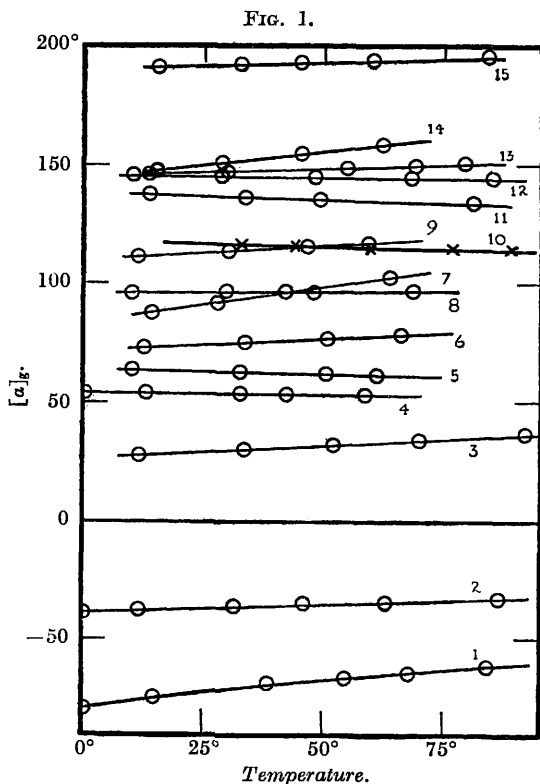**232.** *The Influence of Solvents and of Other Factors on the Rotation of Optically Active Compounds. Part XXX. The Rotation–Dispersion of Various Derivatives of Camphor.*

By THOMAS STEWART PATTERSON and JAMES DALRYMPLE LOUDON.

IN continuation and extension of work described in the foregoing paper, we have prepared, and examined the rotation–dispersion of, the following compounds : Reychler's camphorsulphonic acid; its methyl and ethyl esters; α-chlorocamphor; α-bromocamphor; the Reychler sulphonic acid derivatives from these halogenated camphors; the methyl and ethyl esters prepared in turn from these acids; the α-chloro- and α-bromo-camphorsulphonamides, and camphorsulphonanhydramide, all under various conditions of tem-

perature, solvent, and concentration. Our purpose was to ascertain to what extent, if any, the substitution of new radicals and groups in the camphor molecule may lead to a departure in the funda-
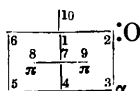
FIG. 1.

1. Camphor-10-sulphonanhydramide in aniline .... $p = 4.84$
2.   ,,   ,,   in tetrachloroethane .... $p = 3.16$
3. Camphor-10-sulphonic acid in water .... $p = 9.71$
4. Methyl camphor-10-sulphonate in ethyl alcohol .... $p = 4.8$
5. Ethyl   ,,   ,,   in benzene .... $p = 3.15$
6. Methyl a-chlorocamphor-10-sulphonate in benzene .... $p = 2.44$
7. a-Chlorocamphor in benzene .... $p = 6.9$
8. a-Chlorocamphor-10-sulphonamide in pyridine .... $p = 3.68$
9. Methyl a-bromocamphor-10-sulphonate in benzene .... $p = 2.62$
10. Methyl a-chlorocamphor-10-sulphonate in ethylene bromide ... $p = 2.0$
11. a-Bromosulphonamide in pyridine .... $p = 2.9$
12. Ethyl a-bromocamphor-10-sulphonate in ethylene bromide ... $p = 1.94$
13. a-Chlorocamphor in ethylene bromide .... $p = 3.2$
14. a-Bromocamphor in benzene .... $p = 6.9$
15.   ,,   in ethylene bromide .... $p = 3.23$

mental constants of rotation from those of camphor itself, and, if possible, to correlate the data.

In spite of the very large amount of work that has been done

upon camphor, there is still some doubt, if not about the structure of the molecule itself, at least about the positions which substituents take up on entering it. The numbering and naming of the camphor molecule adopted here is as shown. The β position has been allocated both to 6 and to 10. Positions 8 and 9 are of course not identical.
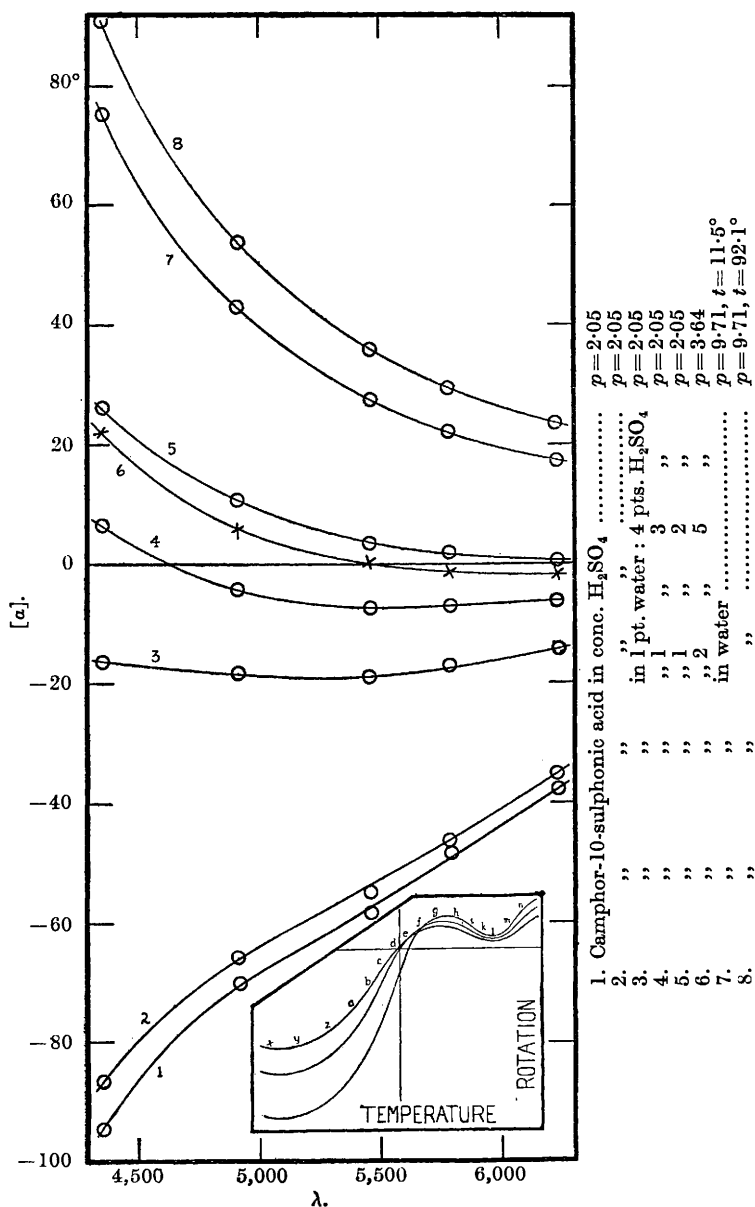
The rotation data for a solution of Reychler's acid (camphor-10-sulphonic acid) in solution in water, $p = 9.71$, are quoted on p. 1738, and those for mercury green are represented by graph 3 of Fig. 1. The rotation increases almost linearly with increase of temperature, and the other data show that the corresponding curves for the other colours spread out rapidly, as the refrangibility of the light increases, in what may be regarded as a fairly normal manner. The data for the temperatures 11·5° and 92·1° are also shown in Fig. 2 as the dispersion curves 7 and 8, which are referred to below.

As mentioned in the foregoing paper (p. 1720), concentrated sulphuric acid as a solvent has a very marked effect in depressing the rotation of camphor, and therefore we investigated its action upon Reychler's acid also. The results are of considerable interest and are shown in Fig. 2 as dispersion curves. The graphs are numbered to correspond to the experimental data on p. 1738. Graphs 1 and 2 on the diagram represent the behaviour of camphor-10-sulphonic acid in two different samples of concentrated sulphuric acid ($p = 2.05$) and at nearly the same temperature, ca. 19°. It will be seen that as the refrangibility of the light diminishes, the rotations of the solutions rapidly rise from ca. $-100°$ for violet light to above $-38°$ for red light. The curves appear to exhibit inflexion. The addition of water to the solvent in the proportion of 1 part to 4 parts of sulphuric acid brings about a considerable change in the form of graph 3, in which the dispersion is visibly anomalous, since there is a definite minimum rotation at a wave-length of $\lambda = 5220$ between blue and green.

Graph 4 shows the behaviour when the solvent contains water in the proportion of 1 part to 3 parts of sulphuric acid. The rotation is now positive for violet light, but diminishes with increasing wave-length, and would be zero for light of about $\lambda = 4650$. Again the dispersion is visibly anomalous since there is a minimum rotation in the neighbourhood of green, the rotation thereafter increasing with increase of wave-length.

By diluting the sulphuric acid further, the curves 6 and 5 were obtained, whilst the rotation–dispersion *in water alone* is shown in curves 7 and 8, which represent respectively the data for the

Fig. 2.

$p = 9.709$ solution at $11.5°$ and at $92.1°$, and have been already referred to.

This diagram, taken as a whole, appears to suggest that curves 8, 7, and 5 would all tend to cut the axis of zero rotation, thus following courses similar to those actually observed for curves 6, 4, and 3; *i.e.*, tending to become asymptotic to the *x*-axis, but on the negative side of it. Presumably curves 2 and 1 would do the same thing.

It seems to us of especial significance that this diagram, if inverted, bears a remarkable general resemblance to the dispersion diagram for ethyl tartrate, in which the dispersion curves seem to become asymptotic to the *x*-axis at high wave-lengths, on the positive side of the axis of zero rotation. Those for camphor-10-sulphonic acid appear to become asymptotic to the *x*-axis on its negative side, and this suggests that, if ethyl tartrate and the other tartrates are to be regarded as *dextro*-compounds, camphor-10-sulphonic acid ought, perhaps, to be regarded as a *lævo*-compound, since its general behaviour would seem to be the inverse of that of tartaric acid (see p. 1735).

These data are plotted as a characteristic diagram (lines A,B) in Fig. 3, and it will be seen that they all lie in a satisfactory fashion upon approximately straight lines. The region of visibly anomalous dispersion for camphor-10-sulphonic acid lies in the region where the rotation for green light is between about zero and $-25°$. The lines for each pair of colours intersect at a different rotational value. At the moment it is not necessary to take account of each of these values; for purposes of later comparison the intersection of the violet and green may be noted. It occurs at the rotational value, for both colours, of $-24·2°$.

We next examined under various conditions the methyl and ethyl esters of camphor-10-sulphonic acid (Reychler's acid), for which we devised improved methods of preparation (see p. 1738). The results are shown below.

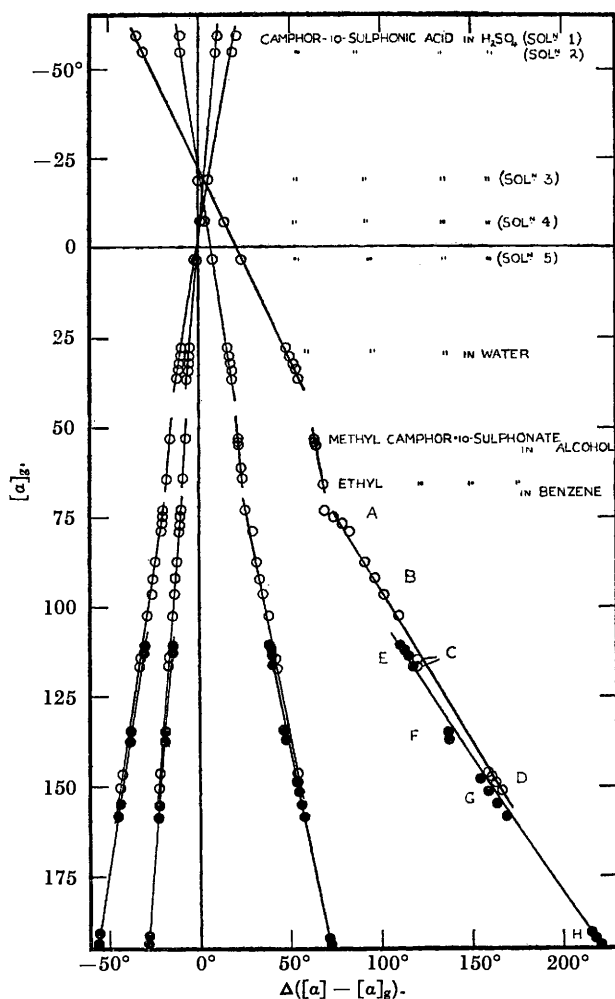*Rotation of methyl camphor-10-sulphonate in different solvents.*

Solvent.	t.	Conc.*	$a_g.$	$[a]_g.$
Benzaldehyde	16·5°	5·113	+2·71°	+53·01°
Ethyl alcohol	16·5	5·021	2·72	54·18
Chloroform	17	4·928	2·77	56·20
Ethylene bromide	16	5·157	2·90	56·23
Nitrobenzene	14·5	5·032	3·00	59·61
Benzene	17	1·030	0·73	70·87

* G. per 100 c.c. of solution.

Rotation of ethyl camphor-10-sulphonate in different solvents.

Ethylene bromide	17	1·03	+0·54	+52·43
Ethyl alcohol	15·5	5·00	2·65	53·00
Chloroform	16·5	1·124	0·60	53·39
Benzene	14	1·116	0·79	70·79

FIG. 3.

A = Methyl a-chlorocamphor-10-sulphonate in benzene .... $p = 2\cdot44$
B = a-Chlorocamphor in benzene .... $p = 6\cdot87$
C = Methyl a-chlorocamphor-10-sulphonate in ethylene bromide $p = 2\cdot01$
D = a-Chlorocamphor in ethylene bromide .... $p = 3\cdot19$
E = Ethyl a-bromocamphor-10-sulphonate in benzene .... $p = 2\cdot39$
F = a-Bromocamphor-10-sulphonamide in pyridine .... $p = 2\cdot90$
G = a-Bromocamphor in benzene .... $p = 6\cdot69$
H = a-Bromocamphor in ethylene bromide .... $p = 3\cdot23$

The rotations of the two esters in each solvent are very similar, but they vary according to the nature of the solvent, as between, e.g., ethyl alcohol and benzene.

We then examined a solution of the methyl ester ($p = 4.8$) in alcohol and one of the ethyl ester in benzene ($p = 3.15$) over a range of temperature up to 60°, and for five colours of light. A sufficient notion of the general behaviour will be obtained from the two curves for mercury green shown on Fig. 1 (graphs 4 and 5, respectively). In each case the specific rotation diminishes slightly with increase of temperature; the curves are very similar, and it seems probable that, at lower temperatures, a maximum value for the rotation would occur.

The rotation of α-chlorocamphor was examined in a similar fashion, the influence of a number of solvents at a single concentration being first ascertained.

Rotation of α-chlorocamphor in different solvents.

Solvent.	t.	Conc.	$a_g.$	$[a]_g.$
H_2SO_4 (conc.)	20°	2·060	+1·35°	+65·52°
Benzene	19·5	2·000	1·75	87·5
Ethyl alcohol	19·5	2·008	2·44	121·5
Tetrachloroethane	20	2·062	2·67	129·5
Ethylene bromide	20	2·036	3·03	148·8

There is here a very considerable variation of rotation according to the solvent employed. Whereas, in concentrated sulphuric acid, the specific rotation for mercury green is only about + 65°, it is raised in ethylene dibromide to 149°. Two of these solutions were then investigated more fully as regards the influence of temperature. In benzene ($p = 6.9$; graph 7, Fig. 1) the rotation for green light increases from 87·34° at 14° to 102·2° at 63·5°. In ethylene bromide ($p = 3.2$; graph 13, Fig. 1), in which the rotation is considerably higher than in benzene, the increase of rotation for green light on heating is distinctly less, the change being from + 146·1° at 13·5° to 150·9° at 89°. The curves for other colours of light show a very similar behaviour. Their general characteristics are what may now be foretold. As is the case with ethyl tartrate, when the rotation reaches gradually higher values the increase of rotation on heating becomes less.

The rotation of the *methyl* and *ethyl* esters of α-chlorocamphor-10-sulphonate, prepared as described on p. 1741, were examined in the same way as before.

Rotation of methyl α-chlorocamphor-10-sulphonate in different solvents.

Solvent.	t.	Conc.	$a_g.$	$[a]_g.$
Benzene	17·5°	1·152	+0·89°	+77·27°
Ethyl alcohol	17	1·112	1·22	109·7
Chloroform	17·5	1·104	1·25	113·2
Ethylene bromide	17·5	1·130	1·36	120·3

Rotation of ethyl α-chlorocamphor-10-sulphonate in different solvents.

Benzene	17	1·068	+0·83	+77·71
Ethyl alcohol	18	1·008	1·11	110·2
Ethylene bromide	17	1·084	1·32	121·7

The rotation of both esters is influenced in very much the same way by these solvents, being highest in ethylene bromide and lowest in benzene; and whereas in benzene solution ($p = 2\cdot44$; see data, p. 1741, and graph 6, Fig. 1) the rotation of the methyl ester for all colours of light examined increases slightly, in ethylene bromide ($p = 2\cdot007$, graph 10, Fig. 1) it quite definitely diminishes on heating, although again not to any very great extent.

The behaviour of the corresponding bromo-derivatives is shown in the table below. With close general similarity there is again a very considerable rise in specific rotation for mercury green, from 113·9° as the solvent is changed from concentrated sulphuric acid to ethylene bromide, in which, for $c = 5\cdot05$, the rotation has risen to 192·9°.

Rotation of α-bromocamphor in different solvents.

Solvent.	$t.$	Conc.	$a_g.$	$[a]_g.$
H$_2$SO$_4$ (conc.)	17°	2·02	+2·30°	+113·9°
Benzene	17·5	14·11	21·57	152·8
Pyridine	17	5·138	8·35	162·5
Ethyl alcohol	16	10·09	17·12	169·3
Tetrachloroethane	17	5·062	9·15	180·7
Ethylene bromide	17	5·050	9·74	192·9

The effects of temperature change, in this case, on a solution in benzene ($p = 6\cdot9$; graph 14, Fig. 1) and one in ethylene bromide ($p = 3\cdot23$; graph 15, Fig. 1) are very similar to those for the chloro-compound, and exhibit the same characteristics. In the benzene solution, in which the rotation is lower for all the different colours, the rotation increases more rapidly with rise in temperature than is the case in the ethylene bromide solution.

Rotation of methyl α-bromocamphor-10-sulphonate in different solvents.

Solvent.	$t.$	Conc.	$a_g.$	$[a]_g.$
Benzene	16°	1·01	+1·14°	+112·9°
Ethyl alcohol	17	1·178	1·65	140·1
Chloroform	16	1·044	1·51	141·4

Rotation of ethyl α-bromocamphor-10-sulphonate in different solvents.

Benzene	18	1·000	+1·13	+113·0
Tetrachloroethane	18	1·002	1·35	134·7
Ethyl alcohol	17	1·000	1·38	138·0
Chloroform	18	1·006	1·41	140·2
Ethylene bromide	17	1·122	1·81	161·4

For the *ethyl* and the *methyl* ester of α-bromocamphor-10-sulphonate there is again a considerable change in rotation in passing from

one solvent to another, and the actual values of the rotation for the two esters in benzene, ethyl alcohol, and chloroform are not merely in the same sequence, but are numerically very close to one another. The $T-R$ curves of the methyl ester in benzene ($p = 2.62$; graph 9, Fig. 1) and of the ethyl ester in ethylene bromide ($p = 1.94$; graph 12, Fig. 1) show the same characteristics as before—a gradual increase of rotation with rise of temperature in benzene, whereas in ethylene bromide, in which the value of the rotation is higher, the $T-R$ curves are clearly very close to a maximum value, and on the whole the rotation tends to diminish slightly with increase of temperature.

The rotation of α-chlorocamphor-10-sulphonamide also was examined in pyridine ($p = 3.68$). The data are given on p. 1743, and are represented by graph 8 of Fig. 1. The curve is evidently in the neighbourhood of a maximum value, and fits in very well between those for methyl α-chlorocamphor-10-sulphonate in benzene ($p = 2.44$; graph 6, Fig. 1) and in ethylene bromide ($p = 2.0$; graph 10, Fig. 1). The rotations are higher for the respective colours of light than is the case for methyl α-chloro-camphor-10-sulphonate in benzene, and, corresponding to this, the increase in rotation on heating is slower. On the other hand, the rotation is not so high as that of methyl α-chlorocamphor-10-sulphonate in ethylene bromide, and again, as might be expected, whereas the rotation of the sulphonamide shows a maximum value at least for green light, the rotation of the methyl sulphonate for all colours of light definitely diminishes on heating.

The α-bromosulphonamide in pyridine solution ($p = 2.9$; graph 11, Fig. 1) gave results much like those for the chloro-derivative. The rotation for all colours of light is higher, and, corresponding to this, it diminishes on heating.

To extend the investigation to a compound of a slightly different type, we examined the rotation of camphorsulphonanhydramide, with the results shown below.

Rotation of camphor-10-sulphonanhydramide in different solvents.

Solvent.	t.	Conc.	α_g.	$[\alpha]_g$.
Tetrachloroethane	17.5°	5.116	−1.9°	−37.15°
Chloroform	14	3.462	1.38	39.56
Nitrobenzene	16.5	3.998	2.19	54.76
Dimethylaniline	16.5	2.308	1.44	62.40
Aniline	16	4.95	3.69	74.54

The rotations are all negative and there is a marked difference in their value in different solvents. Since, for the most part, however, the solvents used were not the same, these data are not very easily comparable with those for the other compounds which we have

examined, but it is noticeable that the rotation is the highest (in an absolute sense) in tetrachloroethane, and that most of the other active compounds we have examined give the highest rotations in this solvent or ethylene bromide.

We then examined the rotation of the compound in tetrachloroethane ($p = 3\cdot16$; graph 2, Fig. 1), which gives it the highest rotation, and in aniline ($p = 4\cdot84$; graph 1, Fig. 1), which gives it the lowest rotation, for various colours of light and at several temperatures. The most noticeable features are that in tetrachloroethane the rotation, very much in accordance with what has been observed in other cases, increases fairly rapidly on heating, in such a way that the curve is convex to the point of origin of the diagram, and in aniline, which depresses the rotation to a greater extent, the rotation increases still more rapidly.

Considering now, as a whole, the data which we have obtained, there appears to be here a general resemblance between the behaviour of camphor and that of ethyl tartrate, which we consider to be perhaps the most fully investigated of active compounds. It has been suggested in previous papers that the $T-R$ curve for this ester, if it could be sufficiently extended, would show at least one maximum and two minima, these singular points being actually observable in special cases : the maximum in certain solvents (like water, nitrobenzene, benzaldehyde), which, at ordinary temperatures, raise the rotation of the dissolved ethyl tartrate; one of the minima in derivatives such as ethyl dibenzoyltartrate, and the other minimum in derivatives such as *iso*butyl diacetyltartrate or ethyl tartrate dissolved in such a solvent as quinoline. This is shown in the inset diagram on Fig. 2.

From our present experiments it appears that for camphorsulphonanhydramide, camphoroxime dissolved in *o*-nitrotoluene or in alcohol, or for camphor in concentrated sulphuric acid :—(1) the rotations for all the various colours, as a group, lie, in an absolute sense, much below those for camphor in the other solvents, examined, *e.g.*, phenol; and (2) in the former group the rotations for violet light are least, again in an absolute sense, and those for red greatest; whereas in the other solvents just the opposite is the case, the rotation for violet being much higher than that for red, the other colours lying in between in the usual order. Therefore, for the low-rotational group of curves, to assume, on further heating, the same sequence as the high-rotational group of curves, it would be necessary for the graph for violet to cross over the intermediate graphs, and so on in sequence. A similar, but opposite, behaviour would be necessary in order that the high-rotational group of curves should assume the sequence of the low-rotational group.

Actual instances of this crossing we have only observed with camphorsulphonic acid in diluted sulphuric acid (Fig. 2, graphs 3 and 4) and with camphor (previous paper, Fig. 1, graph 5), and then only in the dispersion curves; but, although a little difficult, it would, we think, be quite possible to observe the actual intersections in T-R curves for suitable mixtures of sulphuric acid and water. It would thus appear that the former set of graphs corresponds to the low-temperature part of the general curve (region yz of the diagram inset in Fig. 2), and the latter set of graphs to the high-temperature part (region ghi) of the same general curves.

Since the T-R curves for camphor appear to be similar to those for ethyl tartrate, it might seem, following the same line of argument as was used by Clough (J., 1915, **107**, 1517), that the allocation of d-configuration to both substances might be justified. It must be remembered, however, that the actual region of intersection of the T-R curves for camphor has been realised by us with difficulty, and then only in a single solution in aqueous sulphuric acid (see preceding paper, p. 1721), whereas this region for ethyl tartrate may be easily and accurately examined. The characteristics of the former are therefore not so apparent, nor so easily interpreted, as of the latter. The dispersion curves, however, reveal a distinct difference, those shown in Fig. 2 being, in general, of the opposite character to those for ethyl tartrate : the region of visibly anomalous dispersion occurs for positive values of rotation in ethyl tartrate, but for negative values in camphor and camphorsulphonic acid. This naturally applies also to the region of intersection of the T-R curves, and of the lines on the characteristic diagram, and it seems therefore possible that the substance usually called d-camphor ought to be called l-camphor. If a criterion of this sort should prove really to be applicable, it may become possible to allocate two compounds C$abcd$ and C$efgh$—compounds which have nothing at all in common as regards the groups of which they are composed— to the one or the other series of active substances. But the matter cannot be settled at present, and is, indeed, a very difficult one.

Although at first sight it might perhaps be expected that α-chlorocamphor and α-bromocamphor ought to be of the same configuration and family as camphor itself, it is not impossible that the new asymmetric group produced by the introduction of the halogen atom may fundamentally disturb the asymmetry of the molecule; and that the α-chlorocamphor and the camphor from which it is derived may be of opposite configuration. Such a conclusion would be in harmony with the generalisation pointed out by Wood and Nicholas (J., 1928, 1671), $viz.$, that compounds exhibiting anomalous

dispersion in the positive region of rotation possess *dextro*-configurations.

It seems further possible that there may be a class of compound which could be allocated, in this way at least, definitely neither to the *d*- nor the *l*-form, the only examples known at present being, perhaps, the derivatives of mannitol (Patterson and Todd, J., 1929, 2876), and bornyl benzene- and naphthalene-sulphonates, examined by Patterson and McAlpine (J., 1928, 2472).

It seems at least clear that, for the camphor derivatives, there is a maximum in the *T–R* curve in the high-temperature region *ghi* (inset diagram, Fig. 2); but since it is evidently much more difficult in the case of camphor and its derivatives than it is in the case of ethyl tartrate, to shift the general *T–R* curve about, by the use of different solvents, nothing can be said meantime as to the likelihood of a low-temperature minimum corresponding to the region *xy*, or a high-temperature minimum corresponding to the region *klm*, in the tartrates.

The general resemblance of the curves obtained for two compounds so different in constitution as ethyl tartrate and camphor is striking, and it appears to us that, although the various asymmetric centres in the molecule of an optically active compound may, perhaps, be regarded as contributing, each, a certain amount to the total rotation, it is better to consider these partial rotations as completely merged in one another, so that the rotation is the result of the asymmetry of the molecule as a whole, in much the manner adopted by Pasteur. This approximates to the suggestion put forward by one of us (J., 1901, **79**, 188) that the influence of such factors as temperature change and solvent may be due to a deformation of the molecule, an idea which has been in abeyance merely because no satisfactory method of investigating it further has suggested itself.

In this connexion, it is at least worthy of note that the influence of certain solvents upon ethyl tartrate and camphor, respectively, stand in inverse order; quinoline, which enhances the rotation of the former, depresses that of the latter; ethylene bromide, which depresses the rotation of ethyl tartrate, enhances that of camphor, but whether this relationship is definitely connected with the *d*- or *l*-configuration of the active molecule cannot be decided at present.

In Fig. 3 is shown a characteristic diagram for camphor-10-sulphonic acid dissolved in sulphuric acid, in water, and in mixtures of these two solvents. The data lie in satisfactory fashion upon the characteristic diagram, but the lines do not meet at a single point and therefore the rotation dispersion of camphorsulphonic acid is definitely anomalous. The point of intersection of the line for

violet with that for green is $-22\cdot2°$, and the dispersion calculated from this rational zero should be $v/g = 1\cdot95$.* This rational zero for camphor-10-sulphonic acid is therefore a little different from that of camphor itself dissolved in sulphuric acid, a fact which we take to indicate that the introduction of the sulphonic group into the camphor molecule alters the asymmetry of the whole molecule in some rather fundamental fashion.

On the same diagram are also plotted the data for methyl camphor-10-sulphonate in alcohol and for the corresponding ethyl ester in benzene. These, somewhat to our surprise, do not fit in with the other data. It may be noted that the data recorded on the diagram represent the behaviour of the two esters on the descending lines of a $T–R$ curve (graphs 4 and 5 of Fig. 1), *i.e.*, just beyond a maximum value, and it has been pointed out elsewhere (*Proc. Roy. Soc. Edin.*, 1918–19, **39**, 27) that the data on one side of a maximum value of a $T–R$ curve may possibly lie on one characteristic diagram, whilst those on the other may lie upon a different characteristic diagram. Nevertheless, this does not appear to us to cover the present case, and we content ourselves meantime by drawing attention to the discrepancy.

On Fig. 3 are also shown characteristic diagrams for α-chloro- and α-bromo-camphor and some of their respective derivatives. It is clear that neither set of data falls upon the characteristic diagram either for camphor or for camphor-10-sulphonic acid. If, however, it be remembered that the introduction of chlorine or bromine in the α-position in the camphor molecule introduces a new asymmetric carbon atom, and therefore necessarily disturbs to some considerable extent the general asymmetry of the molecule, this will not seem surprising. In addition it is noticeable that the exchange of bromine for chlorine produces data which do not lie upon one and the same characteristic diagram. By extrapolation—necessarily somewhat inexact owing to the considerable extent through which it has to be carried out, since by no means could we obtain data on the negative side of the diagram—the point of intersection of the line for violet on the characteristic diagram for α-chlorocamphor derivatives should cut the line for green at about $+ 11°$, and from this rational zero the average dispersion v/g would have a value of about $2\cdot19$.†

In a similar fashion the line for violet in the characteristic diagram for bromo-derivatives should intersect the line for green at a rotation

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* Thus, when the rotation for g is $25°$ that for v is $70°$, whence $v/g = (22\cdot2 + 70)/(22\cdot2 + 25) = 1\cdot95$.

† When the rotation for g is $150°$ that for v is $315°$, and $(315-11)/(150-11) = 2\cdot19$.

value of about $+ 24.5°$. The dispersion therefore for the bromo-compound would be about $v/g = 2.30$.

<div align="center">EXPERIMENTAL.</div>

The colours of light used were as on p. 1722.

Camphor-10-*sulphonic acid in Water*.—Prepared as described by Reychler (*Bull. Soc. chim.*, 1898, **19**, 120), the product was recrystallised twice from glacial acetic acid and then three times from ethyl acetate. Before measurement of its rotation, it was heated for one hour in an air-oven at 105—110° : prolonged heating at 110° causes charring.

$p = 9.709$. Densities determined : 1.028 at 15.4°; 1.023 at 31.6°; 1.018 at 43.7°; 1.007 at 63°; 0.9970 at 80°; 0.9942 at 85°.

<div align="center">*Rotation data.*</div>

t.	d.	$[a]_{r_2}$.	$[a]_y$.	$[a]_g$.	$[a]_b$.	$[a]_v$.
11.5° •	1.029	$+17.52°$	$+22.21°$	$+27.58°$	$+42.98°$	$+75.44°$
33.2	1.022	19.08	24.31	30.04	45.65	79.86
52.0	1.014	20.76	26.16	31.93	48.32	83.35
70.0	1.004	22.25	27.57	33.86	51.17	86.76
92.1 *	0.9892	23.82	29.74	36.18	53.75	90.97

* These data are shown as dispersion curves in Fig. 2.

Remarks. The density curve shows a very pronounced flattening at the lower temperatures—this was corroborated by a second series of density determinations.

Camphor-10-*sulphonic Acid in Sulphuric Acid–Water Mixtures*.—Concentrated sulphuric acid was distilled from an all-glass distilling flask to remove non-volatile impurities. The first distillate, containing approx. 2 g. of water to 5 g. of acid, was employed in preparing solution 6 (see table). A more concentrated and higher-boiling fraction was employed for solution 2, whilst for solutions 1, 3, 4, and 5 the main bulk of the higher-boiling fractions was employed. The density of this third sample was $d_4^{15.3°}$ 1.84288, which indicates the presence of dissolved trioxide.

Solvent.		Conc., g./100 c.c. soln.	d.	t.	$[a]_{r_2}$.	$[a]_y$.	$[a]_g$.	$[a]_b$.	$[a]_v$.
H_2SO_4, g.	H_2O, g.								
(1) (Conc. H_2SO_4, d 1.84288)		2.052	—	19°	$-38.97°$	$-49.2°$	$-59.44°$	$-70.17°$	$-94.52°$
(2) (Conc. H_2SO_4)		2.052	—	18.8	-37.06	-46.29	-55.07	-65.79	-86.74
(3)* 19.7995	4.8176	2.057	—	19.6	-14.45	-16.87	-18.79	-19.28	-16.39
(4)* 44.2452	15.0878	2.054	—	18.7	-6.327	-6.814	-7.303	-4.38	$+6.566$
(5) 19.7163	9.9753	2.059	—	14.5	$+0.9714$	$+1.942$	$+3.4$	$+10.69$	$+26.23$
(6) Aqueous distillate		3.637†	1.552	0	-1.771	-1.181	0.2952	5.903	22.14
		,,	1.537	18	$+0.2982$	$+1.49$	$+2.683$	$+8.050$	$+25.34$

* Visibly anomalous region. † G. per 100 g. of solution.

The solutions were all colourless, but in the temperature–rotation experiment (6) decomposition set in above 30°.

Preparation of the Methyl and Ethyl Esters of Camphor-10-*sulphonic Acid*.—Our early attempts to prepare these esters according to

Edminson and Hilditch (J., 1910, **97**, 223) by heating the theoretical quantity of sulphonyl chloride with the sodium alkyloxides dissolved in excess of the corresponding alcohol, were completely unsuccessful; other processes were therefore tried, *e.g.*, (*a*) heating together the acid chloride and the alcohol, either alone or in the presence of benzene or of pyridine, (*b*) the silver salt method, (*c*) the Fischer–Speier method, or (*d*) the continuous esterification method of Frankland and Aston (J., 1901, **79**, 517).

These methods also were all more or less unsuccessful, chiefly owing to the fact that the ester first formed reacted very readily, either with the sodium alkyloxide or with the alcohol, to produce an ether (see Ferns and Lapworth, J., 1912, **101**, 273), or that the sulphonyl chloride was hydrolysed to reproduce the sulphonic acid (see Krafft and Roos, *Ber.*, 1892, **25**, 2257; Boyle, J., 1909, **95**, 1683; 1910, **97**, 211). Ultimately, we succeeded completely by using a modification of the Schotten–Baumann reaction originally suggested by Boyle (J., 1909, **95**, 1683), and also used by Foldi (*Ber.*, 1920, **53**, 1836), the latter of whom acted upon molecular proportions of benzene- and substituted benzene-sulphonyl chlorides with 20—30% aqueous caustic potash solution at 0°. A similar reaction was used by Izmailski and Razenov (Abs., 1923, i, 770); whilst in the following year Hahn and Walter (*Ber.*, 1921, **54**, 1531) used solid powdered caustic potash at low temperatures instead of the solution, a method adopted and extended by Gilman and Beaber (*J. Amer. Chem. Soc.*, 1925, **47**, 518).

We found ultimately that a low temperature was essential to the success of the preparation, and also that there was no necessity to have sufficient alcohol present to bring the sulphonyl chloride into complete solution—this, in fact, lowered the yield—a suspension of the acid chloride in the alcohol being quite satisfactory; and that, for the completion of the reaction, the addition of 2 mols. of caustic alkali was necessary.

The general process for all the sulphonic esters described in this paper is thus as follows. The sulphonyl chloride was dissolved by heating in the requisite alcohol (15 c.c. per 10 g. of acid chloride). The solution was then quickly cooled, in order to deposit the sulphonyl chloride in the required finely divided form, surrounded by a freezing mixture, and 2 equivs. of powdered caustic soda were slowly added, in small quantities, with vigorous stirring, the temperature being kept well below 10°. When the addition was complete, the mixture was kept for $\frac{1}{2}$ hour, more alcohol being added, if necessary, to preserve fluidity, after which, excess of water was added to the reaction product. The oil obtained, which, on stirring, immediately solidified, was filtered off at the pump and

washed. By this method the methyl esters were obtained in 90%
yields, and the ethyl esters in 70—85% yields of almost pure
material.

After some experience with these substances we were able to
obtain poor yields of the esters by the method of Edminson and
Hilditch, if the solutions of the reagents were concentrated, and if
heat was only applied for a very short time before pouring into
water.

*Methyl camphor-*10-*sulphonate.* From camphor-10-sulphonic acid
(Reychler, *loc. cit.*), the acid chloride was prepared in 90% yield by
heating with 1 equiv. of thionyl chloride on the water-bath and
under a reflux condenser till the reaction ceased (Reychler, by use
of phosphorus pentachloride, obtained 65% yields, *loc. cit.*).

Methyl camphor-10-sulphonate, obtained as described above in
85—90% yield, was recrystallised twice from methyl alcohol, and
then had constant rotation $[\alpha]_g^{16\cdot5°}$ ($c = 5\cdot021$ in absolute alcohol)
$= + 54\cdot18°$ and m. p. 61°. A mixed m. p. with a specimen obtained
by the method of Edminson and Hilditch showed no depression.

Ethyl camphor-10-sulphonate was obtained in a similar fashion
in 70% yield. Recrystallised five times from methyl alcohol, it
showed a constant rotation of $[\alpha]_g^{15\cdot5°}$ ($c = 5\cdot00$ in absolute alcohol)
$= + 53\cdot00°$ and m. p. 46°.

*Methyl camphor-*10-*sulphonate in ethyl alcohol,* $p = 4\cdot793$. Den-
sities determined : 0·8124 at 10·5°; 0·7996 at 26·4°; 0·7854 at
43·0°; 0·7686 at 62°.

t.	d.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	0·8206	$+38\cdot30°$	$+46\cdot57°$	$+54\cdot51°$	$+76\cdot28°$	$+118\cdot2°$
13	0·8104	37·66	46·5	53·74	75·63	116·9
32·5	0·7945	36·93	44·81	53·51	74·67	116·1
42	0·7862	36·32	44·79	53·08	74·15	116·6
58·5	0·7717	36·16	44·42	52·88	74·01	116·2

Remarks. Since the above values did not lie on the straight lines
of the characteristic diagram for camphor-10-sulphonic acid, a
second temperature–rotation investigation was undertaken using a
specimen of the ester which had been repeatedly recrystallised.
The results clearly indicated that there is no inaccuracy in the
above set of figures, since the new values obtained were in close
agreement and fell on the same region of the characteristic diagram.

*Ethyl camphor-*10-*sulphonate in benzene,* $p = 3\cdot148$. The densities
were determined at the same temperature as the polarimetric read-
ings, the polarimeter bath being used.

t.	d.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
10°	0·8945	$+45\cdot51°$	$+54\cdot61°$	$+63\cdot71°$	$+86\cdot80°$	$+131\cdot4°$
32·2	0·8714	44·21	53·10	62·44	85·45	129·6
50·2	0·8525	43·79	52·64	61·72	84·55	128·3
61	0·8418	43·17	52·13	61·09	83·97	127·4

A check was made here in the same way as with the methyl ester.

α-Chlorocamphor.—This was prepared following Kipping and Pope's modification (J., 1893, **63**, 593) of Cazeneuve's method, and was crystallised four times from benzene.

α-Chlorocamphor in benzene, p = 6·873.

t.	d.	$[a]_{r_a}$.	$[a]_y$.	$[a]_g$.	$[a]_v$.	$[a]_v$.
14°	0·8964	+62·59°	+74·76°	+87·34°	+118·1°	+178·3°
27·8	0·8824	65·63	78·72	91·81	124·7	188·4
42	0·8672	69·52	82·41	96·36	130·1	197·9
63·5	0·8443	72·59	87·34	102·2	139·5	211·6

α-Chlorocamphor in ethylene dibromide, p = 3·193.

13·5	2·124	+103·9	+124·4	+146·1	+200·3	+304·5
29·8	2·093	104·7	125·3	147·3	202·1	307·8
54·4	2·044	104·9	126·9	148·9	204·3	311·6
68·8	2·015	105·7	127·5	149·7	205·0	313·9
89·0	1·974	106·4	128·6	150·9	206·9	317·0

α-Chlorocamphor-10-sulphonyl Chloride.—The sulphonation of α-chlorocamphor was carried out as described by Armstrong and Lowry (J., 1902, **81**, 1451) except that the product was isolated as the barium salt, which was then converted into the sodium salt by means of a solution of sodium sulphate. Equivalent amounts of the sodium salt and phosphorus pentachloride were shaken together, and the α-chlorocamphor-10-sulphonyl chloride was isolated by stirring the product into crushed ice. Recrystallised from ether, it had the properties recorded in the literature, m. p. 65°.

Methyl α-chlorocamphor-10-sulphonate was prepared from 10 g. of α-chlorocamphor-10-sulphonyl chloride, 3 g. of powdered sodium hydroxide, and 20 c.c. of methyl alcohol; yield over 90%. The compound was purified by three crystallisations from spirit, m. p. 61·5° (Found, by Stepanow's method : Cl, 12·87. $C_{11}H_{17}O_4ClS$ requires Cl, 12·66%).

Methyl α-chlorocamphor-10-sulphonate in benzene, p = 2·438.

t.	d.	$[a]_{r_a}$.	$[a]_y$.	$[a]_g$.	$[a]_b$.	$[a]_v$.
12·5°	0·8925	+52·29°	+63·20°	+72·97°	+97·38°	+141·4°
33·5	0·8708	53·89	64·77	74·78	101·0	148·4
50·5	0·8529	55·91	66·41	76·65	104·6	154·8
66	0·8375	57·24	67·97	78·66	107·7	161·4

Methyl α-chlorocamphor-10-sulphonate in ethylene bromide, p = 2·007.

32·5	2·125	+83·22	+99·77	+116·6	+157·9	+235·9
44	2·101	82·56	99·61	116·2	156·7	235·6
59·5	2·070	82·26	98·81	115·3	156·1	234·7
76·5	2·035	81·87	98·37	115·0	156·1	234·4
88·8	2·009	81·37	98·11	114·5	155·6	234·2

Ethyl α-chlorocamphor-10-sulphonate, prepared as for the methyl ester, 25 c.c. of absolute alcohol being used (yield 85%), was crystal-

lised five times from spirit (seeding with crude material being at first necessary); m. p. 56° (Found, by Stepanow's method : Cl, 11·95. $C_{12}H_{19}O_4ClS$ requires Cl, 12·06%).

Ethyl α-chlorocamphor-10-sulphonate in benzene, p = 2·425.

t.	d.	$[a]_{r_s}$.	$[a]_y$.	$[a]_z$.	$[a]_b$.	$[a]_v$.
11°	0·8932	+51·07°	+61·16°	+70·98°	+94·06°	+137·4°
33	0·8708	52·98	64·22	73·98	98·24	144·7
49	0·8541	54·31	66·37	76·03	102·0	150·9
65·1	0·8376	55·69	68·00	77·82	104·6	156·6

α-Bromocamphor.—Prepared as described by Kipping and Pope (*loc. cit.*), the compound was purified by two crystallisations from toluene, followed by recrystallisation from benzene; when dried in an air-bath at 50°, it had m. p. 56°.

α-Bromocamphor in benzene, p = 6·688.

t.	d.	$[a]_{r_s}$.	$[a]_y$.	$[a]_g$.	$[a]_b$.	$[a]_v$.
15°	0·9035	+105·1°	+126·0°	+147·7°	+200·9°	+301·8°
28·7	0·8896	107·3	128·8	151·0	205·0	309·4
45	0·8720	109·6	131·8	154·6	210·1	317·9
61·8	0·8537	111·9	134·8	158·1	215·1	326·9

α-Bromocamphor in ethylene dibromide, p = 3·226.

t.	d.					
15	2·144	+135·2	+162·7	+191·1	+261·6	+406·5
32·5	2·110	136·0	163·9	192·2	264·2	410·1
45	2·084	137·2	164·0	193·0	265·6	412·2
59·5	2·055	137·5	164·3	194·0	266·9	414·6
84·3	2·004	137·8	165·7	195·1	268·1	418·4

α-Bromocamphor-10-sulphonyl Chloride.—This was prepared, from α-bromocamphor, in a manner similar to that described for the α-chloro-compound; m. p. 60°.

Methyl α-Bromocamphor-10-sulphonate.—This *ester* was prepared in 80% yield from 10 g. of the acid chloride, 2 g. of powdered sodium hydroxide, and 20 c.c. of methyl alcohol, and was purified by three crystallisations from methyl alcohol; m. p. 64° [Found (Carius) : Br, 24·8. $C_{11}H_{17}O_4BrS$ requires Br, 24·6%].

Methyl α-bromocamphor-10-sulphonate in benzene, p = 2·62.

t.	d.	$[a]_{r_s}$.	$[a]_y$.	$[a]_g$.	$[a]_b$.	$[a]_v$.
11°	0·8970	+79·52°	+94·95°	+111·2°	+149·7°	+222·1°
30	0·8770	81·06	96·83	113·4	152·9	227·2
46·5	0·8594	82·45	98·26	115·2	155·2	232·4
59	0·8457	83·22	98·74	116·8	156·9	235·8

Ethyl α-Bromocamphor-10-sulphonate.—Prepared as for the methyl ester, but by using 15 c.c. of absolute alcohol, this *ester* was obtained in 75% yield, and after three crystallisations from methylated spirit, had constant rotation and m. p. 61° [Found (Carius) : Br, 23·64. $C_{12}H_{19}O_4BrS$ requires Br, 23·57%].

Ethyl α-bromocamphor-10-sulphonate in benzene, $p = 2.386$.

t.	d.	$[a]_{r_*}$.	$[a]_y$.	$[a]_g$.	$[a]_b$.	$[a]_v$.
11°	0.8952	+79.58°	+94.77°	+110.3°	+148.6°	+220.3°
26.6	0.8790	80.74	96.51	111.7	151.0	224.1
40.8	0.8644	81.81	97.86	113.3	153.6	228.4
63	0.8418	83.70	99.86	116.1	157.1	234.3

Ethyl α-bromocamphor-10-sulphonate in ethylene bromide, $p = 1.939$.

10	2.176	+103.7	+125.0	+145.9	+197.0	+295.6
28.5	2.140	102.8	124.1	145.0	196.2	295.4
48	2.100	102.7	123.4	144.7	196.4	294.8
68	2.059	102.3	123.2	144.3	195.8	295.2
85	2.024	102.5	123.0	144.2	195.8	294.8

α-Chlorocamphor-10-sulphonamide was prepared according to Armstrong and Lowry (J., 1902, **81**, 1451) and crystallised four times from spirit; m. p. 144° (lit., 141°).

Rotation in pyridine, $p = 3.682$.

t.	d.	$[a]_{r_*}$.	$[a]_y$.	$[a]_g$.	$[a]_b$.	$[a]_v$.
10°	1.003	+69.68°	+83.05°	+96.23°	+128.7°	+187.9°
29.5	0.9856	70.09	83.35	96.79	128.8	189.8
47.7	0.9674	70.20	83.70	97.21	130.0	191.3
68.5	0.9464	70.13	83.20	96.85	130.2	192.1

The solution showed signs of slight decomposition.

α-Bromocamphor-10-sulphonamide in pyridine, $p = 2.898$. Prepared as described by Armstrong and Lowry (*loc. cit.*), the compound was crystallised four times from methylated spirits. Its sparing solubility prevented its examination in other solvents.

t.	d.	$[a]_{r_*}$.	$[a]_y$.	$[a]_g$.	$[a]_b$.	$[a]_v$.
13.5°	0.9913	98.56°	118.1°	137.7°	185.1°	273.9°
33.5	0.9809	97.18	116.8	136.1	183.4	271.7
49	0.9656	96.49	116.3	136.0	182.5	271.8
81	0.9322	95.57	114.8	134.0	182.1	271.4

Camphorsulphonanhydramide.—The compound was prepared by the method of Armstrong and Lowry (*loc. cit.*), crystallised four times from glacial acetic acid, washed with water, and dried in the air-oven.

Camphorsulphonanhydramide in tetrachloroethane, $p = 3.162$. Densities determined : 1.606 at 5.5°; 1.578 at 24°; 1.555 at 40°; 1.524 at 61.8°; 1.485 at 86.5°.

t.	d.	$[a]_{r_*}$.	$[a]_y$.	$[a]_g$.	$[a]_b$.	$[a]_v$.
0°	1.614	−29.76°	−34.17°	−38.58°	−47.15°	−59.64°
11.5	1.597	29.09	33.91	37.75	46.06	57.18
31.5	1.567	28.01	32.04	36.21	44.78	55.26
46	1.546	27.36	31.31	35.16	43.6	53.83
63.1	1.522	26.88	30.91	34.54	42.21	51.69
87.5	1.483	26.12	29.72	33.06	39.97	49.04

Camphorsulphonanhydramide in aniline, $p = 4.839$. Densities

determined : 1·037 at 12°; 1·023 at 29°; 1·010 at 44°; 0·9931 at 64·4°; 0·9790 at 81·1°.

0	1·047	−60·33	−69·33	−79·09	−99·56	−131·7
14·7	1·035	55·93	65·40	74·64	94·86	125·1
38·5	1·015	52·30	60·09	68·87	87·58	115·7
54·4	1·001	50·20	58·46	66·73	83·51	110·8
67·8	0·9901	48·15	56·76	64·33	78·87	105·4
84·2	0·9767	46·43	54·50	61·77	76·72	100

Summary.

The strongly depressing solvent action of concentrated sulphuric acid upon the optical rotation of camphor (previous paper) has been found to operate also in a number of camphor derivatives. In particular, camphor-10-sulphonic acid has been shown to exhibit negative rotation in this solvent, whilst in aqueous sulphuric acid solutions the visibly anomalous region of rotation for the compound has been realised.

A satisfactory method for the esterification of camphor-10-sulphonic acid, and its α-chloro- and α-bromo-derivatives, has been described, the methyl and ethyl esters being isolated in each case.

The rotations of these esters and the corresponding amides—with the exception of camphor-10-sulphonamide, for which the anhydramide has been substituted—together with the rotations of α-chloro- and α-bromo-camphor have been examined under different conditions of solvent and temperature, and the data discussed with reference to the characteristic diagram.

The rational zero, v/g, for camphor-10-sulphonic acid is $-22·2°$, i.e., not quite the same as that of camphor, but not far removed from it.

The data for the esters do not appear to lie on the same characteristic diagram as that for camphor-10-sulphonic acid.

The rational zeros, v/g, for the α-chloro- and α-bromo-derivatives are approximately $+11°$ and $+24·5°$ respectively.

By comparison with the behaviour of ethyl tartrate (as a typical d-compound), the results seem to show that, like camphor, camphor-10-sulphonic acid ought, perhaps, to be regarded as possessing a lævo-configuration. The α-halogenated camphor derivatives, on the other hand, are possibly to be classed with compounds of dextro-rotatory configuration.

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