

231. *The Influence of Solvents and of other Factors on the Rotation of Optically Active Compounds. Part XXIX. The Rotation-Dispersion of Camphor, Camphoroxime, isoNitrosocamphor, and Oxymethylenecamphor.*

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ALTHOUGH, for more than a century, camphor has been an important object of study as regards its optical activity, these investigations have never been of the comprehensive kind which alone affords any hope of a successful generalisation of the relative phenomena. Since the rotation of a compound can, and usually does, vary with change of temperature, solvent, or concentration, and in all these cases also with change in the colour of the light used—not to mention the possibility, in addition, of change of pressure, which at the moment is too difficult to attack—it is necessary to take account of all these variables in any investigation likely to be of value. An examination of the variation of rotation with change in any one of these factors can only be of very limited significance, whilst the attempts which are made from time to time to connect casually selected rotation data with conceptions such as dipole moment, specific inductive capacity, etc., without any attempt to show that these phenomena vary sympathetically, are of even less value. We have therefore examined the rotation of camphor as regards its relationship to colour of light, temperature, solvent, and concentration, in the manner adopted for some other substances, notably ethyl tartrate, but since some real advance has now been made in our knowledge of the general behaviour of active compounds, the investigation does not require to be so extensive.* Thus, if the known behaviour of ethyl tartrate allows of any prediction regarding the behaviour of camphor, it is to be expected that, in solvents which confer high rotation, the rotation should diminish or else increase only slowly with rise of temperature, whereas in solvents of depressing influence the rotation should increase fairly rapidly.

Although Biot (*Compt. rend.*, 1852, **35**, 241) seemed to find something peculiar about the rotation-dispersion of camphor dissolved in alcohol and in acetic acid, he did not, as was remarked by Arndtsen (*Ann. Chim. Phys.*, 1858, **54**, 418), explain wherein this

* Our experiments were commenced fully ten years ago, but have been much interrupted.

peculiarity of dispersion lay. Arndtsen himself, who examined the dispersion of camphor in alcoholic solution for six different colours of light, would almost certainly have considered the dispersion normal, inasmuch as the rotation of the substance increases with the refrangibility of the light used, as far as he could examine the problem; and in this he would probably have been followed, until recently, by most chemists.

It has, however, been suggested (Part XXVIII; J., 1929, 2882) that, as tested by some of the methods then in use, the dispersion of certain substances such as cane sugar, tartar emetic, and others, appears to be what is often called "simple" merely because the rotation happens to be great, thus rendering the detection of irregularities in a dispersion curve a difficult matter, especially when the conception of what should be the normal form of the dispersion curve is a purely arbitrary assumption. This first point could only be settled were it possible to examine the dispersion much further beyond the visible spectrum than is practicable at present.* It may, however, at least in our opinion, also be investigated either by lowering the high rotation of the substance in question by means of a depressing solvent, or by conversion of the substance of high rotation into derivatives having rotations in the neighbourhood of zero, whereupon the anomalousness—if any—of the dispersion curves, becomes apparent. Different views may be held as to the validity of this procedure, which involves what seem to be regarded at the present time as the almost absurd assumptions, that a chemical compound retains its individuality when in solution or when heated or cooled to different temperatures, and that the rotatory power of compounds of a mother substance should bear some comparatively simple and graded relationship to that of the mother substance itself.

We first made a rough survey of our field by determining the rotation of camphor at approximately 5% concentration in a number of solvents which have been used in other investigations of this series.† The result is shown in the following table.

* In the case of camphor, however, Lowry and Gore (*Proc. Roy. Soc.*, 1932, A, 135, 13) have measured the rotatory dispersion in and through an absorption band.

† Landolt (*Annalen*, 1877, 189, 333; "Das optische Drehungsvermögen," 1898, pp. 168, 169, §53) examined camphor in a number of solvents at different concentrations. The lowest value he observed was $[\alpha]_D^{20} = 42.95^\circ$, which occurred in benzene solution of $p = 24.32$. By extrapolation from his results, it would appear that the specific rotation of homogeneous camphor, could it exist liquid at ordinary temperature, should be about $[\alpha]_D^{20} = +55^\circ$.

Rotation of camphor in various solvents.

Solvent.	Conc., c.	Temp., t.	α_D (100 mm.).	$[\alpha]_D$.
Quinoline	5.388	18°	+ 1.83°	+ 33.97°
Benzaldehyde	5.209	16	+ 2.28	+ 37.90
Pyridine	6.107	16.5	+ 1.99	+ 38.21
Chloroform	5.236	16.5	+ 2.12	+ 40.49
Nitrobenzene	5.452	16	+ 2.32	+ 42.47
Acetone.....	5.376	17	+ 2.62	+ 48.73
Acetylene tetrabromide	5.506	16	+ 2.8	+ 50.86
Ethylene bromide	5.213	16	+ 2.99	+ 57.37

The data show that the rotation of camphor can be made to vary over a considerable range by the use of different solvents, and it is noticeable that here those solvents, such as quinoline, pyridine, and benzaldehyde, which tend greatly to enhance the rotation of ethyl tartrate, tend to lower that of camphor, whilst others, like acetylene tetrabromide and ethylene bromide, which have a marked depressing effect upon the rotation of ethyl tartrate, have an enhancing effect upon the rotation of camphor.

Guided by the foregoing data, we then examined the rotation of camphor more fully, first using the homogeneous substance at 190° for various colours of light, with the results given on p. 1722. Owing to the easy volatility and the high m. p. of camphor, we were unable accurately to determine the density of the substance, or to calculate values for the specific rotation. It was found, however, that by raising the temperature from 190° to 200°, the observed rotation, in the case of green light, diminished slightly, and this diminution would probably be more marked at higher temperatures. As is shown below, the rotation of camphor in the solvents we have examined increases with rise of temperature, whilst in the homogeneous substance the rotation diminishes; it seems therefore highly probable that at a temperature of about 200° the observed rotation of camphor for green light is in the neighbourhood of a maximum value.

Three solutions of camphor in ethylene bromide were examined, the most dilute ($p = 4.5$) at three different temperatures. It appears that, for all the colours of light used, the rotation diminishes with increasing concentration, and that in the most dilute solution it increases with rise of temperature.

In the case of quinoline ($p = 4.43$), the solvent at the other end of the series, the specific rotation (α) increases at all temperatures between 0° and 99.3° in passing from red to violet light, (b) increases for all colours of light with increase of temperature, and considerably more than in ethylene bromide; and, although we did not examine the point, it would almost certainly increase with increase of concentration in this solvent.

examined; one, moreover, with a comparatively high *b. p.*, so that experiments could be made at rather higher temperatures. In a solution of $p = 25.85$ at 19° , the specific rotation for green light is reduced to 23.07° ; and in this solvent the rotation increases with increasing refrangibility of the light, as well as with increase of temperature and of concentration. It was possible to get a fairly concentrated solution in phenol, of $p = 72.97$, and in this case also the rotation increases with the refrangibility of the light and with the temperature.

None of these solvents, however, produced as great an effect on the rotation of camphor as we had wished; none of them depresses it sufficiently to bring into view the region of visibly anomalous rotation-dispersion, and in order to construct a satisfactory characteristic diagram, we required data lying on the negative side. We therefore resorted to camphoroxime, which has a considerable negative rotation, and we examined it in alcohol ($p = 6.22$) and in *o*-nitrotoluene ($p = 4.38$): the latter solvent produced a lower rotation than did alcohol, and in both cases the rotation rose fairly rapidly with increase in temperature for all the different colours of light.

The dispersion curves for these two solutions at a temperature of approximately 14° are shown as graphs 9 and 8 respectively in Fig. 1. It is true that these dispersion curves are not identical with those which they intersect, representing the dispersion of camphor in concentrated and in slightly diluted sulphuric acid, but considering the difference in constitution and conditions of the active compounds, the similarity is fairly close.

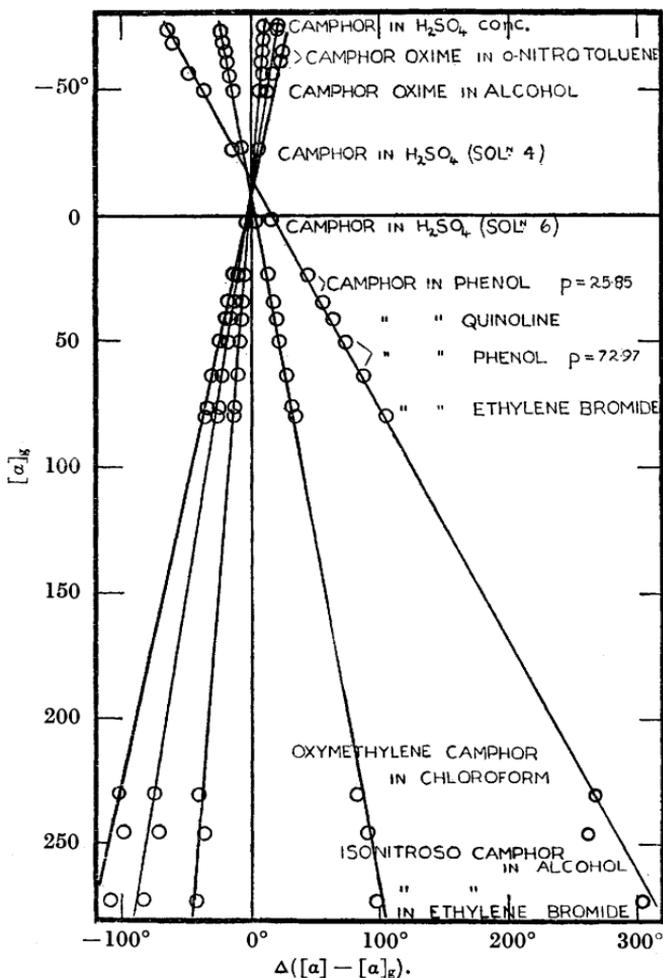
The data for camphoroxime in these two solvents lie completely on the negative side of the characteristic diagram, Fig. 2, and do not themselves exhibit visibly anomalous rotation dispersion.

To complete the characteristic diagram on the positive side we examined also *isonitrosocamphor*—which is known to have a high rotation—at various temperatures, in alcohol and in ethylene bromide. In this case the rotation for all the colours of light used is higher in the latter solvent than in the former, whilst, in addition, the rotation diminishes as the temperature increases, so that the tendency already referred to in the case of homogeneous camphor is definitely realised in this derivative. The data in the case of *isonitrosocamphor* are perhaps a little less definite than in the others, because of the possibility of mutarotation, and, in ethylene bromide, the rotation of the solution did not return to its original value after heating to a temperature of 100° , which, however, is fairly drastic treatment.

At this stage we happened on a passage by the Hon. Robert

Boyle ("The Origin of Formes and Qualities," 2nd. edn., 1667, Sect. II, p. 183), in which he records the interesting facts that camphor is easily soluble in oil of vitriol, with the production of a colour, and that, although its smell then entirely disappears, the camphor is completely reprecipitated from the solution by the

FIG. 2.



addition of an excess of water. This led us to examine the rotation of camphor dissolved in sulphuric acid, whereupon we found that, by this means, the rotation of camphor could be reduced even below that of camphoroxime dissolved either in alcohol or in *o*-nitrotoluene. We found later that Lucas (*Ann. Physique*, 1928, 9, 446), apparently without Boyle's prompting, had already recorded some data for

camphor dissolved in sulphuric acid, and that, by the action of nitric acid, he had succeeded in removing the impurity to which the colour mentioned by Boyle was evidently due.

Our data are given on p. 1724, and are represented by the dispersion curves in Fig. 1.

It will be noticed that the dispersion curve obtained for camphor in our most concentrated sulphuric acid (graph 1) lies, at low rotations, completely on the negative side of the diagram, and that, as the quantity of water present increases, the shape of the dispersion curve gradually alters through graph 2 (8 sulphuric acid to 1 water), graph 3 (6 : 1), and graph 4 (4 : 1), so that, when the proportion of sulphuric acid to water is as 3 : 1 (graph 5), there occurs a distinct minimum in the neighbourhood of Hg_b , and the curve seems to suggest a point of inflexion in the neighbourhood of Hg_g . In this region we obviously have visibly anomalous rotation dispersion. When the proportion of water is raised so as to give a ratio of sulphuric acid to water of 2 : 1, all but one of the points on the curve pass to the positive side of the diagram, but the rotation for Hg_r is still negative. The curve cuts the axis of zero rotation at $\lambda = ca. 6030 \text{ \AA.U.}$

On account of the decreasing solubility of camphor as the amount of water is increased, the behaviour could not be followed further, but on the diagram is shown a dispersion-rotation curve for camphor in quinoline ($p = 4.43$), which appears to be in complete harmony with the others, just as if it forms one—as indeed we think it does—of the same family of curves.

It is obviously not easy to examine the influence of temperature change on solutions of camphor in sulphuric acid, but, by working at low temperatures, we obtained sufficient data, recorded on p. 1724, to show that, as was to be expected, the rotation increases (in an absolute sense) with rise of temperature, which is in agreement with the fairly general regularity mentioned on p. 1715, that when the rotation of any substance has a high value, it diminishes on heating, and *vice versa*.

In Fig. 2 is shown a characteristic diagram representing some of the results recorded above. It is to be noticed that for camphor itself dissolved in phenol or in concentrated or aqueous sulphuric acid, for camphoroxime in *o*-nitrotoluene and in alcohol, and even for isonitrosocamphor and oxymethylenecamphor in solution, the experimental data lie with satisfactory regularity upon straight lines, from which it may be concluded that the dispersion of all the solutions concerned is of the same general type. Since, however, these lines do not meet all at one point, it may be concluded that the anomalousness obvious in the region of intersection persists through-

out the whole diagram. The points of intersection of these lines, taken in pairs, may all be regarded as singular points; but the one upon which, for the moment, attention may chiefly be focused is the intersection of the lines for violet and for green light. On the diagram these two lines intersect at a specific rotation of -16.5° , and this point may be regarded as the rational zero for these two colours for all the compounds in question. If, by any means, e.g., change of solvent or of temperature, the rotation for any one of these compounds for green light can be made to assume the value -16.5° , then the rotation for violet light will have the same value. With oxymethylenecamphor, where definite mutarotation occurs, the end values do not agree with the rest of the diagram.

Finally, the dispersion for these two colours, violet and green, is constant over wide ranges, and should have the approximate value throughout, $v/g = 2.08$.*

EXPERIMENTAL.

The colours of light used were as follows :

λ	r_1 .	r_2 .	y.	g.	b.	v.
	6716	6234	5790	5461	4916	4358

Homogeneous camphor. The camphor used was purified by recrystallisation from methyl alcohol and then by sublimation.

t.	$\alpha_{r_1}(100)$.	$\alpha_{r_2}(100)$.	α_y .	α_g .	α_b .	α_v .
190°	+ 37.38°	46.94°	58.54°	70.00°	99.38°	160.20°
200				69.76		

Camphor in ethylene bromide : I, $p = 4.4940$. Densities determined : 2.0474 at 21.8° ; 2.0176 at 37.4° ; 1.9531 at 70° ; 1.8943 at 99.9° .

t.	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
15°	+ 41.9°	51.12°	63.04°	76.00°	107.87°	176.00°
33.5	42.46	52.06	64.30	77.38	110.58	179.37
61	43.00	53.26	65.85	79.31	113.68	183.47

II, $p = 38.442$. Densities determined : 1.4697 at 10.75° ; 1.4469 at 28.75° .

20	+ 40.85	49.23	60.80	73.24	103.13	170.09
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III, $p = 50.219$. Densities determined : 1.3325 at 14.5° ; 1.3146 at 30° .

20	+ 38.64	46.39	59.75	72.03	102.36	167.7
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It is impossible to obtain a more concentrated solution of camphor in ethylene bromide at ordinary temperature.

* When the rotation for green is $+100^\circ$ that for violet is $+226^\circ$; therefore $v/g = (16.5 + 226)/(16.5 + 100) = 2.08$.

Camphor in quinoline, $p = 4.4278$. Densities determined: 1.09119 at 14.75°; 1.06562 at 46.75°; 1.04287 at 75.5°; 1.02359 at 99°.

t .	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	+ 20.63°	25.57°	32.40°	40.70°	61.09°	105.28°
14.5	22.23	27.81	35.24	43.78	65.31	112.62
45.75	26.87	32.63	40.78	50.09	73.83	124.22
71.5	29.31	36.36	45.61	55.54	79.12	134.5
99.3	32.69	39.76	50.30	61.01	85.88	144.41

Camphor in phenol: I, $p = 25.846$. Densities determined: 1.0411 at 25.5°; 1.0213 at 49.75°; 0.99953 at 75.5°; 0.97836 at 100°.

t .	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
19°	+ 10.59°	13.83°	18.22°	23.07°	35.94°	67.46°
37	12.48	15.87	21.18	26.61	41.51	74.87
71	17.65	21.87	27.19	33.85	50.29	89.67

II, $p = 37.464$. Densities determined: 1.0326 at 18.75°; 1.0231 at 30.5°.

20.5	+ 13.83	17.58	22.80	28.42	43.77	78.18
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III, $p = 47.739$. Densities determined: 1.0255 at 14°; 1.01315 at 29.5°.

20	+ 15.67	21.38	27.55	34.14	50.11	89.43
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IV, $p = 58.773$. Densities determined: 1.0126 at 14.75°; 1.0005 at 29.5°.

20	+ 21.97	27.22	34.42	42.59	62.85	107.6
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V, $p = 72.9718$. Densities determined: 0.99566 at 16°; 0.98363 at 31.5°; 0.96089 at 60.25°; 0.94630 at 78.25°; 0.92918 at 99°.

0	+ 26.19	32.50	41.26	49.94	71.60	122.46
17.5	27.69	34.38	43.23	52.50	75.91	126.85
33.3	28.72	35.80	45.09	54.68	78.06	131.52
60.6	31.18	38.24	48.11	58.21	83.76	139.56
99.75	33.42	41.19	52.42	63.28	90.64	149.73
140.00	36.34	44.41	56.42	68.12	98.67	—

Camphoroxime in alcohol, $p = 6.220$. Densities determined: 0.8088 at 12.5°; 0.7972 at 26.5°; 0.7882 at 37.2°; 0.7800 at 46°; 0.7730 at 54.5°; 0.7650 at 63°.

t .	d .	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	0.8204	—	-36.87°	-42.87°	-50.09°	-63.45°	-86.12°
14.5	0.8076	-31.98°	-36.34	-42.81	-49.40	-62.22	-85.72
34	0.7906	-31.01	-36.74	-43.22	-49.71	-62.55	-84.16
54	0.7732	-30.54	-36.24	-42.09	-48.72	-61.97	-84.07

Camphoroxime in o-nitrotoluene, $p = 4.378$. Densities determined: 1.1596 at 14°; 1.1461 at 27.5°; 1.1405 at 34°; 1.1216 at 54°; 1.1047 at 72°; 1.0890 at 88.2°.

<i>t.</i>	<i>d.</i>	$[\alpha]_{F_1}$	$[\alpha]_{F_2}$	$[\alpha]_Y$	$[\alpha]_G$	$[\alpha]_B$	$[\alpha]_V$
14°	1.1596	-40.14°	-48.14°	-56.75°	-65.13°	-84.33°	—
40	1.1350	-38.99	-47.04	-55.46	-64.40	-81.51	—
60.5	1.1158	-37.37	-45.42	-52.98	-61.30	-79.21	—
78.5	1.0986	-36.67	-44.22	-51.63	-59.43	-76.08	—
100	1.0784	-35.06	-41.96	-49.22	-57.44	-72.93	—

isoNitrosocamphor in alcohol, $p = 2.503$. Densities determined : 0.8015 at 14.5°; 0.7939 at 22.5°; 0.7851 at 33.5°; 0.7749 at 45.2°; 0.7659 at 55.2°; 0.7556 at 65.8°.

<i>t.</i>	<i>d.</i>	$[\alpha]_{F_1}$	$[\alpha]_{F_2}$	$[\alpha]_Y$	$[\alpha]_G$	$[\alpha]_B$	$[\alpha]_V$
0°	0.8142	+147.5°	+174.8°	+209.8°	+245.7°	+336.2°	+505.8
13	0.8038	147.6	173.4	211.3	245.8	335.8	505.4
28	0.7897	143.5	173.6	209.6	245.0	333.3	503.6
39.5	0.7795	145.4	171.4	209.1	243.1	330.9	502.5
53.5	0.7674	144.5	170.8	207.2	243.8	329.6	501.0

isoNitrosocamphor in ethylene bromide, $p = 0.9513$. Densities determined : 2.1267 at 17.5°; 2.1048 at 32.5°; 2.0868 at 43.5°; 2.0609 at 56°; 2.0280 at 72.5°; 1.9911 at 89.5°.

<i>t.</i>	<i>d.</i>	$[\alpha]_{F_1}$	$[\alpha]_{F_2}$	$[\alpha]_Y$	$[\alpha]_G$	$[\alpha]_B$	$[\alpha]_V$
18.5°	2.1250	163.9°	189.9°	231.3°	272.8°	370.1°	576.3°
40	2.0936	141.6	172.4	207.1	246.1	336.6	522.0
60	2.0535	138.2	165.4	202.9	238.4	325.9	507.9
79	2.026	134.0	159.9	192.0	228.3	314.2	497.7
100	1.965	125.4	152.2	190.5	217.3	305.9	488.9

The rotation of the solution did not return to its original value, even on standing over-night. A similar result attended a repetition of the experiment.

Camphor in sulphuric acid. The sulphuric acid was carefully distilled in an all-glass apparatus, and the higher-boiling fraction, *d* 1.844, selected for use. The camphor was purified as described by Lucas (*Ann. Physique*, 1928, 9, 446). Several solutions were made up in this acid, alone and diluted with water, and examined polarimetrically.

	Mixture, g.		Approx. ratio, H ₂ SO ₄ :H ₂ O.	Conc.	Temp.	$[\alpha]_{F_1}$	$[\alpha]_Y$	$[\alpha]_G$	$[\alpha]_B$	$[\alpha]_V$
	H ₂ SO ₄	H ₂ O								
1.	Pure	—	∞	2.156	21.5°	-46.84°	-53.43°	-63.64°	-92.32°	-128.9°
2.	20.49	2.50	8:1	2.132	24	37.99	45.6	56.28	74.11	103.1
3.	12.67	2.07	6:1	2.05	20	35.6	41.95	49.75	67.32	90.72
4.	10.19	2.5	4:1	2.036	19	20.63	24.56	27.02	32.41	40.77
5.	*10.72	3.75	3:1	2.116	17	8.507	8.98	9.913	11.81	8.034
6.	10.03	5.03	2:1	2.02	16	-0.495	+0.99	+1.98	+5.44	+17.82

* Visibly anomalous region.

To get some idea of the effect of temperature change on the rotation of sublimed camphor in sulphuric acid, we made a solution of $p = 2.829$, using a different sample of $d_{18.2}^{20} = 1.8395$.

<i>t.</i>	<i>d.</i>	$[\alpha]_{F_1}$	$[\alpha]_Y$	$[\alpha]_G$
0°	1.817	-54.16°	-65.51°	-75.56°
17.1	1.799	-52.38	-64.18	-74.32
32.9	1.782	-51.90	-62.82	-73.40

Decomposition occurred above 40°. The solution was orange-red in colour : blue and violet could not be read with any accuracy.

Mutarotation of oxymethylenecamphor in chloroform at 0°.

$$c = 0.9815.$$

Time.	$[\alpha]_{11}$.	$[\alpha]_{12}$.	$[\alpha]_5$.	$[\alpha]_6$.	$[\alpha]_b$.	$[\alpha]_c$.
Zero	+127.4°	+153.5°	+188.5°	+229.9°	+312.0°	+496.1°
24 hrs.	74.51	94.26	110.8	133.8	182.2	277.0

On standing for a further 24 hours and cooling to 0°, the solution became turbid and could not be read.

$$c = 0.9725.$$

Zero	+131.1	+160.6	+196.0	+232.7	+330.4	+497.4
After 4 days at room temp.	63.6	69.4	84.2	101.6	142.0	205.0

Summary.

The rotation of camphor alone and in various organic solvents has been examined and found to vary from a maximum of $[\alpha]_{5461}^{19}$ + 76° in ethylene bromide ($t = 15^\circ$, $p = 4.5$) to a minimum of 23.07° in phenol ($p = 25.8$). It has also been examined in concentrated and diluted sulphuric acid, in the former of which the rotation is depressed to - 75.6° ($t = 0^\circ$; $p = 2.83$). *iso*Nitrosocamphor, camphoroxime, and oxymethylenecamphor were also examined.

In general the data lie with satisfactory regularity upon the lines of a characteristic diagram, the greatest discrepancy occurring in the case of *isonitrosocamphor*. The rational zero for camphor, v/g , is - 16.5°.

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