulphonic chloride, and prepared the amide, the sulphonic acid, and some of the salts of the latter; all these substances appeared to be homogeneous, and on analysis gave the results which were expected.

In the meantime we commenced the investigation of the action of chlorosulphonic acid on camphor, and, having isolated the sulphonic chloride in the manner described, we compared it with that obtained by the first method; it separated from boiling light petroleum in lustrous, colourless crystals, which appeared to be identical in ordinary properties with the sulphonic chloride previously studied, and showed the same behaviour as the latter when heated. It was also observed that when the ill-defined crystals obtained from hot light petroleum were dissolved in a mixture of ether and petroleum, well-defined, four-sided plates were deposited, showing a very peculiar behaviour when heated (see later, p. 562); as the sulphonic chlorides from the two sources both gave such plates, we took it as a satisfactory proof of their identity.

It was not until we came to examine the rotatory power of the two preparations that this conclusion was, to some extent at any rate, proved to be erroneous. Some of the salts which had been prepared from the sulphonic chloride obtained by the first method had been found to be optically inactive; although, under these circumstances, it was *a priori* improbable that the sulphonic chloride would be optically active, examination showed it to be feebly dextrorotatory, the sample in question having a specific rotatory power  $[\alpha]_D = +3.73^\circ$  in chloroform solution.

On making an observation with a sample of the sulphonic chloride prepared by the second method, we found that here, also, there was feeble dextrorotation, but that the specific rotatory power was not the same as that of the other preparation, being, in fact,  $[\alpha]_D = +4.7^\circ$  in chloroform solution.

This, however, was not the only fact which optical examination brought out, inasmuch as different samples prepared by the same method had slightly different specific rotations, all being dextrorotatory.

The explanation of these facts seemed to be fairly obvious, namely, that the sulphonic chloride hitherto supposed to be homogeneous was a mixture of an optically active with an optically inactive compound, and that the reason why the preparation obtained by the second method was the more highly dextrorotatory was that the formation of the sulphonic acid from which it was derived had taken place under



conditions generally more favourable to the production, or less favourable to the destruction, of an optically active substance; it appeared very probable, also, in view of the analytical results, that the two optically different substances had the same composition, that is to say, were both camphorsulphonic chlorides.

Under these circumstances we commenced a more careful and searching examination of the sulphonic chloride which had been obtained by the first method of sulphonating, and to which alone the following statements refer, with the object, if possible, of separating the optically different compounds assumed to be present; for this purpose slightly different samples, which had been purified in various ways, were employed. On recrystallising these from cold ethyl acetate, it was found that two kinds of crystals were deposited, namely, small, four-sided plates, evidently identical with the above-mentioned crystals obtained from ethereal petroleum solution, and very large, compact, prismatic masses, rather translucent than transparent; although so different in appearance, both kinds of crystals had practically the same melting point, and were, in fact, simply different forms of one and the same substance. When the flat plates were separated and recrystallised from ethyl acetate, in some cases only one, in others both kinds of crystals were again obtained; the prismatic masses, treated in the same way, yielded either transparent plates or prisms, or a mixture of the two. It was clear, therefore, that the formation of one or other kind of crystals was simply due to a slight alteration in the conditions of the experiment, and that a separation of the optical isomerides was not to be effected in this way.

We next tried fractional crystallisation from a mixture of chloroform and light petroleum, and found that, after a great many operations, a given sample could be separated into fractions of slightly different specific rotation; the process, however, was extremely tedious, and we again resorted to ethyl acetate.

On systematically crystallising samples of the sulphonic chloride from ethyl acetate, the crystals first deposited began to show a behaviour different from that previously noticed; their melting point gradually became less and less definite, although, after having been melted, they liquefied almost completely at  $105.5$ – $106.5^\circ$  when heated for the second time; when a particular stage of the process had been arrived at, well-defined, transparent prisms were obtained, and these, though apparently homogeneous, began to melt at about  $110^\circ$ , and did not liquefy completely until the temperature rose to about  $130^\circ$ . From these crystals, it was a matter of little difficulty, by simply continuing the process, to isolate a substance melting at  $137.5^\circ$ .

This compound is dextrorotatory camphorsulphonic chloride, and

is described later (p. 564); it has a specific rotatory power  $[\alpha]_D = +128.7^\circ$ .

*Evidence of the Existence of Lævorotatory Camphorsulphonic Chloride.*

These experiments having shown that the slight and variable optical activity of different samples of the sulphonic chloride was due to the presence of variable quantities, usually 2 to 4 per cent. of the dextrorotatory compound, attempts were made to isolate the optically inactive substance, of which it seemed the mixture was for the most part composed.

Although, starting with a sample of specific rotation greater than about  $[\alpha]_D = +3^\circ$ , it was possible in the manner described above to obtain from it a small quantity of the pure active compound, we were unable, owing, perhaps, to the small quantities at our disposal, to obtain inactive preparations simply by fractional crystallisation from ethyl acetate; samples which had been systematically treated showed a specific rotation corresponding with the presence of about 0.4 to 1 per cent. of the active modification, and, apparently, this quantity underwent no change on continuing the process.

When such samples were dissolved in ethyl acetate, and the solutions slowly evaporated at the ordinary temperature, the large prisms already mentioned were found to be mixed in some, but not in all, cases, with a few well-defined tetrahedra; the latter melted at about  $136^\circ$ , that is to say, at practically the same temperature as the dextrorotatory compound, which, under the same conditions, was observed to crystallise in tetrahedra.

It seemed probable, therefore, that if the process were repeated several times, we should be able to obtain the inactive substance in a pure condition by separating the different crystals.

This, however, was not the case, as is shown by the following account of the behaviour of a typical sample:—

A preparation (about 5.5 grams) which in chloroform solution showed a specific rotation  $[\alpha]_D = +2.57^\circ$ \* was dissolved in cold ethyl acetate, and the next day all the well-defined tetrahedra which had been deposited were picked out, the process being repeated daily; after five or six operations, the specific rotation, observed as before in chloroform solution, had fallen to  $[\alpha]_D = +1.74^\circ$ . On continuing in the same way, the specific rotation fell to  $1.04^\circ$ , then to  $0.42^\circ$ , and at the end of about two weeks we obtained a preparation (about 4 grams) which showed no rotation.

\* The values of  $[\alpha]_D$  given in this section of the paper are, in some cases, only approximate, as the weight of the substance was frequently obtained by difference, and slight decomposition (hydrolysis) may have occurred during crystallisation.

The tetrahedra which had been separated from the sample of specific rotation  $[\alpha]_D = +0.42^\circ$  were all well-defined crystals, and weighed 0.51 gram; a portion (0.471 gram) of these crystals showed in chloroform solution a specific rotation  $[\alpha]_D = +5.08^\circ$ .

Now if these tetrahedra had consisted of pure dextrorotatory camphorsulphonic chloride, they would have had a specific rotatory power  $[\alpha]_D = +128.7^\circ$ , that is to say, the rotation should have been 22 times greater than the observed value, and, moreover, their elimination from the sample of specific rotation  $[\alpha]_D = +0.42^\circ$  must have been accompanied by a very much greater change in the specific rotation of the latter; in other words, the tetrahedra in question could not be all of the same kind.

Some of the tetrahedra which had not been employed for the optical examination were well washed with petroleum until free from adherent matter, and dried in the air; 10 well-defined, lustrous crystals, when heated singly in separate capillary tubes, had practically the same melting point; one or two of them showed faint signs of melting at about  $130^\circ$ , and completely liquefied at  $135^\circ$ , but all the others melted at  $135$ – $137^\circ$ ; after solidification, they all melted at practically the same temperature as at first.

Other tetrahedra from the same sample were then examined in pairs, two crystals of approximately equal size being taken at random and placed either slightly apart or in loose contact in a capillary tube; 15 pairs were thus treated. On slowly heating, not one out of the 30 crystals showed any signs of melting until the temperature rose to about  $127^\circ$ , but they all liquefied completely below  $137^\circ$ , the majority of them melting at  $135$ – $136^\circ$ . As soon as the fused mixture of two tetrahedra had solidified, the melting point was again taken; the contents of 12 out of the 15 tubes melted at practically the same temperature as at first, namely, at about  $135^\circ$ , but the contents of the remaining three liquefied completely at  $105.5$ – $107.5^\circ$ . Finally, eight small tetrahedra were placed in loose contact in a single tube; signs of melting were visible at about  $125^\circ$ , and at  $134^\circ$  they had all melted; after having solidified, the contents of the tube liquefied completely at  $105.5$ – $107^\circ$ .

These observations prove that there are two kinds of tetrahedra which, when fused together in approximately equal quantities, give a substance melting at about  $106^\circ$ ; since both kinds melt at about  $135^\circ$ , that is to say, at practically the same temperature as dextrorotatory camphorsulphonic chloride, and are identical in other properties, it follows that they represent respectively the dextro- and lævo-rotatory modifications.

The reason that the melting point of the separate crystals was not always the same as that of the pure dextrorotatory compound was,

doubtless, due to the presence of traces of the mixture of lower melting point, the crystals having been taken from a solution which contained a large excess of the latter; the fact that only three out of the 15 pairs examined consisted of the two kinds of crystals, whereas, according to the laws of probability, five pairs should have done so, was, no doubt, partly owing to the fact that the tetrahedra had been obtained from a dextrorotatory solution, which would yield a larger proportion of the modification present in excess. A second experiment with a totally different sample of tetrahedra gave slightly different results. Six crystals, heated singly, melted at 130—136°; after solidification, they showed the same behaviour. 12 crystals heated in pairs all melted at 130—136°; three out of the six pairs melted completely at 105·5—107·5° on heating for the second time.

Although we have not yet succeeded in isolating the levorotatory camphorsulphonic chloride, except in the form of single crystals which could not be identified, we have obtained further evidence of its existence, as will be seen from the facts now to be stated.

The successful preparation in the above mentioned manner of a substance which showed optical inactivity in chloroform solution was simply a matter of chance. On recrystallising the inactive sample already referred to, tetrahedra were again deposited from the solution, the principal portion of the deposits consisting, as before, of transparent prisms; five crystallisations yielded 47 well defined tetrahedra, all of which were removed. The rest of the sample, previously inactive, had now become distinctly dextrorotatory, and the tetrahedra (0·118 gram) which had been taken from the solution had a specific rotation  $[\alpha]_D = -20·7^\circ$ .

Several other samples of sulphonic chloride showing feeble dextrorotation were repeatedly recrystallised, and small quantities of tetrahedra separated. In some cases, the solutions became distinctly levorotatory, the specific rotation of the dissolved substance being in one case as high as  $[\alpha]_D = -0·42^\circ$ ; the mixture of tetrahedra separated from solutions which became less dextrorotatory, consisted, of course, of a larger proportion of dextro- than of levo-crystals, the mixture of the two showing, in some cases, a specific rotation of as much as  $[\alpha]_D = +25^\circ$ . Solutions of samples which showed levorotation still continued to deposit tetrahedra on recrystallisation, and sometimes became dextrorotatory; in such cases, the mixture of tetrahedra, which had been separated, contained the levorotatory modification in excess, and had a specific rotation amounting, in one instance, to as much as  $[\alpha]_D = -20·7^\circ$ .

These observations seem to prove the existence of levorotatory camphorsulphonic chloride.

*Character and Properties of the Mixture of Optically Active Camphor-sulphonic Chlorides.*

The question whether the two optically active compounds combine to form a racemic modification remains to be discussed; it becomes necessary, therefore, to more fully describe the character of the prisms and four-sided plates which have been already mentioned.

Concerning the prisms, it may be stated that the smaller crystals are usually transparent and, to the unaided eye, appear to be well defined and absolutely homogeneous (see Fig. 1, next page), just as much so, in fact, as crystals of zinc sulphate. Larger crystals, which can easily be obtained 20 mm. in length, very frequently show a striated appearance which renders them opaque in places, otherwise they seem to be similar to the smaller prisms, except, perhaps, that they are not quite so well defined; their striated appearance seems to be due to internal fracture because, on carefully watching the crystals, we frequently observed that transparent parts suddenly became opaque, probably owing to a slight change of temperature. These prisms have no constant melting point. Some of them show signs of melting at about  $106^{\circ}$ , and liquefy completely at about  $115^{\circ}$ , that is to say, part of the crystal will melt at the lower temperature and flow to the bottom of the tube, leaving a portion of solid matter which adheres to the side of the tube, and which does not melt until the higher temperature is reached. Others, more especially those obtained from a solution containing a considerable excess of one of the active modifications, begin to melt at about  $110^{\circ}$ , but do not assume a completely liquid form until the temperature has risen to about  $130^{\circ}$ ; the solidified mass, on reheating, usually begins to melt at  $105.5^{\circ}$ , but often does not liquefy completely until about  $130^{\circ}$ .

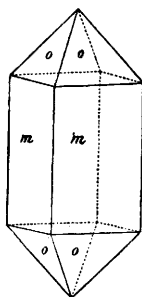
The behaviour here described in the case of two extreme examples is typical of all the prismatic crystals, and may be accounted for by assuming that they are non-homogeneous mixtures of variable proportions of the two optically active substances; the behaviour illustrated by the first example is probably that of crystals in which the constituents are present in approximately equal quantities; if, however, one modification be present in large excess, the crystals would, doubtless, show the behaviour illustrated by the second example.

That these crystals do actually consist of the two optical isomerides is hardly to be doubted; that they may contain unequal quantities of the substances is proved by the following experiment:—A chloroform solution of a sample of well defined tetrahedra (0.116 gram,  $[\alpha]_D = +24.8^{\circ}$ ) was mixed with a solution of a different sample of tetrahedra (0.182 gram,  $[\alpha]_D = -11.2^{\circ}$ ), and evaporated to

dryness; the residue melted at  $107-115^{\circ}$ , and, on reheating, at  $105.5-106.5^{\circ}$ ; it was dissolved in ethyl acetate in a test tube, and the solution allowed to evaporate at the ordinary temperature. Two large, and one small, well defined prisms were deposited, but no tetrahedra; on recrystallising the whole, a number of small, well defined prisms were obtained, but not a single tetrahedron; one of these prisms melted at  $106-120^{\circ}$ , and, after solidification, liquefied completely on reheating at  $105.5-106.5^{\circ}$ ; on recrystallising the remainder, one fairly large tetrahedron was deposited, but, after some time, it was converted into a large prism of irregular form, having become imbedded, as it were, in a mass of the crystalline mixture, a phenomenon which was frequently observed in other cases.

The variable composition of these prisms is also indicated by a crystallographic examination. On attempting to measure the angles, multiple images were obtained from all the faces, and the only result arrived at was that the prism angle  $mm$  (see Fig. 1) was nearly  $90^{\circ}$ , so that the axes  $a$  and  $b$  are almost equal in length, just as in the crystals of the optically active modification described below. The forms present are  $m\{110\}$  and  $o\{111\}$ , and very rarely  $b\{010\}$ . Each face of the form  $m\{110\}$  is generally marked with a fine, irregular line in the direction of the  $c$ -axis, just as is frequently seen on quartz crystals; this line is often continued on to the pyramid form, and probably indicates twinning, as in the case of quartz; in addition to this line, light striæ parallel to  $c$  are also observed. The extinction through  $m\{110\}$  is straight all over the face, and the optic axis plane is  $b\{010\}$ . We were unable to cut a section in order to

FIG. 1.

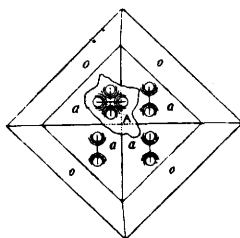


measure the optic axial angle owing to the extremely brittle nature of the crystals, but on carefully chipping a large number, a few chance fragments the sides of which were approximately parallel to  $a\{100\}$  were obtained, and through these the smaller axial angle could be observed; the angle in air was about  $45^{\circ}$ , and the inter-

ference figure exactly similar to that of the four-sided plates referred to below.

All the above observations having shown that the prismatic crystals do not represent a pure racemic form of camphorsulphonic chloride, we carefully examined the four-sided plates already alluded to. These crystals are generally 2—3 mm. in width, and are often observed growing in rows of as many as 10 or 12 individuals, attached to each other by their opposite corners; though at first transparent, they become opaque after some time, even when left in the solution. Their behaviour on heating is practically the same as that of the prisms, but, perhaps, not quite so irregular; they usually show signs of melting at about  $106^{\circ}$  and liquefy at about  $111^{\circ}$ ; the solidified mass generally melts at  $105.5$ — $106.5^{\circ}$  on reheating. They belong to the rhombic system, but attempts to measure them were as unsuccessful as those made with the prisms; the angle of the rhomb is, however, about  $90^{\circ}$ . The forms present are  $o\{111\}$  and  $a\{100\}$ ; the pinacoid is the acute bisectrix, and through it the optic axes are seen. The opposite corners of the crystals are joined by lines reaching across  $a\{100\}$ , these lines being the traces of two of the planes of symmetry upon the third. On examining the plates in convergent polarised light with a  $\frac{1}{4}$ -inch objective, a portion (A) of the crystal often shows two similar biaxial interference figures, superposed at  $90^{\circ}$  (see Fig. 2); this patch is caused by twinning upon  $\{011\}$ , the existence of the four optic axes being due to the composite nature of the crystal in the part (A).

FIG. 2.



These plates are frequently obtained on recrystallising the prisms from ethereal petroleum, sometimes also, but under conditions which we could not satisfactorily determine, when ethyl acetate is employed.

When the large prisms or the four-sided plates are dissolved in light petroleum (b. p.  $80$ — $90^{\circ}$ ) and the solution cooled very slowly, extremely thin, acicular prisms 3—4 cm. in length and about 0.5 mm. in width are deposited; these usually melt at  $106$ — $110^{\circ}$ , and, on reheating, the solidified mass liquefies completely at  $105.5$ — $107^{\circ}$ ; when

crystallisation has taken place quickly from a hot solution, the melting point of the crystal powder appears to be much more regular. In shape, the acicular prisms closely resemble the massive prisms obtained from ethyl acetate solution, but as they exhibit the form  $a\{100\}$ , the apparent optic axial angle in air,  $2E$ , could be measured; the following values were obtained from observations made with three crystals.

| Light.    | No. of obs. | Limits.                           | Mean.            |
|-----------|-------------|-----------------------------------|------------------|
| Sodium.   | 21          | $48^{\circ} 22' - 49^{\circ} 16'$ | $48^{\circ} 53'$ |
| Thallium. | 20          | $48 53 - 50 50$                   | $49 21$          |

The rather wide limits between which the observations lie are due to the extreme thinness of the plates, the brushes on which the cross wires of the polariscope had to be centred being necessarily of considerable breadth. In polarised light, the crystals show interference colours of high orders.

Although, as will be seen, the arguments which can be advanced against the view that one or other of the two forms of crystals just described may represent a true racemic modification are not quite so strong as in the case of the large prisms, we have been unable to adduce any evidence in favour of such an assumption.

It would seem, therefore, that dextro- and lævo-rotatory camphor-sulphonic chlorides have the property of crystallising together in almost any proportion, the crystals so formed being partially resolved into their components on recrystallisation; although these crystals are so different in habit from those of the pure, optically-active modification (see later, p. 566), the ratio of the crystallographic axes seems to be approximately the same in both cases.

The curious behaviour which the various kinds of crystals show when heated, and which at first, when they were thought to be homogeneous, was attributed to dimorphism, appears to be simply the result of admixture, as is shown by the following experiment:—12 well-defined tetrahedra, obtained from an approximately inactive solution, were well washed with ethyl acetate and petroleum successively, and, when dry, reduced to a fine powder. This powder behaved exactly like the well-defined prisms and four-sided plates; it began to melt at about  $106^{\circ}$  and was completely liquid at about  $115^{\circ}$ ; it melted for the second time at  $105.5 - 107^{\circ}$ .

There is little to add to the above account of the properties of the mixture of the two optically active camphorsulphonic chlorides. It is very readily soluble in chloroform and dissolves freely in most ordinary organic solvents except light petroleum, in which it is only sparingly soluble at high temperatures and almost insoluble at low; the appearance of the crystalline deposit obtained on rapidly cooling



a hot light petroleum solution is very characteristic, and is shown in Fig. 3. The behaviour of the sulphonic chloride with water and with ammonia is described later.

FIG. 3.



Hitherto only the sulphonic chloride obtained from the product of the interaction of camphor and anhydrosulphuric acid has been referred to; that obtained with the aid of chlorosulphonic acid has not yet been very carefully examined, but appears to be, on the whole, very similar in composition to the other. A dextrorotatory compound, identical in optical and in general properties, with that obtained by the first method has been separated from it; the principal portion of the product consists of a substance which crystallises in compact prisms, four-sided plates, and acicular prisms, apparently identical with those described above, and which is, therefore, in all probability, a mixture of dextro- and lævo-rotatory camphorsulphonic chlorides.

*Dextrorotatory Camphorsulphonic Chloride,  $C_{10}H_{15}O \cdot SO_2Cl$ .*

The isolation of this substance having been already described, we will pass at once to an account of its properties, its composition having been determined by the following analytical results.

0.1535 gave 0.2683  $CO_2$  and 0.0854  $H_2O$ .      $C = 47.65$ ;  $H = 6.18$ .  
 0.2265    ,,    0.1287  $AgCl$  and 0.2180  $BaSO_4$ .     $Cl = 14.04$ ;  $S = 13.21$ .  
 $C_{10}H_{15}O \cdot SO_2Cl$  requires  $C = 47.92$ ;  $H = 5.99$ ;  $Cl = 14.14$ ;  
 $S = 12.78$  per cent.

It melts at  $137.5^{\circ}$ , and its melting point is the same on reheating. It crystallises from boiling light petroleum in very peculiar, dendritic forms much the same in appearance as the crystals of the mixture shown in Fig. 3; it separates from cold chloroform in well-defined, transparent prisms. On crystallisation from hot ethyl acetate, it is deposited in curious, opaque masses, which have usually a more or less triangular form; when, however, crystallisation takes place slowly at the ordinary temperature, it is obtained in well-defined tetrahedra, Fig. 4, which are represented and described below (p. 566). The solubility of this substance in most ordinary solvents seems to be rather less than that of the mixture already described, nevertheless, it dissolves freely in most of the ordinary solvents with the exception of light petroleum. It is only slowly hydrolysed by boiling water, giving a colourless solution; it is readily acted on by warm potash.

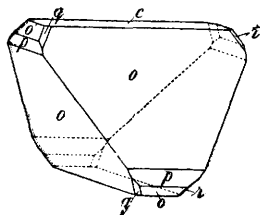
In determining its specific rotation, 1.3372 grams of substance melting at  $131.5^{\circ}$  were dissolved in chloroform, the solution diluted to 25 c.c., and examined at  $14^{\circ}$  in a 200 mm. tube; the average of seven concordant observations was  $[\alpha]_D = +13^{\circ} 46'$ ; the specific rotatory power is, therefore,  $[\alpha]_D = +128.7^{\circ}$ , a value higher than those of the bromo- and chloro-derivatives described below. Although great care was taken in purifying the sample employed in the rotation determination, we have hitherto had at our disposal such very small quantities of the pure substance that the value given above may not be quite accurate; it may be stated, however, that a carefully purified sample of the dextrorotatory sulphonic chloride obtained from the product of the interaction of camphor and chlorosulphonic acid gave a value practically the same as the other preparation, namely,  $[\alpha]_D = +127.6^{\circ}$ .

The crystals deposited from ethyl acetate solution are indistinguishable by mere inspection from cubic tetrahedra; the edges are generally a millimetre or so long. Such small crystals as these, show, as a rule, only the hemihedral octahedron, but on microscopic examination, the corners are frequently seen to be replaced by the complementary tetrahedron. Crystals having edges a centimetre or so in length may, however, be readily cultivated; these crystals ordinarily exhibit only the one tetrahedron form, but occasionally the combination of forms represented in Fig. 4 is obtained. The form  $o, \kappa\{111\}$  is always the largest present; it gives rather poor reflections on the goniometer, owing to a somewhat irregular habit of growth by which it is characterised. The complementary tetrahedron,  $o', \kappa\{1\bar{1}1\}$ , is, as before stated, only seldom present; its faces are, however, very bright and give good measurements. The pinacoid  $c\{001\}$  is more often observed; it is somewhat irregularly developed, but generally gives pretty fair results on measurement. The

prism form  $p\{110\}$  is very seldom exhibited and gives indifferent reflections. The two remaining forms,  $r\{011\}$  and  $q\{101\}$ , which are rarely observed, are very small, and their faces reflect so little light that the one,  $q\{101\}$ , is measured with difficulty, even when the lowest power of the larger Fuess goniometer is used; the other,  $r\{011\}$ , could not be measured at all.

The crystals are very brilliant, possess a glassy lustre, and are extremely brittle, breaking apparently with equal facility in all directions and showing a conchoidal fracture. It was impossible to cut sections for optical examination, but on crushing the crystals on the microscope stage, a few irregular fragments were obtained, showing a biaxial interference figure on examination under a wide-angled immersion objective in polarised light. The apparent optic axial angle in air is about  $45^\circ$ , that is to say, of about the same magnitude as the angle measured on the prismatic crystals of the mixture of optically active isomerides described above. The double refraction is positive and very strong.

FIG. 4.



Crystalline System : Orthorhombic. Sphenoidal hemihedrim.

$$a : b : c = 0.9980 : 1 : 1.0368$$

Forms observed :

|              |                               |            |
|--------------|-------------------------------|------------|
| $c$ . . . .  | $\{001\}$ . . . .             | $oP$       |
| $o$ . . . .  | $\kappa\{111\}$ . . . .       | $+P$       |
| $o'$ . . . . | $\kappa\{1\bar{1}1\}$ . . . . | $-P$       |
| $p$ . . . .  | $\{110\}$ . . . .             | $\infty P$ |
| $r$ . . . .  | $\{011\}$ . . . .             | $P\infty$  |
| $q$ . . . .  | $\{101\}$ . . . .             | $P\infty$  |

The following angular measurements were obtained :—

| Angle.                             | Number of observations. | Limits.                       | Mean.          | Calculated.      |
|------------------------------------|-------------------------|-------------------------------|----------------|------------------|
| $co = 001 : 111$                   | 17                      | $55^\circ 19' - 56^\circ 12'$ | $55^\circ 44'$ | —                |
| $op = 111 : 110$                   | 6                       | $33 \ 57 - 34 \ 31$           | $34 \ 15$      | $34^\circ \ 16'$ |
| $oc = 111 : 00\bar{1}$             | 15                      | $124 \ 1 - 124 \ 29$          | $124 \ 14$     | $124 \ 16$       |
| $oo = 111 : \bar{1}\bar{1}\bar{1}$ | 24                      | $108 \ 9 - 108 \ 51$          | $108 \ 34$     | —                |
| $oq = 111 : 101$                   | 8                       | $35 \ 16 - 36 \ 2$            | $35 \ 38$      | $35 \ 43$        |

Notwithstanding the close agreement between the observed and calculated values of the angles given in the above table, the small difference in length of the  $a$  and  $b$  axes is practically within the limits of experimental error; the angle  $bp(010 : 110)$ , the tangent of which measures the ratio  $b : a$ , is calculated as  $45^{\circ} 3' 30''$ ; if this angle were  $3\cdot5'$  smaller, the axes  $a$  and  $b$  would be equal in length. We should, therefore, have had considerable doubt as to whether the crystals belonged to the orthorhombic or to the tetragonal system had it not been for the conclusive evidence afforded by the observation of the biaxial interference figure. This point will be again referred to in connection with the sulphonamide derived from this substance.

*Dextrorotatory Camphorsulphonamide*,  $C_{10}H_{16}O\cdot SO_2\cdot NH_2$ .

In preparing this substance, a small quantity (1 gram) of the pure, finely-divided dextrorotatory sulphonic chloride melting at  $137\cdot5^{\circ}$  was placed in a stoppered bottle together with a little concentrated aqueous ammonia, and the mixture well shaken; a slight development of heat seemed to occur, but the powder did not dissolve completely even on prolonged shaking, although it distinctly underwent a change in appearance. After keeping for about six hours, the contents of the bottle were transferred to a dish and the ammonia allowed to escape at the ordinary temperature, during which process the amide was slowly deposited in a crystalline form; the next day the product was separated by filtration, washed with a little cold water, and dried at  $100^{\circ}$ ; the yield was  $0\cdot75$  gram, and, on evaporating the mother liquors, a further small quantity was obtained, so that but little of the chloride had been converted into the ammonium salt of the sulphonic acid.

For the analysis, the substance was recrystallised from ethyl acetate and dried at  $100^{\circ}$

$0\cdot1570$  gave  $0\cdot2988$   $CO_2$  and  $0\cdot1079$   $H_2O$ . C = 51·90; H = 7·63.

$C_{10}H_{16}O\cdot SO_2\cdot NH_2$  requires C = 51·95; H = 7·36 per cent.

Dextrorotatory camphorsulphonamide separates from cold ethyl acetate in well-defined crystals which are described below; these crystals show faint signs of melting at  $135^{\circ}$ , and liquefy completely at  $137\cdot5^{\circ}$ , that is to say, at the same temperature as the sulphonic chloride from which they are derived; the solidified mass melts at  $136$ — $137^{\circ}$  on reheating.

When the amide is slowly crystallised from its solution in concentrated ammonia, it separates in small, compact, six-sided plates which seem to contain water of crystallisation; when these crystals are heated, they begin to melt at about  $105^{\circ}$ , and at the same time effervesce, but they do not liquefy completely until the temperature rises to

about  $120^\circ$ ; after solidification, the melting point is  $136$ — $137^\circ$ . The amide is moderately easily soluble in hot water and in chloroform, separating from the latter in well-defined plates.

For the determination of its rotatory power,  $0.5629$  gram was dissolved in alcohol, the solution diluted to  $25$  c.c., and examined at  $13^\circ$  in a  $200$  mm. tube;  $\alpha_D = +4^\circ 13'$  as the mean of  $10$  concordant observations, or  $[\alpha]_D = +93.6^\circ$ .

The crystals of dextrorotatory camphorsulphonamide deposited on spontaneous evaporation of its solution in ethyl acetate are colourless and transparent, and belong to the tetragonal system; they are remarkable both for their great beauty and their very unsymmetrical development. They grow in a great variety of forms, the particular shape of any individual apparently depending on which face rests on the bottom of the vessel. In a few instances the pinacoid  $c\{001\}$  is the lowest face, and the crystal then develops into a double pyramid having its lower end much more truncated than the upper one, as shown in Fig. 5. If the crystal happens to grow on one of the dome faces  $p\{hok\}$ , a very unsymmetrical figure, which at first sight would seem to belong to the rhombohedral system, is obtained. At other times, four-sided, flattened pyramids, possessing  $a\{100\}$  as the basal plane, are formed. The crystallographic identity of these and several other habits assumed by the substance was fully proved by careful goniometrical measurements.

The form  $c\{001\}$  is the only one of the pinacoids which attains any considerable size; it is very frequently absent, but, when present, it gives pretty fair reflections on the goniometer. The form  $p\{101\}$  is always present, is generally very well developed, and gives very perfect images, so that it can be measured with considerable accuracy. The occurrence of the vicinal forms  $p'\{403\}$  and  $p''\{20\ 0\ 19\}$  is very remarkable, forms of such high orders being so rarely observed on crystals of artificial origin, and particularly on crystals of organic substances, which usually consist of but a few simple forms. The form  $p'\{403\}$  is very well defined and usually gives very perfect images; it is generally of about the same size as  $p\{101\}$ . The form  $p''\{20\ 0\ 19\}$  is, as a rule, much smaller, and does not give such sharp measurements as  $p'\{403\}$ ; compared, however, with the reflections ordinarily obtained from artificial crystals, the images are good.

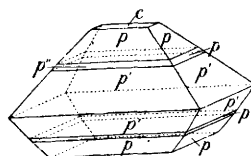
In addition to the forms enumerated above, several others vicinal to  $p\{101\}$ ,  $p'\{403\}$ , and  $p''\{20\ 0\ 19\}$  are generally observed, one of these in particular, which lies about  $6^\circ$  from  $p\{101\}$ , being very sharply defined. As will be seen from the data given below, measurements of a very exact nature may be made on these crystals. As the study of such vicinal forms seems likely to lead to results of great crystallographic importance, a careful investigation of this substance is

being undertaken with the object of ascertaining whether any regularities exist such as have been pointed out by former investigators in the cases of the minerals quartz, adularia (Websky, *Zeit. d. d. geolog Ges.*, 15, 677) and pyrrargyrite (Miers, *Zeit. f. Kryst.*, 15, 129).

On examination in convergent polarised light, the optic axis is seen through the basal pinacoid  $c\{001\}$ . The double refraction is positive in sign and weak, but both refraction and dispersion are strong.

Since this substance exhibits circular polarisation in solution, it should crystallise in hemihedral forms; as, however, the forms observed up to the present cannot be affected by hemihedrism, its non-appearance is accounted for. It is intended to compare the crystalline form of this dextrorotatory amide with that of the lævo-modification, if the latter can be prepared.

FIG. 5.



Crystalline System : Tetragonal.

$$a : c = 1 : 1.1253.$$

Forms present :

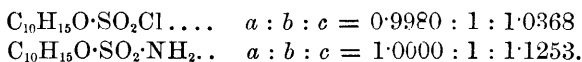
$$\begin{aligned} c & \dots \{001\} \dots oP \\ p & \dots \{101\} \dots P_{\infty} \\ p' & \dots \{403\} \dots \frac{2}{3}P_{\infty} \\ p'' & \dots \{20019\} \dots \frac{2}{9}P_{\infty}. \end{aligned}$$

The following angular measurements were obtained:—

| Angle.                   | Number of observations. | Limits.          | Mean.       | Calculated. |
|--------------------------|-------------------------|------------------|-------------|-------------|
| $cp = 001 : 101$         | 54                      | 48° 12'— 48° 35' | 48° 22' 30" | —           |
| $pp = 101 : \bar{1}01$   | 27                      | 96 38— 96 51     | 96 45 0     | 96° 45' 0"  |
| $pp = 101 : 10\bar{1}$   | 17                      | 83 9— 83 27      | 83 18 0     | 83 15 0     |
| $pp = 101 : 011$         | 10                      | 63 44— 63 53     | 63 48 30    | 63 49 0     |
| $pp = 101 : 01\bar{1}$   | 7                       | 116 4— 116 18    | 116 10 0    | 116 11 0    |
| $pp' = 101 : 403$        | 63                      | 7 50— 8 0        | 7 55 0      | 7 56 30     |
| $pp' = 101 : 40\bar{3}$  | 9                       | 75 10— 75 26     | 75 17 0     | 75 18 0     |
| $p'p' = 403 : 40\bar{3}$ | 48                      | 67 15— 67 30     | 67 22 30    | 67 22 0     |
| $pp'' = 101 : 20019$     | 7                       | 1 26— 1 29       | 1 27 0      | 1 27 30     |
| $p'p'' = 403 : 20019$    | 5                       | 6 27— 6 32       | 6 29 0      | 6 29 0      |
| $p'p' = 403 : 043$       | 4                       | 72 4— 72 7       | 72 5 0      | 72 5 0      |
| $p'p' = 403 : 04\bar{3}$ | 3                       | 107 54— 107 58   | 107 57 0    | 107 55 0    |

On comparing the axial ratios of the active sulphonamide with

those of the corresponding active sulphonic chloride, considerable similarity will be seen to exist:—



The ratio  $a : b$  is almost the same in both cases: that there is, however, a slight difference between these ratios for the two substances is shown by the fact that the amide is tetragonal, and hence has its two axes  $a$  and  $b$  equal in length, whilst the chloride, which is orthorhombic, necessarily has these two axes of different lengths. The difference between the ratio  $a : b$  in the two cases is very small, corresponding to a difference of only  $3'$  or so of arc; it is, however, somewhat curious that this difference is of such a nature as to change the crystalline system from a uniaxial to a biaxial one. The ratio  $b : c$  is, as will be seen from the above figures, considerably altered by the change from the sulphonic chloride to the sulphonamide.

There is apparently no crystallographic relationship between the active and inactive amides; the latter crystallises in the monosymmetric system and its axial ratios differ considerably from those of its active and tetragonal isomeride, although the crystalline form is not masked in either case by the presence of solvent.

*Inactive Camphorsulphonamide*,  $\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_2\cdot\text{NH}_2$ .

We prepared this compound by the same method as that described in the case of the dextrorotatory amide, using for this purpose a sample (1 gram) of the sulphonic chloride which had a specific rotatory power  $[\alpha]_D = +0.21^\circ$ , and which melted, when heated for the first time, at  $106.5\text{--}111^\circ$ , afterwards at  $105.5\text{--}106.5^\circ$ . The appearances and behaviour of the sulphonic chloride during the action were the same as in the case of the active compound; the crude product when dried at  $100^\circ$  was free from ammonium salts and weighed 0.7 gram; as a small quantity remained in the mother liquors, from which, on evaporating, it was deposited in well-defined plates, it is evident that the formation of ammonium camphorsulphonate takes place, if at all, only to a very slight extent.

The analyses were made with a sample which had been recrystallised from alcohol and dried at  $100^\circ$ .

0.1628 gave 0.3096  $\text{CO}_2$  and 0.1106  $\text{H}_2\text{O}$ .  $\text{C} = 51.86$ ;  $\text{H} = 7.54$ .

0.1856 ,, 0.1876  $\text{BaSO}_4$ .  $\text{S} = 13.59$ .

$\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_2\cdot\text{NH}_2$  requires  $\text{C} = 51.95$ ;  $\text{H} = 7.36$ ;  $\text{S} = 13.85$  per cent.

On examining an alcoholic solution of 0.6341 gram of the substance in 25 c.c. in a 200 mm. tube, it was found to be inactive; this observa-

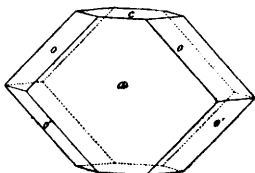
tion, and the generally well-defined character of the substance, point to the conclusion that the two optically active amides combine to form a stable racemic compound, a view which is confirmed by the crystallographic examination.

The crystals of the amide obtained from ethyl acetate solution show signs of melting at about  $133\cdot5^{\circ}$ , but do not melt completely until the temperature has risen to  $136\cdot5^{\circ}$ . When the capillary tube containing the liquid substance is cooled, crystallisation does not take place at all readily, but can sometimes be brought about by plunging the tube into the hot sulphuric acid (at about  $130^{\circ}$ ) and immediately withdrawing it; the opaque, crystalline mass obtained in this way melts sharply at  $122\text{--}123^{\circ}$  if it be heated almost immediately. When, on the other hand, the liquid or vitreous substance in the tube is allowed to crystallise slowly, or the substance melting at  $122\text{--}123^{\circ}$  is kept for some time, the melting point is found to be  $131\cdot5\text{--}132\cdot5^{\circ}$ . This behaviour is doubtless due to dimorphism; that it is not the result of the presence of excess of one of the optically active amides seems to be proved by the fact that a mixture of the crystals of this substance with those of the dextrorotatory amide melts at practically the same temperature as the separate constituents, namely, at  $133\cdot5\text{--}136\cdot5^{\circ}$  when heated for the first time, afterwards either partially at  $122\text{--}123^{\circ}$ , or not until  $131\cdot5\text{--}132\cdot5^{\circ}$ .

The solubility of this substance in various organic liquids seems to be approximately the same as that of the active amide; it dissolves freely in boiling water, from which it is deposited, on cooling, in small rhombs; it is moderately easily soluble in chloroform, but almost insoluble in boiling light petroleum.

It crystallises from alcohol in small, colourless, transparent, six-sided tablets, Fig. 6, which are generally less than 2 mm. in width. On examining these crystals in convergent polarised light, an optic axis is seen emerging from the form  $a\{100\}$ ; the axis is not central, however, but lies in the obtuse  $\beta$ -angle  $100 : 00\bar{1}$ . The extinction in  $a\{100\}$  is, of course, the trace of the plane of symmetry on that form, so that the plane of symmetry is also the optic axial plane; the double refraction is weak, and the dispersion strong. The crystals are unaffected by exposure to the atmosphere.

FIG. 6.





The pinacoid  $a\{100\}$  is very irregularly developed, and multiple images are obtained from it; this form is the largest present. The other pinacoid  $c\{001\}$  comes next in point of size, and also gives poor reflections. The pyramid forms  $o\{111\}$  and  $o'\{\bar{1}\bar{1}\bar{1}\}$  are smaller than the pinacoids, and generally give better images.

The following results were obtained on measurement:—

Crystalline System : Monosymmetric.

$$a : b : c = 0.821 : 1 : 1.047.$$

$$\beta = 81^\circ 4'.$$

Forms observed:

$$\begin{aligned} a & \dots \{100\} \dots \infty P \infty \\ c & \dots \{001\} \dots oP \\ o & \dots \{111\} \dots -P \\ o' & \dots \{\bar{1}\bar{1}\bar{1}\} \dots +P. \end{aligned}$$

| Angle.                                    | No. of measurements. | Limits.                       | Mean observed value. | Calculated.   |
|---|----------------------|-------------------------------|----------------------|---------------|
| $ac = 100 : 001$                          | 7                    | $80^\circ 59' - 82^\circ 24'$ | $81^\circ 48'$       | $81^\circ 4'$ |
| $ac = 100 : 00\bar{1}$                    | 6                    | $97 32 - 99 8$                | $98 17$              | $98 56$       |
| $ao = 100 : 111$                          | 15                   | $44 24 - 45 16$               | $44 50$              | $45 0$        |
| $oo' = 111 : \bar{1}\bar{1}\bar{1}$       | 21                   | $82 43 - 83 20$               | $83 3$               | —             |
| $ao' = 100 : \bar{1}\bar{1}\bar{1}$       | 19                   | $51 30 - 52 22$               | $51 57$              | —             |
| $co = 001 : 111$                          | 12                   | $53 24 - 54 31$               | $53 57$              | $53 41$       |
| $oo' = 111 : \bar{1}\bar{1}\bar{1}$       | 10                   | $61 43 - 62 36$               | $62 6$               | $62 31$       |
| $co' = 00\bar{1} : \bar{1}\bar{1}\bar{1}$ | 18                   | $63 12 - 64 27$               | $63 48$              | —             |

#### *Optically Inactive Camphorsulphonic Derivatives.*

The sulphonic derivatives of camphor which are now to be described were prepared from the sulphonic chloride previous to the discovery of its composite nature; it is very probable, therefore, that the samples employed were feebly dextrorotatory. Under these circumstances, it is possible that some of the preparations, even after having been purified, were mixtures consisting of a large proportion of a racemic with a very small proportion of a dextrorotatory compound; as, however, fairly concentrated aqueous solutions of the sodium and barium salts of the sulphonic acid showed no appreciable rotation on examination in a 200 mm. tube, and as, moreover, the ammonium and zinc salts, which form well-defined crystals, appeared to be homogeneous, we do not think that the dextrorotatory substance, even if it were present at all, could have been in sufficient quantity to cause any appreciable errors, except perhaps in the determinations of the water of crystallisation of some of the salts.

*Camphorsulphonic acid*,  $C_{10}H_{16}O \cdot SO_3H$ .

Although this compound is the product of the action of either anhydrosulphuric or chlorosulphonic acid on camphor, it cannot be directly isolated from the solutions, but must first be converted into the sulphonic chloride. In preparing the pure acid, the finely-divided, pure sulphonic chloride (about 10 grams) is placed in a flask containing about 20 c.c. of distilled water, and provided with a reflux condenser; the flask is then heated on a sand-bath. Apparently no change takes place at first, but after boiling for some time the crystals begin to change to a colourless oil which slowly passes into solution. As soon as the whole is dissolved, the colourless solution is transferred to a dish and evaporated on the water-bath until it begins to smell distinctly of hydrochloric acid; it is now diluted with alcohol, and again evaporated to a small bulk; this process having been continued until a portion of the syrupy residue gives no precipitate with a dilute solution of silver nitrate, a little water is added, and the solution heated on the water-bath to expel the alcohol.

The aqueous solution of camphorsulphonic acid thus prepared has usually a yellowish colour, due, apparently, to the decomposition of some of the acid by the hydrochloric acid which becomes concentrated during the first evaporations; when care is taken not to concentrate too far before adding alcohol, only very slight charring occurs, and a practically pure solution of the sulphonic acid is obtained.

When the syrupy, aqueous solution is kept for some days over sulphuric acid, the sulphonic acid is deposited in colourless, leaf-like crystals which are hygroscopic; although in very dry weather the crystals seem to undergo little change on exposure to the air, they rapidly deliquesce in a moist atmosphere; for this reason the acid was not analysed, and the properties of the solid substance were not very fully examined.

A small quantity of the crystalline substance which had been kept for some days on porous earthenware over sulphuric acid melted at  $56-58^\circ$ ; when the capillary tube containing the liquid acid was slowly heated to  $105^\circ$ , no effervescence was observed, and, some time afterwards, the tube having been kept in a desiccator, the melting point was again found to be  $56-58^\circ$ ; these observations seem to show that the crystalline acid is anhydrous, or that it does not lose its water at  $105^\circ$  (compare the behaviour of bromocamphorsulphonic acid, p. 585).

The crystals of camphorsulphonic acid are very readily soluble in water and in alcohol; they seem, also, to be soluble to a slight extent in dry ether.

The aqueous solution of the acid has a sour, rather bitter taste, turns blue litmus red, and rapidly decomposes carbonates with effervescence; granulated zinc placed in a cold, moderately concentrated solution is slowly acted on with evolution of gas, and, on warming, the metal is rapidly dissolved; magnesium in the form of ribbon is also readily acted on when the solution is warmed, but silver and copper seem not to be attacked even by boiling, concentrated solutions.

In concentrated solutions of the ammonium salt, solutions of copper, lead, silver, mercuric, and stannous salts produce no precipitate; the addition of a drop of ferric chloride produces a faint yellow coloration, and on warming a distinct reddish colour, which changes again to a faint yellow on cooling.

*Ammonium camphorsulphonate*,  $C_{10}H_{15}O \cdot SO_2 \cdot ONH_4$ .—This salt is easily obtained by adding a slight excess of ammonia to an aqueous solution of the acid, prepared as described above, and then evaporating on the water-bath. During this process the solution, which is at first slightly coloured, but clear, rapidly becomes turbid owing to the separation of a very small quantity of a brownish, flocculent substance; on filtering from this impurity, a colourless solution of the salt is obtained. The formation of this precipitate is observed in preparing all the salts of the sulphonic acid, and is doubtless due to the presence of traces of some decomposition product of the acid originating in the manner already suggested.

The ammonium salt crystallises from its concentrated aqueous solutions in colourless needles or prisms which, when thoroughly air dried, do not lose in weight when heated at  $130^\circ$ ; it is very readily soluble in water, alcohol, and acetone, but seems to be insoluble in ether and benzene.

*Sodium camphorsulphonate*,  $C_{10}H_{15}O \cdot SO_2 \cdot ONa$ .—This compound is formed when the aqueous solution of the acid is neutralised with pure sodium carbonate; on evaporating the filtered solution to a syrup and then allowing to cool, the salt is obtained in ill-defined, colourless plates.

For analysis, the crystals were first dried on porous earthenware and then exposed to the air for many days until approximately constant in weight; it may be here stated that many of the salts of camphorsulphonic acid, and of the corresponding chloro- and bromo-acids described below, are very sensitive to changes in the hygrometric state of the atmosphere, and on exposure to the air they gain or lose in weight according as the air is damp or dry; this variation is not very great, but is probably sufficient to cause slight errors in the determinations of the water of crystallisation of some of the salts.

0.3134 gave 0.0739  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 7.64$ .

0.7768 lost 0.0899 at  $100^\circ$ .  $\text{H}_2\text{O} = 11.57$ .

$\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_2\cdot\text{ONa} + 3\text{H}_2\text{O}$  requires  $\text{Na} = 7.46$ ; 2 out of  $3\text{H}_2\text{O} = 11.69$  per cent.

Judging by these results, the salt contains 3 mols.  $\text{H}_2\text{O}$ , but, as it slowly decomposes at  $130^\circ$ , the water could not be estimated directly.

Sodium camphorsulphonate is very readily soluble in water, alcohol, and acetone, but seems to be insoluble in benzene; it does not melt in its water of crystallisation when heated at  $100^\circ$ , as do the sodium salts of chloro- and bromo-camphorsulphonic acids.

*Potassium camphorsulphonate*,  $\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_2\cdot\text{OK} + 1\frac{1}{2}\text{H}_2\text{O}$ , was prepared in the same way as the sodium salt; it crystallises from hot concentrated aqueous solutions in colourless, striated needles, and is readily soluble in alcohol and acetone.

Analyses of the air-dried salt gave the following results.

0.6657 lost 0.0599 at  $100^\circ$ , and no further loss occurred at  $140\text{--}145^\circ$ , although the salt turned slightly brown.  $\text{H}_2\text{O} = 9.0$ .

0.3081 gave 0.0873  $\text{K}_2\text{SO}_4$ .  $\text{K} = 12.7$ .

$\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_2\cdot\text{OK} + 1\frac{1}{2}\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 9.1$ ;  $\text{K} = 13.1$  per cent.

*Barium camphorsulphonate*,  $(\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_2\cdot\text{O})_2\text{Ba} + 3\frac{1}{2}\text{H}_2\text{O}$ .—In preparing this salt, an aqueous solution of the acid was boiled for some time with excess of pure barium carbonate, and the slightly acid, filtered solution evaporated on the water-bath; on cooling, the solution slowly changed into a colourless, crystalline mass, which was then spread on biscuit ware and finally dried in the air until it ceased to continuously lose in weight. Various preparations were analysed with the following results.

I. 0.7759 lost 0.0714 at  $150^\circ$ .  $\text{H}_2\text{O} = 9.20$ .

0.2775 gave 0.0976  $\text{BaSO}_4$ .  $\text{Ba} = 20.69$ .

II. 0.4643 lost 0.0436  $\text{H}_2\text{O}$  at  $150^\circ$ .  $\text{H}_2\text{O} = 9.39$ .

0.2755 gave 0.0975  $\text{BaSO}_4$ .  $\text{Ba} = 20.67$ .

III. 0.5198 lost 0.0417 at  $100^\circ$ , a further loss of 0.0067 gram occurring at  $135\text{--}140^\circ$ .  $\text{H}_2\text{O} = 8.02$  (at  $100^\circ$ ); 1.4 (between  $100^\circ$  and  $130^\circ$ ).

0.2847 gave 0.1000  $\text{BaSO}_4$ .  $\text{Ba} = 20.65$ .

$(\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_2)_2\text{Ba} + 3\frac{1}{2}\text{H}_2\text{O}$  requires  $\text{Ba} = 20.69$ ;  $3\frac{1}{2}\text{H}_2\text{O} = 9.51$ ; 3 out of  $3\frac{1}{2}\text{H}_2\text{O} = 8.15$ ,  $\frac{1}{2}\text{H}_2\text{O} = 1.46$  per cent.

These results seem to show that the salt crystallises with  $3\frac{1}{2}$  mols.  $\text{H}_2\text{O}$ , of which three are expelled at  $100^\circ$ , the remaining  $\frac{1}{2}$  mol. being lost between  $100^\circ$  and  $130^\circ$ .

The sodium, potassium, and barium salts which have been heated

at 100°, are very hygroscopic, and rapidly gain in weight on exposure to the air, but without liquefying; for this reason the determinations of the percentage of metal were all made with air-dried samples, a portion of the preparation being taken at the same time for estimating the water of crystallisation.

*Zinc camphorsulphonate* is obtained in beautiful, colourless, transparent prisms, when granulated zinc is dissolved in an aqueous solution of the acid, and the filtrate slowly evaporated; when crystallisation takes place quickly from hot solutions, the salt is deposited in lustrous plates; it is readily soluble in water, alcohol, and acetone.

*Magnesium camphorsulphonate*, prepared in a similar manner, crystallises from water in colourless, lustrous plates, or in peculiar cauliflower-like masses; it dissolves freely in alcohol.

#### *Sulphonic Derivatives of Bromocamphor.*

*Preparation of bromocamphor.*—The best method of preparing bromocamphor is, without doubt, that described by Armstrong and Matthews (*Chem. News*, 1878, **37**, 4), as it has the advantage of being very simple in operation and of affording a good yield of pure product; it seems, nevertheless, to have been overlooked by all subsequent workers in this field. The following are the details of the process:—Powdered camphor, in quantities of about 150 grams, is placed in a large flask, heated on a water-bath, and a little bromine gradually added from a stoppered funnel; the mass soon liquefies, forming an almost colourless oil, hydrogen bromide being rapidly evolved; as soon as the evolution of gas slackens, more bromine is added, the process being continued until the theoretical quantity (160 grams) of halogen has been employed. During bromination we frequently observed the formation of a readily volatile substance, which sublimes into the neck of the flask, and is there deposited in light orange needles; this compound rapidly liquefies on exposure to the air, and is probably identical with Laurent's "bromure de camphre,"  $C_{10}H_{16}OBr_2$  (Gerhardt, *Traité de Chimie Org.*, **3**, 696), which was investigated by Swarts (*L'Institut*, 1862, 63). As soon as bromination is complete, the contents of the flask are poured into a large volume of water, the almost colourless solid product separated by filtration, washed with water, and crystallised from boiling methylated spirit; two crystallisations generally give pure bromocamphor, melting at 74°; the immediate yield usually amounts to about 180 grams, and further quantities can be obtained from the mother liquors. The character of the residual oily substance will be considered on a subsequent occasion.

*Sulphonation of Bromocamphor with Anhydrosulphuric acid.*

Bromocamphor readily dissolves in 10 per cent. anhydrosulphuric acid with slight development of heat, giving an amber-coloured solution of bromocamphorsulphonic acid; sulphonation occurs without any appreciable charring, and on pouring the solution into water no separation of bromocamphor is observed. In preparing large quantities of the sulphonic acid, pure bromocamphor (100 grams) is treated with five times its weight of 10 per cent. anhydrosulphuric acid, and after a few minutes the solution is poured on to ice; after diluting with water, the solution is neutralised with calcium carbonate and milk of lime, the calcium sulphate separated by filtration, and the filtrate treated with sodium carbonate as long as a precipitate is produced; the solution of the sodium salt is evaporated, any calcium sulphate which is deposited during the process being separated, and the syrupy residue is then heated in an air-bath at 130—135°, until it is transformed into a brown, friable, hygroscopic mass, similar in appearance to the crude sodium salt of camphorsulphonic acid. The yield of crude anhydrous salt is about 100 grams.

For obvious reasons, we made no attempt to obtain bromocamphorsulphonic acid from the crude calcium or sodium salt, but proceeded at once to the preparation of the sulphonic chloride. When the crude anhydrous sodium salt is triturated with phosphorus pentachloride, as described in the preparation of camphorsulphonic chloride, a dark pasty mass results, and on pouring this product on to powdered ice, the bromosulphonic chloride separates in the form of sticky, dirty grey clots. After stirring well, the mixture is transferred to a separating funnel, and shaken two or three times with a considerable quantity of chloroform; the chloroform extract is then well washed with small quantities of water, dried with calcium chloride, filtered, and evaporated; the residue is a thick, dark brown or black oil, the weight of which is, on the average, about 40 per cent. of the crude sodium salt employed.

*Bromocamphorsulphonic Chloride, C<sub>10</sub>H<sub>14</sub>OBrSO<sub>2</sub>Cl.*

After a very short time the crude oily sulphonic chloride begins to solidify, and slowly changes into a dark brown, semi-solid mass, which contains a large proportion of crystalline substance. The pure sulphonic chloride is very easily isolated; on repeatedly washing the tarry mass with small quantities of dry ether, the oily and tarry matters are, to a great extent, removed, and a brown crystalline substance remains; the latter is obtained in large, well-defined, transparent crystals, by repeated crystallisation from hot chloroform.

Analyses of the purified compound showed it to be bromocamphorsulphonic chloride; lead chromate was used for the combustions, a silver spiral being placed at the front of the tube; the chlorine and bromine were estimated together by Carius' method, and the sulphuric acid in the filtrate from the silver salts was determined by precipitation with barium nitrate.

- I. 0.1622 gave 0.2171 CO<sub>2</sub> and 0.0661 H<sub>2</sub>O.  
 II. 0.1633 „ 0.2157 CO<sub>2</sub> „ 0.0631 H<sub>2</sub>O.  
 III. 0.2024 „ 0.2036 Ag(ClBr) and 0.1438 BaSO<sub>4</sub>.  
 IV. 0.2293 „ 0.2337 Ag(ClBr) „ 0.1609 BaSO<sub>4</sub>.  
 V. 0.1912 „ 0.1905 Ag(ClBr).

|           | Calculated for<br>C <sub>10</sub> H <sub>14</sub> OBr·SO <sub>2</sub> Cl. | Found. |       |       |       |       | p. c. |
|-----------|---|--------|-------|-------|-------|-------|-------|
|           |   | I.     | II.   | III.  | IV.   | V.    |       |
| C . . . . | 36.42   | 36.50  | 36.02 | —     | —     | —     | p. c. |
| H . . . . | 4.26  | 4.52   | 4.30  | —     | —     | —     | „     |
| O . . . . | —   | —      | —     | —     | —     | —     | „     |
| S . . . . | 9.73  | —      | —     | 9.76  | 9.64  | —     | „     |
| Cl + Br   | 35.03   | —      | —     | 35.05 | 35.52 | 34.72 | „     |

Bromocamphorsulphonic chloride, prepared from the product of the action of anhydrosulphuric acid on bromocamphor, separates from cold chloroform in magnificent, transparent octahedra, and from hot alcohol in small, well-defined crystals, apparently of the same form as those obtained from chloroform. It melts at 136—137° without visible decomposition, but at higher temperatures it slowly decomposes, a large quantity of gas being evolved. It is very readily soluble in hot chloroform, glacial acetic acid, benzene, and acetone; it also dissolves freely in these liquids at the ordinary temperature, but is much less readily soluble in ether, and only very sparingly in cold light petroleum boiling at 80—90°. It is rather slowly hydrolysed by boiling water, but when warmed with moderately concentrated potash, it is almost immediately attacked, yielding potassium chloride and potassium bromocamphorsulphonate; quantitative experiments showed that, after acidifying with nitric acid, the chlorine which is precipitated on adding silver nitrate is 10.89 per cent. of the sulphonic chloride employed, theory demanding 10.74 per cent.

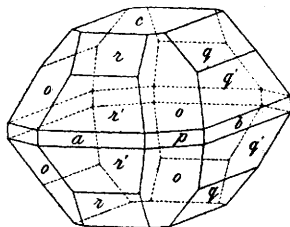
Bromocamphorsulphonic chloride is a very stable substance; it can be crystallised from a hot glacial acetic acid solution of chromic acid; when a small quantity is dissolved in hot concentrated nitric acid, the solution boiled for a few minutes and then poured into cold water, practically the whole of the sulphonic chloride is precipitated unchanged.

The sulphonic chloride is optically active. For the determination

of its specific rotatory power, we dissolved 1.3714 grams of the pure substance in chloroform and made the solution up to 25 c.c.; the observations were made at  $14^{\circ}$ ;  $l = 20$  cm. The rotatory power  $\alpha_D$  was found to be  $+14^{\circ} 23'$  as the average of 17 readings, all lying within  $4'$  of the mean; the specific rotatory power is, therefore,  $[\alpha]_D = +131^{\circ}$ . Observations of the rotatory power made with the rays  $L_{1a}$  and  $T_{1a}$  showed that the dispersion was very large, but the measurements were not very concordant, owing to the feeble illumination.

The crystals deposited from a chloroform solution belong to the orthorhombic system, Fig. 7, the pinacoid  $c\{001\}$  being normal to a bisectrix. The dome forms  $r\{101\}$ ,  $r'\{201\}$ ,  $q\{011\}$ , and  $q'\{021\}$  are generally the largest present, but give rather poor reflections on the goniometer, owing to the faces being somewhat uneven in character; this is, perhaps, to be attributed to the great solubility of the substance in the solvent employed. The pinacoids  $a\{100\}$  and  $b\{010\}$  are not always developed; they are very small and give indifferent images. The basal plane is also frequently absent, but is sometimes of considerable size and then gives very good reflections. The pyramid  $o\{111\}$  is generally well developed and yields good measurements. The form  $k\{221\}$  is seldom observed, but when present it is very bright and gives good images. In the case of a particularly well formed crystal which exhibited nearly all the other forms, the

FIG. 7.



pyramid  $k\{221\}$  showed only one-half the full number of faces; these were  $(221)$ ,  $(\bar{2}21)$ ,  $(2\bar{2}\bar{1})$ , and  $(\bar{2}\bar{2}\bar{1})$ ; this, however, was probably only fortuitous, such a selection of the faces of this form not according with the hemihedrism of the orthorhombic system.

Although the substance shows circular polarisation in solution, the crystals do not seem to be hemihedral; this is, however, by no means a unique case, as ordinary camphor, menthol, and patchouli camphor do not crystallise in hemihedral forms. Pyroelectricity could not be detected, and attempts to obtain corrosion figures, which so frequently indicate hemihedral structure, by etching the faces of large



crystals with ether or chloroform, were unsuccessful. The crystals exhibit no definite cleavage, but on rapid heating, tend to split up along surfaces approximately parallel to the basal plane  $c\{001\}$ ; the fracture is, however, very conchoidal.

Crystalline System : Orthorhombic.

$$a : b : c = 1.0518 : 1 : 0.8912.$$

Forms present :—

|      |      |           |      |                       |
|------|------|-----------|------|-----------------------|
| $a$  | .... | $\{100\}$ | .... | $\infty\bar{P}\infty$ |
| $b$  | .... | $\{010\}$ | .... | $\infty\bar{P}\infty$ |
| $c$  | .... | $\{001\}$ | .... | $oP$                  |
| $r$  | .... | $\{101\}$ | .... | $\bar{P}\infty$       |
| $r'$ | .... | $\{201\}$ | .... | $2\bar{P}\infty$      |
| $q$  | .... | $\{011\}$ | .... | $\bar{P}\infty$       |
| $q'$ | .... | $\{021\}$ | .... | $2\bar{P}\infty$      |
| $o$  | .... | $\{111\}$ | .... | $P$                   |
| $p$  | .... | $\{110\}$ | .... | $\infty P$            |
| $k$  | .... | $\{221\}$ | .... | $2P$                  |

The following angular measurements were obtained :—

| Angle.                   | No. of obser-<br>vations. | Limits. |           | Mean.   | Calculated. |
|--------------------------|---------------------------|---------|-----------|---------|-------------|
| $ar' = 100 : 201$        | 4                         | 30° 16' | — 30° 31' | 30° 24' | 30° 33'     |
| $r'r = 201 : 101$        | 17                        | 19      | 1— 19 20  | 19 8    | 19 11       |
| $cr = 001 : 101$         | 14                        | 39 58   | — 41 7    | 40 34   | 40 17       |
| $cr' = 001 : 201$        | 18                        | 58 45   | — 60 29   | 59 35   | 59 27       |
| $ar = 100 : 101$         | 5                         | 49 38   | — 49 56   | 49 46   | 49 44       |
| $r'r' = 201 : 20\bar{1}$ | 11                        | 59 46   | — 61 52   | 60 57   | 61 5        |
| $q'q = 021 : 011$        | 21                        | 18 47   | — 19 11   | 18 57   | 19 0        |
| $cq = 001 : 011$         | 24                        | 40 57   | — 42 6    | 41 39   | 41 42       |
| $cq' = 001 : 021$        | 16                        | 59 4    | — 61 18   | 60 13   | 60 42       |
| $q'q' = 021 : 02\bar{1}$ | 12                        | 58 1    | — 59 33   | 58 49   | 58 35       |
| $co = 001 : 111$         | 29                        | 50 3    | — 51 47   | 50 53   | —           |
| $ok = 111 : 221$         | 5                         | 16 42   | — 17 3    | 16 51   | 16 59       |
| $ko = 221 : 11\bar{1}$   | 8                         | 61 4    | — 61 43   | 61 22   | 61 15       |
| $ro = 101 : 111$         | 7                         | 33 57   | — 34 36   | 34 18   | 34 13       |
| $oo = 111 : 1\bar{1}1$   | 4                         | 68 6    | — 68 44   | 68 29   | 68 26       |
| $qo = 011 : 111$         | 34                        | 31 48   | — 32 30   | 32 19   | —           |
| $oo = 111 : 1\bar{1}1$   | 7                         | 64 10   | — 64 52   | 64 34   | 64 38       |
| $ao = 100 : 111$         | 4                         | 57 28   | — 57 54   | 57 45   | 57 41       |
| $bo = 010 : 111$         | 5                         | 55 21   | — 56 1    | 55 40   | 55 47       |
| $oo = 111 : 1\bar{1}1$   | 17                        | 77 49   | — 78 37   | 78 13   | 78 14       |
| $or' = 111 : 201$        | 7                         | 38 34   | — 38 51   | 38 42   | 38 39       |
| $oq' = 111 : 021$        | 9                         | 36 49   | — 37 1    | 36 56   | 36 57       |
| $r'q' = 201 : 02\bar{1}$ | 6                         | 104 18  | — 104 30  | 104 23  | 104 24      |

*Sulphonation of Bromocamphor with Chlorosulphonic acid.*

The bromocamphorsulphonic chloride, prepared in the above-mentioned manner, showed so great a tendency to assume a crystalline form, and separated from solvents in such beautiful, colourless crystals, that

it seemed difficult to believe it to be identical with the substance obtained by Marsh and Cousins from the product of the action of chlorosulphonic acid on bromocamphor, and described by them (*loc. cit.*) as a "black, semi-crystalline solid." It was, therefore, with considerable interest that we undertook a repetition of Marsh and Cousins' experiments, thinking it possible that we might obtain an isomeride of the sulphonic chloride described above.

Following the directions given by Marsh and Cousins, we dissolved pure bromocamphor (82 grams) in pure chloroform (164 grams) in a flask provided with a reflux condenser fitted with a calcium chloride drying tube, and added freshly-distilled chlorosulphonic acid (82 grams), boiling at 154—158°, to the solution from a tap-funnel fitting into the cork of the flask. The solution, which became slightly warm and gave off a little hydrogen chloride, was then heated on a water-bath for about nine hours, at the end of which time the evolution of gas was practically over, and the solution, previously homogeneous, had separated into two layers; a considerable quantity of a crystalline substance, which was, doubtless, the sulphonic acid, was frequently deposited during this process, but it was not found advantageous to separate it.

When cold, the contents of the flask were slowly poured on to powdered ice, the chloroform solution separated with the aid of a funnel, and the aqueous solution extracted twice with chloroform; the combined chloroform solutions were washed with water, dried with calcium chloride, and the chloroform evaporated, when a thick, dark yellow oil remained. This residue, according to Marsh and Cousins (*loc. cit.*, p. 971), is "nearly all  $\alpha$ -bromocamphorsulphonic chloride, together with an insignificant amount of unaltered bromocamphor," but the grounds on which this statement is based are not mentioned; the oil we obtained showed no signs of crystallising when agitated with a crystal of the pure sulphonic chloride already described, and remained liquid even after keeping for many weeks; we have not yet examined it very carefully, but from its behaviour we should infer that it contains a relatively small proportion of bromocamphorsulphonic chloride.

The aqueous solution of the sulphonic acid, which had been extracted with chloroform, was neutralised with barium carbonate, the filtrate treated with the necessary quantity of sodium carbonate, and the clear, yellowish-brown solution of the sodium salt evaporated to a syrup on the water-bath; this residue was then dried at 130—140°, until it became crisp and friable, reduced to a powder, and treated with phosphorus pentachloride in the usual manner, the theoretical quantity of the latter being used.

The dark pasty or liquid mass was slowly poured on to powdered

ice, and the crude sulphonic chloride, which separated in grey clots, extracted by shaking the mixture two or three times with chloroform; finally, the chloroform extract was dried with calcium chloride, filtered, and evaporated. The crude sulphonic chloride thus prepared was a thick oil, rather lighter in colour than that obtained by the first process we employed; the yield was about 70 grams. After a short time, the oil began to crystallise, and gradually solidified to a dark brown mass, in which, after long keeping, a considerable quantity of oily impurity was still present; the semi-solid product was stirred with a little dry ether, the mixture filtered on the pump, and the residue purified by washing with ether and recrystallising from hot chloroform.

The pure bromocamphorsulphonic chloride prepared in this way melted at 136—137°, and crystallised from cold chloroform in large, transparent octahedra; the analyses of this preparation gave the following results.

I. 0.1771 gave 0.1768 Ag(Cl,Br) and 0.1237 BaSO<sub>4</sub>.

II. 0.2070 „ 0.2065 Ag(Cl,Br).

|                   | Calculated for<br>C <sub>10</sub> H <sub>14</sub> OBr·SO <sub>2</sub> Cl. | Found. |             |
|-------------------|---|--------|-------------|
|                   |   | I.     | II.         |
| Cl + Br . . . . . | 35.03 p. c.   | 34.81  | 34.76 p. c. |
| S . . . . .       | 9.73 „  | 9.59   | — „         |

The bromocamphorsulphonic chloride obtained from the product of the action of anhydrosulphuric acid on bromocamphor was identical with the compound produced by the method employed by Marsh and Cousins; the identity of the two preparations was proved by the ordinary methods of examination, and also by the following crystallographic measurements:—

| Angle.                           | No. of obser-<br>vations. | Limits.         | Mean.   | Calculated. |
|----------------------------------|---------------------------|-----------------|---------|-------------|
| <i>cr</i> = 001 : 101            | 11                        | 39° 58'—40° 54' | 40° 28' | 40° 17'     |
| <i>r'r'</i> = 201 : 20 $\bar{1}$ | 7                         | 60 47—61 34     | 61 9    | 61 5        |
| <i>rr'</i> = 101 : 201           | 9                         | 18 52—19 27     | 19 12   | 19 11       |
| <i>cq</i> = 001 : 011            | 9                         | 40 56—41 53     | 41 33   | 41 42       |
| <i>q'q'</i> = 021 : 02 $\bar{1}$ | 3                         | 58 10—59 16     | 58 53   | 58 35       |
| <i>qq'</i> = 011 : 021           | 8                         | 18 47—19 28     | 19 4    | 19 0        |
| <i>co</i> = 001 : 111            | 7                         | 50 21—51 4      | 50 47   | 50 53       |
| <i>qo</i> = 011 : 111            | 5                         | 32 4—32 46      | 32 25   | 32 19       |

A number of other angles were measured, but the crystallographic identity of the samples prepared by the two methods is sufficiently obvious. The calculated values are taken from the table on page 580, as the measurements made on the sulphonic chloride prepared from the anhydrosulphuric acid product were much the more numerous, and consequently the more accurate.

The quantity of pure bromocamphorsulphonic chloride which is obtained from the crude product by the above method of purification is only small, amounting on the average to about 40 per cent.; the ethereal washings give, on evaporation, a dark oil, from which only small quantities of the crystalline substance are deposited on keeping. We have not yet examined this oily bye-product, so that at present its composition is a matter of conjecture; since, however, Marsh and Cousins' analysis, which appears to have been made with a sample of their "black, semi-crystalline solid," gave results\* agreeing very closely with those required by the pure sulphonic chloride, it would seem that the oily bye-product contains the same percentage of halogens, and is, therefore, possibly an isomeride.

*Bromocamphorsulphonamide*,  $C_{10}H_{14}OBrSO_2NH_2$ .

When pure, finely-divided bromocamphorsulphonic chloride is gradually added to a cold, saturated alcoholic solution of ammonia, a slight development of heat occurs, and the chloride dissolves with separation of ammonium chloride, the solution remaining colourless. When, after the lapse of about 12 hours, the ammonium chloride is separated by filtration and the filtrate evaporated to dryness on the water-bath, a semi-solid, very sticky, almost colourless mass is obtained; on washing this residue with chloroform, a thick, yellowish oil, which we have not examined, passes into solution, a colourless, crystalline powder remaining. Bromocamphorsulphonamide can be easily obtained in a pure condition by recrystallising this powder from boiling water; as, however, the yield is poor, probably owing to the formation of ammonium salt as well as to that of the oily substance, in preparing larger quantities of the amide we adopted a method similar to that made use of in the case of camphorsulphonamide, and proceeded as follows:—

The powdered sulphonic chloride, in quantities of about 5 grams, was treated with about 50 c.c. of concentrated aqueous ammonia in a stoppered bottle at the ordinary temperature, and the mixture was shaken at intervals during about two days; at the end of this time the powder had to a great extent dissolved, and even the portions which had not passed into solution seemed to be free from sulphonic chloride. The contents of the bottle were now transferred to a basin,

\* There is evidently some mistake in the numbers given by Marsh and Cousins; the weight of the mixed chloride and bromide of silver obtained from the given quantity of substance corresponds with 12.98 per cent. of chlorine and 29.33 per cent. of bromine, and not with 10.70 per cent. and 24.11 per cent. respectively, as stated; we assume, of course, that the substance analysed contained equivalent quantities of the two halogens.

and, after 24 hours' exposure to the air, the precipitated amide was separated by filtration; the crude product, nearly 4 grams, seemed to be practically pure.

Analyses of samples which had been recrystallised from boiling water and dried at 105—110° gave the following results.

- I. 0.1672 gave 0.2362 CO<sub>2</sub> and 0.0863 H<sub>2</sub>O.  
 II. 0.1676 „ 0.2374 CO<sub>2</sub> and 0.0820 H<sub>2</sub>O.  
 III. 0.2062 „ 0.1235 AgBr and 0.1528 BaSO<sub>4</sub>.  
 IV. 0.1872 „ 8.0 c.c. N<sub>2</sub> at 18° and 755 mm.

|              | Calculated for<br>C <sub>10</sub> H <sub>11</sub> OBr·SO <sub>2</sub> ·NH <sub>2</sub> . | Found. |       |       |      | p. c. |
|--------------|--|--------|-------|-------|------|-------|
|              |  | I.     | II.   | III.  | IV.  |       |
| C . . . . .  | 38.71  | 38.53  | 38.63 | —     | —    | p. c. |
| H . . . . .  | 5.16   | 5.73   | 5.43  | —     | —    | „     |
| Br . . . . . | 25.80  | —      | —     | 25.50 | —    | „     |
| S . . . . .  | 10.32  | —      | —     | 10.17 | —    | „     |
| N . . . . .  | 4.52   | —      | —     | —     | 5.00 | „     |
| O . . . . .  | —  | —      | —     | —     | —    | „     |

Bromocamphorsulphonamide crystallises from boiling water in long, colourless, lustrous needles, and from cold alcohol in compact, transparent prisms; it melts at 145°. It is readily soluble in hot alcohol, but only moderately easily in boiling water, and sparingly in benzene and chloroform; it seems to dissolve far more readily in a concentrated aqueous solution of ammonia than in water.

The preparation of this amide has been previously attempted by Marsh and Cousins, but they obtained it in a very impure condition, as it is described as “a brown, viscid oil” (*loc. cit.*, p. 974).

In measuring the rotatory power of the amide, we dissolved 2.2978 grams of substance in alcohol, and diluted to 50 c.c.;  $t = 11^\circ$ ,  $l = 4$  dm. The average of several concordant observations gave  $\alpha_D = 4.20^\circ 4'$ , so that  $[\alpha]_D = +112.4^\circ$ .

*Bromocamphorsulphonic acid*, C<sub>10</sub>H<sub>11</sub>OBr·SO<sub>3</sub>H.

This sulphonic acid is most conveniently prepared in a pure condition by hydrolysing the pure sulphonic chloride with boiling water as described in the case of camphorsulphonic acid (p. 573). No visible change takes place for some time on boiling the finely-divided crystalline powder with water, but, after about half an hour, the quantity of solid becomes visibly smaller, and on continued boiling the sulphonic chloride gradually disappears; the crystals do not liquefy.

The aqueous solution is then evaporated on the water bath, the residue taken up with alcohol, and the process repeated until a portion of the syrup gives no precipitate with a solution of silver

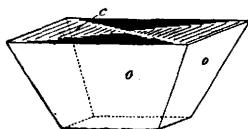
nitrate; care has to be taken that the first two or three evaporations are not carried too far, otherwise the solution turns yellow or brown, as is the case in the preparation of camphorsulphonic acid, and probably from the same cause. When the solution is found to be free from hydrochloric acid, it is evaporated once more with water to expel the alcohol, and then placed over sulphuric acid to crystallise.

According to Marsh and Cousins (*loc. cit.*, p. 974), bromocamphorsulphonic chloride "is remarkably stable towards water, and is not completely converted into acid, even after prolonged boiling with it;" we found that 7 grams of the pure, not very finely powdered, substance were completely hydrolysed after about two hours' boiling with 50 c.c. of distilled water.

When the concentrated aqueous solution of the sulphonic acid is kept over sulphuric acid, it gradually solidifies to a mass of transparent crystals which deliquesce in moist air; crystals are also occasionally deposited when the aqueous solution is evaporated in the air at the ordinary temperature, but only in very dry weather, and they disappear again when the atmosphere becomes damp. Crystals of the acid which have been kept for some time on porous earthenware over sulphuric acid melt at about 195–196°, apparently decomposing, when slowly heated from about 20°; when they are quickly heated to 165°, they melt with effervescence, due doubtless to the escape of water vapour, and then immediately solidify, melting for the second time at 195–196°; when quickly heated to 155°, they do not melt until the temperature rises to 195–196°. These observations seem to show that the hydrated acid melts at about 155–165°, losing water, the partially or completely dehydrated acid at 195–196°.

Bromocamphorsulphonic acid crystallises from water in transparent, tetragonal pyramids which frequently measure 4–5 mm. in the greatest dimension (see Fig. 8).

FIG. 8.



Forms present:

$c \dots \{001\} \dots oP. \quad o \dots \{101\} \dots P\infty.$

Crystalline System: Tetragonal.

$a : c > 1.$

The faces present on the crystals are always much corroded and pitted, owing, apparently, to re-resolution by the mother liquor; the larger of the two pinacoid faces is always striated parallel to its edges in the manner indicated in the figure. The crystals generally grow point downwards in the solution, and this fact may account for the appearance of only one-half of the dome  $\{101\}$  faces; this may, however, be due to hemimorphism. On a microscope slide the substance crystallises in thin, square plates which frequently have two opposite corners of the larger pinacoid face cut off by another form, probably  $\{110\}$ . There is a perfect cleavage parallel to  $c\{001\}$ , through which form the optic axis is visible, the double refraction being fairly strong.

No goniometric measurements could be made owing to the imperfect nature of the crystals, and to the fact that they are somewhat hygroscopic.

Crystals of the acid which had been freed from adherent water by pressure between folds of bibulous paper slowly and continuously lost weight during about four weeks when kept over sulphuric acid, and then did not undergo any further change in weight when heated at  $100^\circ$ ; the loss amounted to very nearly 16 per cent.

Bromocamphorsulphonic acid is very readily soluble in water and in alcohol; its aqueous solution has a strongly acid reaction to litmus, and a sour, very astringent, rather bitter taste.

This acid was prepared by Marsh and Cousins (*loc. cit.*, p. 971), who described it as "a black, tarry mass . . . which solidified on standing over sulphuric acid in a vacuum;" we can confirm Marsh and Cousins' observations regarding the solvent action of an aqueous solution of the acid; both zinc and magnesium are readily acted on, especially on warming, gas being evolved.

The acid is optically active; for the determination of its rotatory power, we employed a sample of the crystalline substance which had been kept over sulphuric acid until its weight became constant.

0.6443 gram of substance was dissolved in water, the solution made up to 25 c.c., and examined at  $14^\circ$  in a 20 cm. tube; the rotation was found to be  $\alpha_D = +4^\circ 33'$  as the average of eight concordant observations, from which  $[\alpha]_D = +88.27^\circ$ . This value may, possibly, be incorrect, because it was afterwards found that the aqueous solution of the acid had attacked the brass tube which was employed in the determination; as, however, the rotation was taken a few minutes after the solution was put into the tube, and did not undergo any appreciable change after keeping for about 15 hours, we did not think it necessary to repeat the observations, especially as we were not quite sure that the sample of acid taken was anhydrous.

Several salts of bromocamphorsulphonic acid were prepared by

neutralising the aqueous solution, obtained in the manner described above, with alkalis or alkali carbonates; in all cases we observed the formation of a slight brown turbidity on boiling the neutral solutions, but after this had been separated by filtration, colourless solutions, from which no further precipitation took place, were obtained. The salts all crystallise well and, with the exception of the ammonium salt, all those we examined contain water of crystallisation; as the wholly or partially dehydrated salts are hygroscopic, the analyses were almost invariably made with samples which had been exposed to the air until approximately constant in weight, portions of the same samples being taken at the same time for the rotatory power determinations. The hydrated salts, like those of camphorsulphonic acid, are rather sensitive to change in the hygrometric condition of the atmosphere, and undergo slight alterations in weight from day to day even after many weeks exposure to the air.

*Ammonium bromocamphorsulphonate*,  $C_{10}H_{14}OBr \cdot SO_2 \cdot ONH_4$ , seems to be less soluble in water than any of the other salts examined; an air-dried sample of the salt lost only 0.14 per cent. in weight when heated at  $100^\circ$ , and gave on analysis results agreeing with those required by the anhydrous compound.

0.2054 gave 0.1162 AgBr. Br = 24.09.

Calculated, Br = 24.38 per cent.

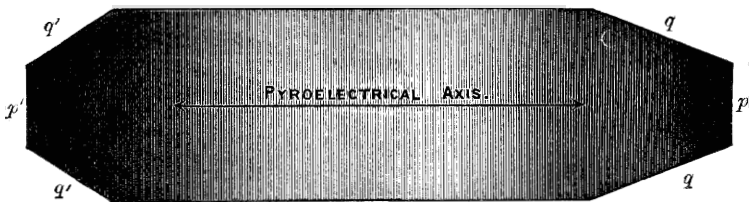
It separates from its cold aqueous solution in colourless, transparent, flattened prisms having the lustre of calcite, Fig. 10 (p. 588), and often attaining a length of several centimetres. The crystals are very brittle, breaking readily across their length and exhibiting a conchoidal fracture; there is a very good cleavage parallel to the pinacoid  $a\{100\}$ , the normal to which is a bisectrix, probably the obtuse one. Prisms showing both ends well developed are but rarely obtained, the crystals tending to grow in clusters from a common centre, one end being, therefore, imperfect. The pinacoids  $a\{100\}$  and  $c\{001\}$ , together with the prism  $r\{101\}$ , are faintly striated in the direction of the axis  $b$ . The other forms are never striated, but all the faces except  $a(100)$  give very poor reflections, owing partly to their bad development and partly to their small size. The substance being optically active in solution, evidence of hemihedral structure was naturally looked for, and it was found that the crystals were hemimorphic, the forms  $p\{110\}$  and  $q\{011\}$  on the one end of the prism being replaced by  $p'\{210\}$  and  $q'\{okl\}$ , where  $k > l$ , at the other end. The two latter forms are badly developed, and the form  $q'\{okl\}$  is so poor in character that measurements cannot be obtained from it; it is in all probability  $\{021\}$ .

Complete confirmation of the hemimorphic nature of the crystals



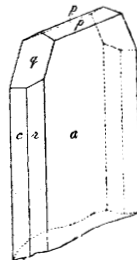
was obtained by an examination of their pyroelectrical properties, which are strongly marked, and may be readily shown by Kundt's method, in the following manner:—A crystal plate, supported on a piece of paper or a microscope slide, is warmed over a Bunsen burner; the heated plate is then placed on a piece of cork and lightly dusted over with an electrified mixture of red lead and sulphur, such as is used for the preparation of the so-called Lichtenberg's figures. The powder being projected from a rubber bellows-shaped vessel, the nozzle of which contains a piece of gauze, its two constituents become oppositely electrified by friction in the orifice. The red lead attaches itself to the negatively electrified end of the crystal plate, whilst the sulphur adheres to the positively charged end, the thickness of the layer increasing from the centre towards the ends, as shown in Fig. 9;

FIG. 9.



on subsequently examining the plate under the microscope, the positive and negative ends are recognised by their different colours. On dusting the powder on to the plate during cooling, the end of the crystals showing the forms  $p\{110\}$  and  $q\{011\}$  becomes yellow, owing to the sulphur being drawn to it, whilst the other end assumes the red colour of the lead oxide. The pyroelectrical axis is, therefore, identical with the geometrical axis  $b$ ; according to the nomenclature proposed by Rose, the end at which the forms  $p\{110\}$  and  $q\{011\}$  appear is the antilogous pole, while the end showing  $p'\{210\}$  and  $q'\{okl\}$  is the analogous pole.

FIG. 10.



The following crystallographic data were obtained :—

Crystalline System : Monosymmetric : Hemimorphic.

$$a : b : c = 1.9155 : 1 : 1.0252.$$

$$\beta = 74^\circ 37'.$$

Forms observed :

$$\begin{aligned} a &\dots \{100\} \dots \infty P\infty \\ c &\dots \{001\} \dots oP \\ r &\dots \{101\} \dots -P\infty \\ q &\dots \{011\} \dots P\infty \\ q' &\dots \{okl\} \dots mR\infty \\ p &\dots \{110\} \dots \infty P \\ p' &\dots \{210\} \dots \infty P2 \end{aligned}$$

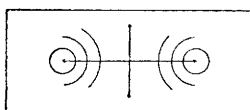
| Angle.                       | No. of observations. | Limits. |             | Mean.   | Calculated. |
|------------------------------|----------------------|---------|-------------|---------|-------------|
| $ar = 100 : 101$             | 17                   | 49°     | 11'—51° 30' | 50° 18' | —           |
| $rc = 101 : 001$             | 12                   | 23      | 41—24 43    | 24 19   | —           |
| $ac = 100 : 00\bar{1}$       | 19                   | 104     | 13—106 50   | 105 29  | 105° 23'    |
| $aq = 100 : 011$             | 8                    | 78      | 54—79 43    | 79 21   | 79 8        |
| $aq = \bar{1}00 : 011$       | 7                    | 99      | 56—101 6    | 100 33  | 100 52      |
| $cq = 001 : 011$             | 6                    | 44      | 16—45 21    | 44 55   | 44 40       |
| $qq = 011 : 01\bar{1}$       | 4                    | 89      | 45—90 41    | 90 7    | 90 40       |
| $qp = 011 : \bar{1}10$       | 3                    | 44      | 26—45 43    | 45 1    | 44 56       |
| $qp = 011 : \bar{1}10$       | 5                    | 57      | 22—58 25    | 57 54   | 58 6        |
| $rq = 101 : 011$             | 6                    | 49      | 3—50 2      | 49 30   | 49 36       |
| $rq = \bar{1}0\bar{1} : 011$ | 4                    | 130     | 2—130 57    | 130 35  | 130 24      |
| $ap = 100 : \bar{1}10$       | 21                   | 60      | 8—62 54     | 61 34   | —           |
| $pp = 110 : \bar{1}10$       | 10                   | 55      | 53—57 58    | 56 59   | 56 52       |
| $rp = 101 : \bar{1}10$       | 3                    | 71      | 50—72 49    | 72 10   | 72 18       |
| $rp = 101 : \bar{1}10$       | 4                    | 107     | 12—108 25   | 107 49  | 107 42      |
| $ap' = 100 : 210$            | 5                    | 41      | 37—42 54    | 42 19   | 42 43       |
| $p'p' = 210 : \bar{2}10$     | 3                    | 94      | 46—95 37    | 95 2    | 94 34       |
| $cp = 001 : \bar{1}10$       | 5                    | 82      | 7—83 12     | 82 17   | 82 45       |

Ammonium bromocamphorsulphonate shows circular polarisation in solution. For the rotatory power determination, 1.1500 grams of the salt, dried at 100°, were dissolved in water, the solution made up to 25 c.c., and examined at 9° in a 20 cm. tube; the mean of eight concordant readings gave  $\alpha_D = +7^\circ 48'$ , from which  $[\alpha]_D = +84.78^\circ$ , a result which is in fair agreement with that obtained by Marsh and Cousins.

Sodium bromocamphorsulphonate,  $C_{10}H_{14}OBr \cdot SO_2 \cdot ONa + 5H_2O$ , crystallises from cold water in large, thin, rectangular plates, sometimes as much as 10 mm. in length. The crystals are very brittle, and, as ordinarily obtained, show interference colours of high orders in polarised light. The large face is a bisectrix, and the optic axes emerge just outside the microscope field, as shown in Fig. 11. The

extinction is parallel to the sides of the plate, so that the crystals probably belong to the orthorhombic system.

FIG. 11.



Analyses of various samples of the air-dried salt gave the following results.

- I. 0.2931 lost 0.0624 at 135°, and gave 0.0471 Na<sub>2</sub>SO<sub>4</sub>.  
 II. 0.8658 ,, 0.1865 at 135—140°.  
 0.2583 gave 0.0443 Na<sub>2</sub>SO<sub>4</sub>.  
 III. 0.9251 lost 0.1961 at 135—140°.

|                        | Calculated for<br>C <sub>10</sub> H <sub>14</sub> OBr·SO <sub>3</sub> Na + 5H <sub>2</sub> O. | Found. |       |             |
|------------------------|---|--------|-------|-------------|
|                        |   | I.     | II.   | III.        |
| H <sub>2</sub> O ..... | 21.28 p. c.   | 21.29  | 21.54 | 21.19 p. c. |
| Na .....               | 5.44 ,,   | 5.21   | 5.56  | —           |

Our analyses, like those of Marsh and Cousins, show that the salt contains 5 mols. H<sub>2</sub>O; we cannot, however, confirm Marsh and Cousins' statement, that the salt retains 1 mol. H<sub>2</sub>O at 100°. When heated at this temperature, it first loses weight very rapidly, but after some time the expulsion of the water takes place only very slowly, doubtless owing to the fact that the salt melts to a vitreous mass; on prolonged heating at 100°, it loses about 20.6 per cent., and even then is not quite constant in weight.

For the rotatory power determination, 1.0326 grams of the air-dried salt were dissolved in water, and the solution made up to 25 c.c.;  $t = 9^\circ$ ,  $l = 20$  cm. The average of the observations gave  $\alpha_D = +5^\circ 13'$ , so that the specific rotatory power of the hydrated salt is  $[\alpha]_D = +63.1^\circ$ , that of the anhydrous salt  $[\alpha]_D = +80.2^\circ$ . The latter value appears to agree fairly well with that given by Marsh and Cousins, namely,  $[\alpha]_D = +76.4^\circ$ .\*

*Barium bromocamphorsulphonate*, (C<sub>10</sub>H<sub>14</sub>OBr·SO<sub>2</sub>·O)<sub>2</sub>Ba + 5½H<sub>2</sub>O, is very readily soluble in water, and could not be obtained in well-defined crystals, as the highly concentrated aqueous solutions gradually change to a colourless mass of a buttery consistency, which, however, becomes hard and crisp when spread on porous earthenware. Analyses of the air-dried salt gave the following results.

\* The value for the anhydrous salt, calculated from Marsh and Cousins' data, is, however,  $[\alpha]_D = +88.53^\circ$ , not  $76.4^\circ$ , so that the actual disagreement is considerable.

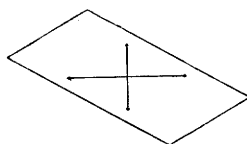
- I. 0.5675 salt lost 0.0656 at 140°.  
 0.1653 salt gave 0.0447 BaSO<sub>4</sub>.  
 II. 0.4699 salt lost 0.0551 at 135°.  
 0.2553 salt gave 0.0677 BaSO<sub>4</sub>.

|                        | Calculated for<br>(C <sub>10</sub> H <sub>14</sub> OBr·SO <sub>3</sub> ) <sub>2</sub> Ba + 5½H <sub>2</sub> O. | Found. |       |
|------------------------|--|--------|-------|
|                        |  | I.     | II.   |
| H <sub>2</sub> O ..... | 11.56  | 11.56  | 11.73 |
| Ba .....               | 16.00  | 15.89  | 15.59 |

To determine its rotation, we dissolved 1.4732 grams of the air-dried salt in water, and diluted to 25 c.c.;  $t = 9^\circ$ ,  $l = 20$  cm.;  $\alpha_D$  was found to be  $+7^\circ 34'$  as the mean of eight concordant readings, so that the specific rotatory power of the hydrated salt is  $[\alpha]_D = +64.23^\circ$ , and of the anhydrous salt  $[\alpha]_D = +72.5^\circ$ .

*Potassium bromocamphorsulphonate*, C<sub>10</sub>H<sub>14</sub>OBr·SO<sub>2</sub>·OK + 1½H<sub>2</sub>O, separates from cold water in large, flat, colourless, transparent plates, of the shape shown in Fig. 12. The faces are much broken up by

FIG. 12.



striae, hence no measurements could be made. When the salt is quickly deposited from its aqueous solution, an hour-glass-shaped structure is often seen inside the crystal; the angle of the rhomb is about  $60^\circ$ , and is bisected by the extinction; the large face is normal to a bisectrix. The edges of the plate are replaced by pyramid faces, and there is an imperfect cleavage parallel to the sides.

The hydrated crystals are stable in the air, but effloresce at  $100^\circ$ , and also when kept over sulphuric acid; the salt is very readily soluble in water and in hot alcohol.

Analyses of the substance gave the following results.

0.3433 air-dried salt lost 0.0248 at  $130^\circ$ . H<sub>2</sub>O = 7.22.

0.2826 salt dried at  $135^\circ$  gave 0.0686 K<sub>2</sub>SO<sub>4</sub>. K = 10.88.

C<sub>10</sub>H<sub>14</sub>OBr·SO<sub>3</sub>K + 1½H<sub>2</sub>O requires H<sub>2</sub>O = 7.18 per cent.

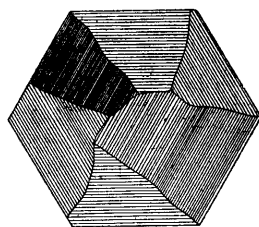
C<sub>10</sub>H<sub>14</sub>OBr·SO<sub>3</sub>K requires K = 11.18 per cent.

In measuring the rotatory power, a sample of the air-dried salt was employed, 1.2303 grams being dissolved in water, the solution made up to 25 c.c., and examined at  $10^\circ$  in a 200 mm. tube. The average of eight concordant observations gave  $\alpha_D = +7^\circ 2'$ , from which the

specific rotatory power is calculated to be  $[\alpha]_D = +71.44^\circ$ ; that of the anhydrous salt is, therefore,  $[\alpha]_D = +76.96^\circ$ .

*Zinc bromocamphorsulphonate* is easily prepared by dissolving the metal in an aqueous solution of the acid. It separates from its cold, aqueous solution, in six-sided, colourless, transparent plates, which frequently attain a length of 5—10 mm.; the crystals do not change in appearance at  $100^\circ$ , but melt with effervescence when heated on platinum in a Bunsen flame. On microscopic examination, the plates are seen to be striated with fine lines running parallel to the edges, and to consist of six twin fragments, as shown in Fig. 13; the

FIG. 13.



individual twinned pieces can be readily distinguished by examination in polarised light. Each twin fragment shows a biaxial figure of moderately large angle; the interference figure, however, is complicated by further twinning on the plane of the large face, as is shown by the absence of definite extinction in any of the six divisions of the crystals. The complete crystal would, therefore, seem to be built up of twelve individuals. The dispersion is strong, and the crystals are highly refractive.

*Magnesium bromocamphorsulphonate*, like the zinc salt, can be readily obtained by dissolving the metal in an aqueous solution of the acid; it separates in colourless, lustrous plates on concentrating the solution, and is readily soluble in water.

*Lithium bromocamphorsulphonate* can be prepared by saturating an aqueous solution of the acid with lithium carbonate. On filtering and evaporating the solution, a colourless mass, consisting of minute needles, is obtained. The salt is readily soluble in water, and seems to contain 2 mols.  $H_2O$ , as is shown by the following analysis.

0.5504 gram of substance lost 0.0550 gram at  $135^\circ$ .  $H_2O = 10.0$ .

$C_{10}H_{14}OBr \cdot SO_2 \cdot OLi + 2H_2O$  requires  $H_2O = 10.2$  per cent.

It will be seen from the above account of the salts of bromocamphorsulphonic acid that Marsh and Cousins' description of their properties

is entirely misleading; the dehydrated salts are, no doubt, highly hygroscopic and difficult to deal with, but they do not liquefy on exposure to the air. "As to their capability or not of crystallising," the only general conclusion to be drawn is that they all crystallise readily.

*Sulphonic Derivatives of Chlorocamphor.*

The study of the compounds obtained from bromocamphor having shown that the halogen substitution products of camphor, as well as camphor itself, are readily converted into well-defined, crystalline sulphonic derivatives, we should not have thought it necessary to carry out a similar investigation in the case of chlorocamphor had it not been for the recent work of Marsh and Cousins (*loc. cit.*). Their account of the sulphonic derivatives of chlorocamphor, when viewed in the light of our experience with the corresponding bromo-derivatives, seemed, however, to give such a wrong impression of the character of these compounds, that we thought it advisable to submit them to a fresh and extended investigation.

*Preparation of chlorocamphor.*—In preparing this substance, we followed Cazeneuve's directions (*Compt. rend.*, **94**, 1530), except that we employed dehydrated methylated spirit instead of absolute alcohol, and found it to answer almost as well as the more costly solvent; the following is a brief description of the process:—

Chlorine is passed into 500 grams of dehydrated methylated spirit containing 1000 grams of powdered camphor in suspension, the stream of gas being regulated so that but little hydrogen chloride escapes; after rather more than the theoretical weight of chlorine has been absorbed, the solution is poured into a large volume of water and the mixture kept for a day or two. During this time the semi-solid precipitate becomes considerably harder, and can be more easily dealt with; it is then freed, as far as possible, from hydrochloric acid by washing with water. If the product be now crystallised from alcohol, it is deposited as a camphor-like substance from which pure chlorocamphor is obtained only with difficulty; it is therefore boiled for some hours with alcoholic potash (500 grams of methylated spirit containing 100 grams of potash), the brown solution poured into water, the crude product separated by filtration, washed with water, and crystallised from methylated spirit; the first crystallisation gives a somewhat camphor-like substance, but, on recrystallising, pure chlorocamphor is obtained in long, hard, brittle prisms. The crude product separated from the solution in alcoholic potash is about 80 per cent. by weight of the camphor employed, but a further quantity may be obtained from the mother liquors. Cazeneuve gives the melting point of chlorocamphor as 83—84°, but according to our observations, the pure

substance melts sharply at  $93.5^{\circ}$ ; Balbiano (*Gazzetta*, **17**, 96) found the melting point to be  $92-92.5^{\circ}$ .

*Sulphonation of chlorocamphor.*—As we have not studied the action of anhydrosulphuric acid on chlorocamphor, and have hitherto only prepared small quantities of chlorocamphorsulphonic acid by sulphonating with chlorosulphonic acid in chloroform solution, it will be unnecessary to enter into the details of the process; the sulphonation and the subsequent preparation of the crude sodium salt were carried out substantially as described in the case of bromocamphor, and one point only seems to require notice, namely, that we frequently observed the separation of a considerable quantity of a crystalline substance during sulphonation. An examination of the properties of this product left little doubt that it was the sulphonic acid, but, being deliquescent and difficult to purify, it was not separated from the solution. The yield of crude sodium salt dried at  $130^{\circ}$  was usually about 65 grams from 50 grams of chlorocamphor.

*Chlorocamphorsulphonic Chloride*,  $C_{10}H_{14}O \cdot SO_2Cl$ .

The preparation of this compound from the crude sodium salt, by treating the latter with phosphorus pentachloride in the manner previously described, can be accomplished without difficulty; as in the case of the bromosulphonic chloride, the pasty or liquid product is poured on to powdered ice, the mixture stirred well, transferred to a separating funnel, and extracted with chloroform. The chloroform solution is then washed several times with small quantities of water, dried with calcium chloride, and the chloroform distilled from a water-bath. The yield of crude product is about one-half by weight of the sodium salt used.

The yellow or brown oil obtained in this way begins to crystallise after some time, but even on long standing it does not solidify completely; in some cases, apparently, when sulphonation has been carried too far, the crude sulphonic chloride is nearly black, and gradually changes to a pasty, tarry mass which is difficult to deal with. The " $\alpha$ -chlorocamphorsulphonic chloride," described by Marsh and Cousins as a "microcrystalline, black solid," was evidently a product of this kind, so that the result of their chlorine determination, which gave approximately the theoretical numbers, seems, as in the case of the crude bromocamphorsulphonic chloride, to indicate the presence of isomerides of the crystalline substance.

The pure compound can be easily isolated by washing the semi-solid mass on the pump with a little ether and crystallising the residue two or three times from a mixture of chloroform and ether, but we have not yet sufficiently investigated the matter to be able to

give a good method of purification. The process just mentioned is very rapid, but apparently a considerable proportion of the crystalline substance is dissolved during the washing with ether, and is not easily recovered from the oily mother liquors; the method of extracting with light petroleum, described in the case of camphorsulphonic chloride, was tried, but without much success, owing to the slight solubility of the chlorosulphonic chloride.

The following analyses were made with samples of the colourless crystalline compound prepared in this way.

0.1637 gave 0.2516  $\text{CO}_2$  and 0.0743  $\text{H}_2\text{O}$ . C = 41.92; H = 5.04.  
 0.1947 „ 0.1950  $\text{AgCl}$  and 0.1610  $\text{BaSO}_4$ . Cl = 24.74; S = 11.35.  
 $\text{C}_{10}\text{H}_{14}\text{O}\cdot\text{SO}_2\text{Cl}$  requires C = 42.14; H = 4.91; Cl = 24.85; S = 11.24.

Chlorocamphorsulphonic chloride resembles the corresponding bromo-derivative, not only in the readiness with which it crystallises, but also in most of its properties. It separates from cold chloroform in magnificent, colourless octahedra, which are fully described below; it is deposited from a mixture of ether and light petroleum in long, prismatic needles, and from ether containing a little chloroform in transparent crystals which seem to retain some of the solvent, since they become opaque when heated at  $100^\circ$ . It melts at  $123\text{--}124^\circ$ , and decomposes when strongly heated, with evolution of very irritating vapours. It is readily soluble in cold chloroform, ether, glacial acetic acid, and ethyl acetate, but only sparingly in boiling petroleum (b. p.  $80\text{--}90^\circ$ ), from which it separates almost completely on cooling. It seems to be insoluble in boiling water, by which it is hydrolysed rather slowly; it is, however, readily acted on by hot potash, with formation of potassium chloride and the potassium salt of chlorocamphorsulphonic acid.

Chlorocamphorsulphonic chloride exhibits circular polarisation in solution, its specific rotatory power being almost as high as that of the corresponding bromo-derivative. The following observations were made with a solution prepared by dissolving 2 grams of the pure substance in chloroform and diluting to 50 c.c. with the same solvent;  $l = 400$  mm.;  $t = 7^\circ$ .

$$\begin{array}{ll} \alpha_{\text{Li}} = +16^\circ 20', & \text{whence } [\alpha]_{\text{Li}} = +102.0^\circ \\ \alpha_{\text{Na}} = +17 \quad 41 & [\alpha]_{\text{Na}} = +110.5 \\ \alpha_{\text{Tl}} = +23 \quad 26 & [\alpha]_{\text{Tl}} = +146.5 \end{array}$$

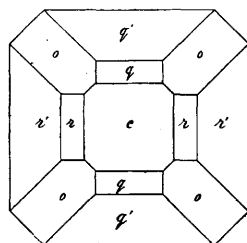
The observations made with the rays  $\text{Li}_\alpha$  and  $\text{Tl}_\alpha$  are only approximate, the difficulty of obtaining monochromatic light, and the fact that no screen can be used as with  $\text{Na}_\alpha$ , rendering it impossible to accurately ascertain the rotation with an ordinary polariscope.

The crystals separating from chloroform solution are magni-



ficent, colourless and transparent octahedra, Fig. 14, indistinguishable by mere inspection from those of the corresponding bromosulphonic chloride. Like the latter, they belong to the orthorhombic system, the optic axes emerging almost normally to the form  $q'\{021\}$ ; the optic axial angle is hence about  $59^\circ$ . The description

FIG. 14.



given above of the habit of the bromosulphonic chloride serves also for the chloro-compound, the most considerable difference being that, in the crystals of the latter, the zone  $a:c[100:001]$  gives rather more concordant measurements; the physical properties of both kinds of crystals are very similar. No hemihedrism could be detected.

Crystalline System: Orthorhombic.

$$a : b : c = 1.0494 : 1 : 0.8795.$$

Forms observed :

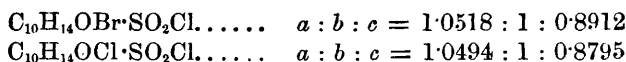
|              |                   |                       |
|--------------|-------------------|-----------------------|
| $a$ . . . .  | $\{100\}$ . . . . | $\infty\bar{P}\infty$ |
| $b$ . . . .  | $\{010\}$ . . . . | $\infty\bar{P}\infty$ |
| $c$ . . . .  | $\{001\}$ . . . . | $oP$                  |
| $r$ . . . .  | $\{101\}$ . . . . | $\bar{P}\infty$       |
| $r'$ . . . . | $\{201\}$ . . . . | $2\bar{P}\infty$      |
| $q$ . . . .  | $\{011\}$ . . . . | $\bar{P}\infty$       |
| $q'$ . . . . | $\{021\}$ . . . . | $2\bar{P}\infty$      |
| $o$ . . . .  | $\{111\}$ . . . . | $P$                   |
| $p$ . . . .  | $\{110\}$ . . . . | $\infty P$            |

The angular measurements are given on the next page.

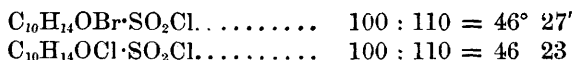
The crystallographic properties of chlorocamphorsulphonic chloride clearly show the great chemical relationship which this substance bears to the bromosulphonic chloride. Hemihedrism, which is rarely absent from crystalline substances exhibiting circular polarisation in the liquid state, was not observed in the case of the crystals of either

| Angle.                      | No. of observations. | Limits.         | Mean.   | Calculated. |
|-----------------------------|----------------------|-----------------|---------|-------------|
| $ar'$ = 100 : 201           | 4                    | 30° 26'— 31° 2' | 30° 41' | 30° 49'     |
| $r'r$ = 201 : 101           | 14                   | 18 54— 19 31    | 19 12   | 19 13       |
| $cr$ = 001 : 101            | 32                   | 39 10— 40 36    | 39 58   | —           |
| $cr'$ = 001 : 201           | 15                   | 58 41— 59 28    | 59 9    | 59 11       |
| $r'r'$ = 201 : 20 $\bar{1}$ | 8                    | 60 59— 62 34    | 61 44   | 61 38       |
| $rr$ = 101 : 10 $\bar{1}$   | 6                    | 79 14— 80 22    | 79 48   | 79 56       |
| $q'q$ = 021 : 011           | 9                    | 18 21— 19 6     | 18 45   | 19 3        |
| $cq$ = 001 : 011            | 27                   | 40 36— 42 5     | 41 20   | —           |
| $cq'$ = 001 : 021           | 12                   | 59 47— 60 42    | 60 16   | 60 23       |
| $q'q'$ = 021 : 02 $\bar{1}$ | 21                   | 58 34— 59 37    | 59 10   | 59 14       |
| $co$ = 001 : 111            | 7                    | 49 58— 50 47    | 50 26   | 50 32       |
| $ro$ = 101 : 111            | 6                    | 33 48— 35 21    | 34 4    | 33 59       |
| $oo$ = 111 : 1 $\bar{1}$ 1  | 5                    | 67 41— 68 25    | 68 1    | 67 58       |
| $oo$ = 111 : 11 $\bar{1}$   | 5                    | 78 49— 79 20    | 79 2    | 78 55       |
| $or'$ = 111 : 201           | 4                    | 38 6— 38 43     | 38 22   | 38 28       |
| $oq'$ = 111 : 021           | 4                    | 36 4— 37 6      | 36 39   | 36 52       |
| $r'q'$ = 201 : 02 $\bar{1}$ | 3                    | 104 37—104 59   | 104 51  | 104 40      |

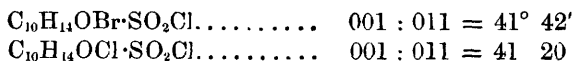
of the sulphonic chlorides. The axial ratio  $a : b$  is, moreover, nearly the same in both cases.



The prism angle 100 : 110, which is a function of the ratio  $a : b$ , has the following values:—



The small difference between these angles, namely, 4', is probably within the limits of experimental error. The lengths of the  $c$ -axis, however, differ pretty considerably in the two cases, the angles connecting the axes  $b$  and  $c$  having the following values:—



The conclusion is, therefore, arrived at that on substituting chlorine for bromine in bromocamphorsulphonic chloride the relative lengths of the axes  $a$  and  $b$  remain practically unaltered whilst the  $c$ -axis decreases in length. A slight alteration in crystallographic dimensions of course frequently attends a change of the halogen in crystalline substances, but morphotropic relations between compounds of the same type are seldom so well marked as in the series of derivatives of camphor crystallographically examined by Zepharovich, Cazeneuve, and Morel. These compounds have the axial ratios given below, and it will be seen that, as in the case of the sulphonic chlorides here described, the ratio  $a : b$  is almost constant, whilst the  $c$ -axis undergoes considerable alteration in length.

|                           |                                   |
|---------------------------|-----------------------------------|
| $C_{10}H_{14}OBr_2$ ..... | $a : b : c = 0.7925 : 1 : 0.5143$ |
| $C_{10}H_{14}OBrCl$ ..... | $a : b : c = 0.8040 : 1 : 0.5228$ |
| $C_{10}H_{14}OCl_2$ ..... | $a : b : c = 0.8074 : 1 : 0.5448$ |

*Chlorocamphorsulphonamide*,  $C_{10}H_{14}OCl \cdot SO_2 \cdot NH_2$ .

Finely divided chlorocamphorsulphonic chloride is readily acted on by concentrated aqueous ammonia at the ordinary temperature, being converted into a well-defined crystalline amide, with slight evolution of heat; when a comparatively small quantity of ammonia is employed, only partial solution occurs, most of the powder caking together to a pasty mass which afterwards becomes crystalline and brittle. After three or four hours, the mixture having been occasionally shaken, the ammonia is allowed to evaporate spontaneously, during which process the dissolved amide is deposited in colourless needles; as soon as the solution smells only slightly of ammonia, the amide is separated by filtration, washed with a little cold water, and dried in the air.

For the following analyses we employed a preparation which had been recrystallised from boiling water and dried at  $100^\circ$ .

0.1687 gave 0.2778  $CO_2$  and 0.0943  $H_2O$ . C = 44.91; H = 6.20.

0.2208 „ 0.1192 AgCl. Cl = 13.33.

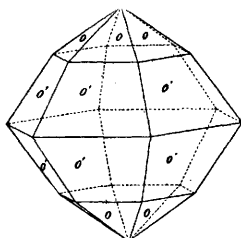
$C_{10}H_{14}OCl \cdot SO_2 \cdot NH_2$  requires C = 45.22; H = 6.03; Cl = 13.34 p. c.

Chlorocamphorsulphonamide crystallises from boiling water in long, flat, colourless needles, melting at  $149.5$ – $150.5^\circ$ ; it is moderately easily soluble in hot alcohol, but only very sparingly in boiling chloroform, and almost insoluble in boiling light petroleum; it is much more readily soluble in cold, concentrated ammonia than in cold water. It crystallises from warm alcohol in transparent plates or prisms forming fern-like masses; these crystals seem to contain alcohol, as they become opaque when heated at  $100^\circ$ , frothing up and melting to a turbid liquid at about  $149^\circ$ ; on heating to about  $175^\circ$ , the liquid becomes clear, and after solidification melts sharply at  $149.5$ – $150.5^\circ$ . The amide is optically active in solution; for the rotatory power determination 2.5328 grams of substance were dissolved in absolute alcohol, and the solution made up to 50 c.c.;  $l = 400$  mm.,  $t = 11^\circ$ . The rotation was  $\alpha_D = 18^\circ 16'$ ; the specific rotatory power is therefore  $[\alpha]_D = +90.16^\circ$ .

When the amide separates slowly from a cold alcoholic solution, it is deposited in small, hexagonal crystals, Fig. 15; these are at first quite colourless and transparent, but on removal from the solution they immediately begin to turn opaque and after a short time the faces become very dull. The transparent crystals were rapidly dried

with filter paper and examined as quickly as possible. The measurements obtained indicated that the crystals belonged to the hexagonal system; owing, however, to their very brittle and unstable character, this could not be confirmed by grinding a section parallel to the

FIG. 15.



basal plane and examining the interference figure. The extinctions in all the faces of the forms  $o\{10\bar{1}1\}$  and  $o''\{40\bar{4}1\}$  were in the direction of the  $c$ -axis. The rhombohedra  $o\{10\bar{1}1\}$  and  $o''\{40\bar{4}1\}$  were generally large, whilst the forms  $c\{0001\}$ ,  $m\{10\bar{1}0\}$ , and  $o'\{20\bar{2}1\}$  were frequently absent, and, as a rule, small. The rapidity with which the crystals effloresced rendered it very difficult to obtain good images; owing to this fact and to the lack of confirmatory evidence, the hexagonal character of the crystals cannot be regarded as fully established. No cleavage was observed.

Crystalline System : Hexagonal.

$$a : c = 1 : 0.917.$$

Forms observed :

$$\begin{aligned} c \dots & \{0001\} \dots oR \\ o \dots & \{10\bar{1}1\} \dots +R \\ o' \dots & \{20\bar{2}1\} \dots +2R \\ o'' \dots & \{40\bar{4}1\} \dots +4R \\ m \dots & \{10\bar{1}0\} \dots \infty R. \end{aligned}$$

The following angular measurements were obtained :—

| Angle.                                   | No. of observations. | Limits.          | Mean.   | Calculated. |
|--|----------------------|------------------|---------|-------------|
| $o' o'' = 40\bar{4}1 : 40\bar{4}\bar{1}$ | 19                   | 34° 4' — 35° 56' | 34° 57' | —           |
| $oo'' = 10\bar{1}1 : 40\bar{4}1$         | 12                   | 33 59 — 35 46    | 34 43   | 34° 4'      |
| $o''o = 40\bar{4}1 : \bar{1}011$         | 4                    | 109 27 — 111 42  | 110 35  | 110 59      |
| $o''o = 40\bar{4}1 : 10\bar{1}1$         | 1                    | —                | 69 17   | 69 1        |

*Chlorocamphorsulphonic acid*,  $C_{10}H_{11}OCl \cdot SO_3H$ .

For the preparation of this acid, we adopted the method which had been found to give such satisfactory results in previous cases, the

pure, finely-divided sulphonic chloride being boiled with a small quantity of water until complete solution ensued; it seemed to be rather more readily hydrolysed than the corresponding bromo-compound, and, like the latter, did not liquefy, even towards the end of the operation. The solution was freed from hydrochloric acid by repeated evaporation with alcohol, the same precautions as before being taken to avoid decomposition of the acid by the hydrochloric acid. The yellowish, syrupy solution of the acid prepared in this way began to crystallise on evaporation at  $100^{\circ}$ , and soon became semi-solid, but, on exposure to the air at the ordinary temperature, the mixture rapidly liquefied; the acid is, in fact, more hygroscopic than the corresponding bromo-derivative, and, for this reason, it was not analysed.

A portion of the crystalline substance which had been kept over sulphuric acid on porous earthenware for two days seemed still to contain water of crystallisation; it melted, but apparently not completely, at about  $125^{\circ}$ , at the same time frothing up considerably, owing, doubtless, to the escape of water vapour. After it had been heated to about  $190^{\circ}$  and then allowed to solidify, it melted at about  $185^{\circ}$ , which is probably, therefore, the melting point of the anhydrous acid.

When the syrupy aqueous solution is slowly evaporated over sulphuric acid, large, flat plates, several millimetres in length, are deposited; these crystals are colourless and transparent, and their faces are covered with striæ. They seem to be rectangular in shape, but the ends are usually rounded, as if re-resolution had occurred. Examination in convergent polarised light shows that the crystals belong to one of the biaxial systems, the large, tabular face being a bisectrix—the optic axes emerge just at the edges of the microscope field.

It will be seen that these crystals are not similar to those of the corresponding bromo-acid, the latter crystallising in the tetragonal system, which is uniaxial; this is probably due to a difference in the degree of hydration of the two acids.

The crystalline acid is very readily soluble in alcohol; its aqueous solution turns blue litmus red, and has a sour taste. In a neutral solution of the ammonium salt, ferric chloride produces no precipitate, but, on warming, the solution becomes reddish-brown, this colour disappearing on cooling; the lead, tin, mercuric, copper, and silver salts of the sulphonic acid are readily soluble, because, even in concentrated solutions of the ammonium salt, solutions of the salts of these metals produce no precipitation.

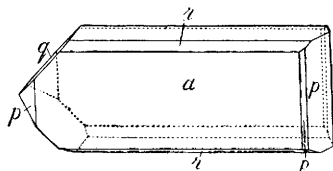
*Salts of chlorocamphorsulphonic acid.*—All the following salts were prepared from portions of the sulphonic acid which had been repeatedly evaporated with alcohol until free from hydrogen chloride; as

the methods of preparation have been already described in the case of other acids, details may be advantageously omitted. It may, however, be stated that the formation of a slight brown, flocculent precipitate on boiling the solution of the acid after neutralisation, was invariably observed; after filtration, the colourless solutions were concentrated on the water-bath, and allowed to cool. The salts were deposited on keeping for some time, and were dried on biscuit-ware in the air; like many of the salts of the other acids, some of them did not become constant in weight, even after prolonged keeping.

*Ammonium chlorocamphorsulphonate*,  $C_{10}H_{14}OCl \cdot SO_2 \cdot ONH_4$ , is a colourless, crystalline compound, and dissolves freely in water, alcohol, and acetone, although it appears to be less readily soluble than the other salts examined. According to Marsh and Cousins, it blackens and decomposes at  $200^\circ$ ; our preparation underwent no visible change when heated at  $215^\circ$  for a short time in a capillary tube, but it melted and then decomposed when heated on a platinum spatula in the Bunsen flame.

The transparent prisms or prismatic needles which are deposited on slowly crystallising an aqueous solution of this salt at the ordinary temperature are easily obtained a centimetre or so in length, and greatly resemble the crystals of ammonium bromocamphorsulphonate; they are very brittle, and have a glassy lustre. The form  $a\{100\}$  is generally the largest present, and its faces give good images; as in the case of the ammonium salt of the bromo-acid, the forms in the zone  $[a, b]$  are lightly striated in the direction of the  $c$ -axis. The form  $r\{101\}$ , though usually small, and the prism  $r'\{201\}$ , which is, in most cases, larger, give good measurements. The form  $q\{011\}$  is very well developed and brilliant, but the forms  $p\{110\}$  and  $p'\{210\}$  are generally poor in character, and do not give good measurements. The pinacoid  $c\{001\}$  is usually small, but gives fairly sharp images.

FIG. 15.



The crystals are hemimorphic. At one end of the prism appear the forms  $p\{110\}$  and  $p'\{210\}$ , and at the other  $q\{011\}$  and  $p'\{210\}$ . One or more of these forms is frequently absent, and in no case, were the two forms  $p\{110\}$  and  $q\{011\}$  seen on the same or on both ends of the crystal. So far as the number of faces ex-

hibited is concerned, the form  $p'\{210\}$  seems to be unaffected by the hemimorphism. The crystals are very irregularly developed, faces of the same form seldom being even approximately equal in point of size. So symmetrically developed a crystal as that represented in Fig. 15 was never met with; frequently the blunt end of the crystal shows only the form  $p\{110\}$ , and one or other of the remaining forms, with the exception of those which lie parallel to the  $b$ -axis, is often absent.

The pinacoid  $a\{100\}$  is normal to a bisectrix, probably the obtuse one; there is a good cleavage parallel to this form.

As would be expected from their hemimorphic nature and their great similarity to the crystals of the ammonium salt of bromocamphorsulphonic acid, these crystals become strongly pyroelectric when heated. On warming a crystal and then dusting it with the electrified mixture of red lead and sulphur during cooling, the pointed end becomes red, owing to the lead oxide adhering to it, whilst the square end of the plate assumes the yellow colour of the sulphur particles which are attracted.

Crystalline System: Monosymmetric. Hemimorphic.

$$a : b : c = 1.9260 : 1 : 1.0471.$$

$$\beta = 74^\circ 56'.$$

Forms observed:

|      |       |           |       |                   |
|------|-------|-----------|-------|-------------------|
| $a$  | ..... | $\{100\}$ | ..... | $\infty P_\infty$ |
| $c$  | ..... | $\{001\}$ | ..... | $oP$              |
| $r$  | .. .. | $\{101\}$ | ..... | $-P_\infty$       |
| $r'$ | ..... | $\{201\}$ | ..... | $+2P_\infty$      |
| $p$  | ..... | $\{110\}$ | ..... | $\infty R$        |
| $p'$ | ..... | $\{210\}$ | ..... | $\infty P_2$      |
| $q$  | ..... | $\{011\}$ | ..... | $R_\infty$        |

The following angular measurements were obtained.

| Angle.            | No. of obser-<br>vations. | Limits.                       | Mean.          | Calculated.    |
|-------------------|---------------------------|-------------------------------|----------------|----------------|
| $ar' = 100 : 201$ | 21                        | $48^\circ 17' - 50^\circ 28'$ | $49^\circ 25'$ | —              |
| $r'c = 201 : 001$ | 12                        | $54 47 - 55 59$               | $55 33$        | $55^\circ 39'$ |
| $ac = 100 : 001$  | 12                        | $74 5 - 75 42$                | $75 1$         | $74 56$        |
| $ar = 100 : 101$  | 8                         | $49 38 - 50 47$               | $50 12$        | $50 14$        |
| $cr = 001 : 101$  | 11                        | $24 6 - 25 21$                | $24 44$        | $24 42$        |
| $aq = 100 : 011$  | 14                        | $78 47 - 79 56$               | $79 28$        | —              |
| $aq = 100 : 011$  | 9                         | $99 54 - 100 58$              | $100 29$       | $100 32$       |
| $cq = 001 : 011$  | 17                        | $44 39 - 45 50$               | $45 19$        | —              |
| $qq = 011 : 011$  | 15                        | $88 42 - 90 1$                | $89 22$        | $89 22$        |
| $ap = 100 : 110$  | 12                        | $61 15 - 62 7$                | $61 44$        | $61 44$        |
| $pp = 110 : 110$  | 7                         | $56 3 - 56 39$                | $56 26$        | $56 31$        |
| $pp' = 110 : 210$ | 5                         | $18 27 - 18 56$               | $18 44$        | $18 49$        |
| $ap' = 100 : 210$ | 8                         | $42 22 - 43 16$               | $42 51$        | $42 55$        |
| $pp' = 210 : 210$ | 6                         | $93 49 - 94 57$               | $94 16$        | $94 9$         |

As will be seen from the axial relations given below, this salt and the ammonium salt of bromocamphorsulphonic acid are very similar in crystalline form.

$C_{10}H_{14}OBr \cdot SO_2 \cdot ONH_4$ .  $a : b : c = 1.9155 : 1 : 1.0252$ .  $\beta = 74^\circ 37'$ .

$C_{10}H_{14}OCl \cdot SO_2 \cdot ONH_4$ .  $a : b : c = 1.9260 : 1 : 1.0471$ .  $\beta = 74^\circ 56'$ .

*Potassium chlorocamphorsulphonate*,  $C_{10}H_{14}OCl \cdot SO_2 \cdot OK + 4H_2O$ , crystallises from cold water in colourless, bifurcated needles, and is readily soluble in alcohol and acetone, but apparently insoluble in ether; the air-dried salt was analysed.

0.6417 lost 0.0009 at  $100^\circ$ , and 0.0124 between  $100^\circ$  and  $145^\circ$ .

0.2528 gave 0.0600  $K_2SO_4$ .

$H_2O$  in salt dried at  $100^\circ = 19.35$ ; K in air-dried salt = 10.64.

$C_{10}H_{14}OCl \cdot SO_2 \cdot OK + 4H_2O$  requires  $H_2O = 19.18$ ; K = 10.34 p. c.

It would seem, therefore, that the salt does not lose any of its water of crystallisation at  $100^\circ$ .

*Barium chlorocamphorsulphonate*,  $(C_{10}H_{14}OCl \cdot SO_2 \cdot O)_2Ba + 5\frac{1}{2}H_2O$ , like the barium salt of the bromo-acid, does not form very well-defined crystals, but separates from its concentrated aqueous solution in colourless, felted masses; it is readily soluble in water and alcohol. The analyses were made with the air-dried salt.

0.5875 lost 0.0640 at  $100^\circ$  and 0.0768 at  $135-140^\circ$ .

0.3627 gave 0.1094  $BaSO_4$ .

$H_2O$  at  $100^\circ = 10.89$ , at  $140^\circ = 13.07$ ; Ba = 17.74.

$(C_{10}H_{14}OCl \cdot SO_2)_2Ba + 5\frac{1}{2}H_2O$  requires  $H_2O = 12.89$ ; Ba = 17.86 p.c.

The salt becomes constant in weight at  $100^\circ$ , at which temperature it seems to lose  $4\frac{1}{2}$  mols.  $H_2O$ ; it turns brown at  $150-160^\circ$ .

The rotatory power of the air-dried salt was measured by dissolving 1.0407 grams in water, diluting to 50 c.c., and examining it in a 400 mm. tube at  $10^\circ$ . The mean of eight good observations gave  $\alpha_D = +3^\circ 54'$ , so that the specific rotation of the salt was about  $[\alpha]_D = +46.8^\circ$ .

*Sodium chlorocamphorsulphonate*,  $C_{10}H_{14}OCl \cdot SO_2 \cdot ONa + 5H_2O$ , separates from cold water in concentrically grouped needles, and is readily soluble in alcohol, but apparently insoluble in ether; the air-dried salt was analysed.

I. 0.3925 lost 0.0972 at  $130^\circ$ .  $H_2O = 24.76$ .

0.1664 gave 0.0310  $Na_2SO_4$ . Na = 6.03.

II. 1.1284 lost 0.2779 at  $145^\circ$ .  $H_2O = 24.6$ .

$C_{10}H_{14}OCl \cdot SO_2 \cdot ONa + 5H_2O$  requires  $H_2O = 23.81$ ; Na = 6.08 p. c.

The salt melts in its water of crystallisation when heated to  $100^\circ$  and the last traces of water are expelled with difficulty, even at  $135^\circ$ .



The rotatory power of the salt was determined with an air-dried preparation containing 24.6 per cent. of water, 1.0052 grams being dissolved in water, the solution diluted to 50 c.c. and examined at  $10^{\circ}$  in a 400 mm. tube; the rotation was  $\alpha_D = +3^{\circ} 52'$ , so that the specific rotatory power of the anhydrous salt was about  $[\alpha]_D = +64^{\circ}$ .

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