

STUDIES ON THE DEPENDENCE OF OPTICAL ROTATORY POWER ON CHEMICAL CONSTITUTION

Part XXX. Rotatory Dispersion of Camphor Carboxylic Acids, Camphors and 1-Borneol

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IN the present communication, we give our determinations of the rotatory dispersion of camphor carboxylic acids in 8 solvents. The influence of the wavelength of light and the nature of the solvent on rotatory power has been briefly discussed. We have also corrected the rotatory dispersion formula of camphor in alcoholic solution, given in an earlier paper.¹ Tables XII and XIII for *l*-borneol are calculated from data given in that paper.

NATURE OF ROTATORY DISPERSION

The rotatory dispersion of camphor carboxylic acids in all the solvents is "simple" and can be expressed by the one-term Drude equation, $[\alpha] = \frac{k_0}{\lambda^2 - \lambda_0^2}$. On plotting $1/\alpha$ against λ^2 a straight line is obtained in each case. The dispersion equations have been worked out and the results are given in Tables III to X. It is seen that the differences between the observed specific rotatory powers (*o*) and those calculated from the equation (*c*) agree within the limits of experimental error.

THE EFFECT OF THE NATURE OF THE SOLVENT ON ROTATORY POWER

The specific rotatory powers, $[\alpha]_{5461}^{35^\circ}$, of camphor carboxylic acids in eight solvents are given in Table I. The sequence of decreasing rotatory powers is as follows:

Glacial acetic acid > chloroform > water > ethyl alcohol > methyl alcohol > acetone > pyridine > benzene. A comparison of the rotatory powers with the dielectric constants of these solvents [water (80) > methyl alcohol (31.2) > ethyl alcohol (25.8) > acetone (21.5) > pyridine (12.4) > glacial acetic acid (6.4) > chloroform (5.2) > benzene (2.28)] shows that there is a close parallelism between them, only glacial acetic acid and chloroform being anomalous in behaviour. The order of methyl and ethyl alcohols is reversed, but the difference in rotatory power is negligible.

The above order of decreasing rotatory power for the Hg green line (5461 Å.U.) does not hold good for all wavelengths. For mercury violet (4358) it is glacial acetic acid > chloroform > water > methyl alcohol > ethyl alcohol > acetone > pyridine > benzene, the first two not falling in the sequence of decreasing dielectric constants. The order of decreasing

TABLE I

Rotatory Power of Camphor Carboxylic Acid in Different Solvents at 35° C.

Solvent	Dielectric constant	$[\alpha]_{5461}^{35^\circ}$	Absolute Rotation (K_0)
Water ..	78.0	81.50°	19.02
Methyl alcohol ..	31.2	72.50	16.46
Ethyl alcohol ..	25.8	72.58	16.94
Acetone ..	21.5	70.08	16.92
Pyridine ..	12.4	47.58	10.42
Glacial acetic acid ..	6.4	90.58	22.54
Chloroform ..	5.2	85.42	21.15
Benzene ..	2.28	42.00	11.40

TABLE II

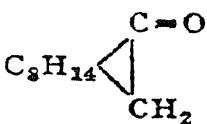
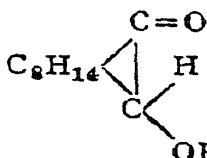
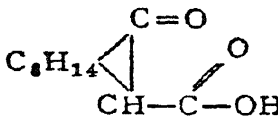
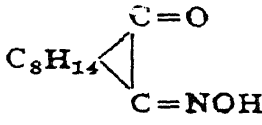
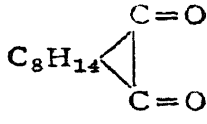
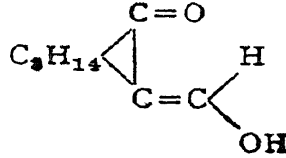
Compound	Structural formula	$[\alpha]_{5461}^{35^\circ}$ in ethyl alcohol
1 Camphor ..		59.61°
2 Borneol ..		43.45
3 Camphorcarboxylic acid ..		72.5
4 Isonitroso camphor ..		241.2 (stable) 214.28 (unstable)
5 Camphorquinone ..		165.54
6 Oxymethylenecamphor ..		243.35

TABLE III

Camphorcarboxylic Acids in Water

$$[\alpha] = \frac{19.02}{\lambda^2 - 0.0614} \quad \lambda_0 = 2478 \text{ \AA.U.}$$

Dextro Conc. : 0.5000 gm./100 c.c.		Wavelength	[α] _{cal.} (c)	Lævo Conc. : 0.5000 gm./100 c.c.	
[α] _{obs.} (o)	$\alpha - c$			$\alpha' - c$	[α] _{obs.} (o')
48.50°	-0.49°	Li ₆₇₀₈	±48.99°	+0.01°	49.00°
..	..	Cd ₆₄₃₈	53.92	-0.42	53.50
62.00	+0.81	Li ₆₁₀₄	61.19	+0.48	61.67
66.50	-0.12	Na ₅₈₉₃	66.62	+0.38	67.00
71.33	+1.52	Hg ₅₇₈₀	69.81	+1.36	71.17
81.50	+1.16	Hg ₅₄₆₁	80.34	+1.16	81.50
90.67	-0.02	Ag ₅₂₀₉	90.69	-0.19	90.50
97.17	+0.70	Cd ₅₀₈₆	96.47	+0.37	96.84
114.0	+1.30	Cd ₄₈₀₀	112.7	+0.90	113.6
120.5	-0.40	Cd ₄₆₇₈	120.9	-0.60	120.3
127.0	+0.40	Li ₄₆₀₂	126.6	+0.70	127.3
145.0	-3.00	Hg ₄₃₅₈	148.0	+0.50	148.5

TABLE IV

Camphorcarboxylic Acids in Methyl Alcohol

$$[\alpha] = \frac{16.46}{\lambda^2 - 0.0680} \quad \lambda_0 = 2608 \text{ \AA.U.}$$

Dextro Conc. : 0.5000 gm./100 c.c.		Wavelength	[α] _{cal.} (c)	Lævo Conc. : 0.5000 gm./100 c.c.	
[α] _{obs.} (o)	$\alpha - c$			$\alpha' - c$	[α] _{obs.} (o')
41.67°	-1.41°	Li ₆₇₀₈	±43.08°	-0.08°	43.00°
48.00	+0.50	Cd ₆₄₃₈	47.50	±0.00	47.50
54.00	-0.05	Li ₆₁₀₄	54.05	+0.12	54.17
59.00	+0.05	Na ₅₈₉₃	58.95	+0.05	59.00
62.17	-0.67	Hg ₅₇₈₀	61.84	±0.00	61.84
72.67	+1.17	Hg ₅₄₆₁	71.50	+0.83	72.33
81.00	+0.03	Ag ₅₂₀₉	80.97	-0.47	80.50
86.17	-0.13	Cd ₅₀₈₆	86.30	+1.03	87.33
102.0	+0.60	Cd ₄₈₀₀	101.4	-0.40	101.00
110.3	+1.20	Cd ₄₆₇₈	109.1	+0.20	109.30
113.0	-1.50	Li ₄₆₀₂	114.5	-0.50	114.0
133.0	-1.90	Hg ₄₃₅₈	134.9	+0.10	135.0

TABLE V

Camphorcarboxylic Acids in Ethyl Alcohol

$$[\alpha] = \frac{16.94}{\lambda^2 - 0.065}$$

$$\lambda_0 = 2550 \text{ \AA.U.}$$

Dextro Conc. : 0.5000 gm./100 c.c.		Wavelength	[α] _{cal.} (c)	Lævo Conc. : 0.5000 gm./100 c.c.	
[α] _{obs.} (o)	$\sigma - c$			$\sigma' - c$	[α] _{obs.} (o')
43.50°	-0.50°	Li ₆₇₀₈	±44.00°	-0.33°	43.67°
49.00	+0.51	Cd ₆₄₃₈	48.49	+0.51	49.00
55.00	-0.11	Li ₆₁₀₄	55.11	+0.06	55.17
60.00	-0.03	Na ₅₈₉₃	60.03	-0.03	60.00
63.00	+0.05	Hg ₅₇₈₀	62.95	+0.05	63.00
72.50	-0.14	Hg ₅₄₆₁	72.64	+0.03	72.67
82.37	+0.24	Ag ₅₂₀₉	82.13	+0.37	82.50
87.33	-0.13	Cd ₅₀₈₆	87.46	-0.46	87.00
103.5	+1.10	Cd ₄₈₀₀	102.4	-0.40	102.0
110.0	-0.10	Cd ₄₆₇₈	110.1	+0.40	110.5
116.7	+1.13	Li ₄₆₀₃	115.4	+0.10	115.5
132.5	-3.00	Hg ₄₃₅₈	135.5	-0.50	135.0

TABLE VI

Camphorcarboxylic Acids in Acetone

$$[\alpha] = \frac{16.92}{\lambda^2 - 0.0564}$$

$$\lambda_0 = 2375 \text{ \AA.U.}$$

Dextro Conc. : 0.5000 gm./100 c.c.		Wavelength	[α] _{cal.} (c)	Lævo Conc. : 0.5008 gm./100 c.c.	
[α] _{obs.} (o)	$\sigma - c$			$\sigma' - c$	[α] _{obs.} (o')
43.00°	+0.02°	Li ₆₇₀₈	±42.98°	-0.14°	42.84
48.84	+1.59	Cd ₆₄₃₈	47.25	+0.29	47.54
53.50	-0.03	Li ₆₁₀₄	53.53	-0.57	52.96
58.84	+0.65	Na ₅₈₉₃	58.19	-0.23	57.96
61.00	+0.08	Hg ₅₇₈₀	60.92	+0.04	60.96
70.00	+0.02	Hg ₅₄₆₁	69.98	+0.18	70.16
79.17	+0.43	Ag ₅₂₀₉	78.74	-0.10	78.64
83.00	-0.64	Cd ₅₀₈₆	83.64	+0.32	83.96
97.17	-0.08	Cd ₄₈₀₀	97.25	-0.45	96.80
104.3	+0.20	Cd ₄₆₇₈	104.1	+0.10	104.2
108.5	+0.40	Li ₄₆₀₃	108.9	-1.00	107.9
125.0	-1.70	Hg ₄₃₅₈	126.7	+0.60	127.3

TABLE VII

Camphorcarboxylic Acids in Pyridine

$$[\alpha] = \frac{10.42}{\lambda^2 - 0.078} \quad \lambda_0 = 2793 \text{ \AA.U.}$$

Dextro Conc. : 0.5004 gm./100 c.c.		Wavelength	[α] _{cal.} (c)	Lævo Conc. : 0.5000 gm./100 c.c.	
[α] _{obs.} (o)	$\sigma - c$			$\sigma' - c$	[α] _{obs.} (o')
28.04°	+0.03°	Li ₆₇₀₈	±28.01°	-0.01°	28.00°
30.96	±0.00	Cd ₆₄₃₈	30.96	-0.79	30.17
35.32	-0.06	Li ₆₁₀₄	35.38	+0.62	36.00
38.94	+0.24	Na ₅₈₉₃	38.70	+0.14	38.84
40.48	-0.20	Hg ₅₇₈₀	40.68	-0.01	40.67
47.64	+0.32	Hg ₅₄₆₁	47.32	+0.18	47.50
53.32	-0.57	Ag ₅₂₀₉	53.89	-0.22	53.67
57.16	-0.50	Cd ₅₀₈₆	57.66	-1.16	56.50
69.52	+1.15	Cd ₄₈₀₀	68.37	-0.04	68.33
73.08	-0.88	Cd ₄₆₇₈	73.96	+0.21	74.17
78.16	+0.31	Li ₄₆₀₃	77.85	+0.15	78.00
94.32	+1.29	Hg ₄₃₅₈	93.03	-0.03	93.00

TABLE VIII

Camphorcarboxylic Acids in Glacial Acetic Acid

$$[\alpha] = \frac{22.54}{\lambda^2 - 0.0449} \quad \lambda_0 = 2119 \text{ \AA.U.}$$

Dextro Conc. : 0.5000 gm./100 c.c.		Wavelength	[α] _{cal.} (c)	Lævo Conc. : 0.5000 gm./100 c.c.	
[α] _{obs.} (o)	$\sigma - c$			$\sigma' - c$	[α] _{obs.} (o')
53.84°	-1.80°	Li ₆₇₀₈	±55.64°	-1.47°	54.17°
61.00	+0.01	Cd ₆₄₃₈	60.99	+0.34	61.33
67.84	-0.98	Li ₆₁₀₄	68.82	-0.82	68.00
75.50	+1.17	Na ₅₈₉₃	74.33	+1.34	75.67
78.00	+0.06	Hg ₅₇₈₀	77.94	+0.23	78.17
90.84	+1.84	Hg ₅₄₆₁	89.00	+1.33	90.33
100.00	+0.44	Ag ₅₂₀₉	99.56	+0.61	100.17
105.3	-0.07	Cd ₅₀₈₆	105.4	-0.40	105.0
120.5	-1.00	Cd ₄₈₀₀	121.5	-0.50	121.0
130.0	+0.40	Cd ₄₆₇₈	129.6	-0.10	129.5
135.0	-0.10	Li ₄₆₀₃	135.1	+0.40	135.5
158.0	+2.70	Hg ₄₃₅₈	155.3	-0.30	155.0

TABLE IX

Camphorcarboxylic Acids in Chloroform

$$[\alpha] = \frac{21.15}{\lambda^2 - 0.0454}$$

$$\lambda_0 = 2031 \text{ \AA.U.}$$

Dextro Conc. : 0.5000 gm./100 c.c.		Wavelength	[α] _{cal.} (c)	Lævo Conc. : 0.5000 gm./100 c.c.	
[α] _{obs.} (o)	<i>o-c</i>			<i>o'-c</i>	[α] _{obs.} (o')
+50.50°	-1.78°	Li ₆₇₀₃	±52.28°	-1.78°	-50.50°
..	..	Cd ₆₄₃₈	57.31
64.00	-0.68	Li ₆₁₀₄	64.68	-1.01	63.67
70.17	+0.09	Na ₅₈₉₃	70.08	-0.08	70.00
73.84	+0.60	Hg ₅₇₈₀	73.24	+0.60	73.84
85.33	+1.67	Hg ₅₄₆₁	83.66	+1.84	85.50
92.50	-1.13	Ag ₅₂₀₉	93.63	-0.96	92.67
100.0	+0.62	Cd ₅₀₈₆	99.38	+0.46	99.84
114.0	-0.30	Cd ₄₈₀₀	114.3	-0.30	114.0
121.5	-0.40	Cd ₄₆₇₈	121.9	-0.90	121.0
127.0	-0.10	Li ₄₆₀₃	127.1	+0.20	127.3
148.0	+1.80	Hg ₄₃₅₈	146.2	+2.80	149.0

TABLE X

Camphorcarboxylic Acids in Benzene

$$[\alpha] = \frac{11.40}{\lambda^2 - 0.028}$$

$$\lambda_0 = 1673 \text{ \AA.U.}$$

Dextro Conc. : 4.0000 gm./100 c.c.		Wavelength	[α] _{cal.} (c)	Lævo Conc. : 4.0000 gm./100 c.c.	
[α] _{obs.} (o)	<i>o-c</i>			<i>o'-c</i>	[α] _{obs.} (o')
+27.25°	+0.23°	Li ₆₇₀₃	±27.02°	+0.02°	-27.04
..	..	Cd ₆₄₃₈	29.49
33.00	-0.09	Li ₆₁₀₄	33.09	+0.16	33.25
35.75	+0.03	Na ₅₈₉₃	35.72	-0.12	35.60
37.25	±0.00	Hg ₅₇₈₀	37.25	±0.00	37.25
42.00	-0.19	Hg ₅₄₆₁	42.19	-0.19	42.00
47.00	+0.14	Ag ₅₂₀₉	46.86	+0.14	47.00
49.25	-0.17	Cd ₅₀₈₆	49.42	+0.08	49.50
56.50	+0.18	Cd ₄₈₀₀	56.32	-0.07	56.25
59.50	-0.23	Cd ₄₆₇₈	59.73	+0.02	59.75
62.00	-0.01	Li ₄₆₀₃	62.01	-0.01	62.00
70.75	+0.38	Hg ₄₃₅₈	70.37	+0.13	70.50

TABLE XI

Camphors in Ethyl Alcohol

$$[\alpha] = \frac{21.91}{\lambda^2 - 0.087} - \frac{11.50}{\lambda^2 - 0.037} \quad \lambda_0 = 2950 \text{ \AA.U.}$$

$$\lambda_0' = 1924 \text{ \AA.U.}$$

Dextro Conc. : = 33.5415 gm./100 c.c.		Wavelength	[α] _{cal.} (c)	Lævo Conc. : 33.5423 gm./100 c.c.	
[α] _{obs.} (o)	$\sigma - c$			$\sigma' - c$	[α] _{obs.} (o')
+32.52°	±0.00°	Li ₆₇₀₈	±32.52°	+0.08°	-32.60
36.41	-0.01	Cd ₆₄₃₈	36.42	+0.18	36.60
42.11	-0.34	Li ₆₁₀₄	42.45	-0.25	42.20
46.93	-0.20	Na ₅₈₉₃	47.13	-0.28	46.85
49.87	-0.07	Hg ₅₇₈₀	49.94	-0.08	49.86
59.61	-0.06	Hg ₅₄₆₁	59.67	-0.18	59.49
70.10	+0.28	Ag ₅₂₀₉	69.82	+0.16	69.98
75.98	+0.24	Cd ₅₀₈₆	75.74	+0.36	76.10

TABLE XII

[-Borneol in Benzene

$$[\alpha] = \frac{11.80}{\lambda^2 - 0.03692} \quad \lambda_0 = 1921 \text{ \AA.U.}$$

Conc. = 6.9010 gm./100 c.c.

Wavelength	[α] _{cal.} (c)	[α] _{Obs.} (o)	$\sigma - c$
Li ₆₇₀₈	28.56°	-29.34°	+0.78°
Cd ₆₄₃₈	31.25	31.88	+0.63
Li ₆₁₀₄	35.18	35.13	-0.05
Na ₅₈₉₃	38.03	38.11	+0.08
Hg ₅₇₈₀	39.70	39.70	±0.00
Hg ₅₄₆₁	45.16	45.21	+0.05
Ag ₅₂₀₉	50.35	50.28	-0.07
Cd ₅₀₈₆
Hg ₄₃₅₈	77.09	77.09	±0.00

rotatory power for Li 6708 is glacial acetic acid > chloroform > water > ethyl alcohol > acetone > methyl alcohol > pyridine > benzene. Here acetic acid, chloroform and methyl alcohol do not follow the sequence of their dielectric constants.

TABLE XIII

l-Borneol in Ethyl Alcohol

$$[\alpha] = \frac{11.40}{\lambda^2 - 0.03767} \quad \lambda_0 = 1940 \text{ \AA.U.}$$

Conc. = 10.6015 gm./100 c. c.

Wavelength	$[\alpha]_{\text{cal.}}$ (c)	$[\alpha]_{\text{Obs.}}$ (o)	<i>o</i> - <i>c</i>
Li ₆₇₀₈	27.64°	27.64°	±0.00°
Cd ₆₄₃₈	30.28	30.25	+0.03
Li ₆₁₀₄	33.82	34.04	-0.22
Na ₅₈₉₃	36.42	36.81	-0.39
Hg ₅₇₈₀	38.25	38.46	-0.21
Hg ₅₄₆₁	43.45	43.76	-0.31
Ag ₅₂₀₉	49.24	48.77	+0.47
Cd ₅₀₈₆	51.71	51.58	+0.13
Hg ₄₃₅₈	74.90	74.90	±0.00

In view of the contradictory results which are obtained with different wavelengths as in the above discussion, it becomes necessary for a strict comparison that the effects of dispersion should be eliminated. This elimination is easy and fairly accurate in the case of compounds showing "simple" rotatory dispersion. In the Drude equation, if we make $\lambda^2 - \lambda_0^2 = 1$ square micron, the angle of rotation becomes numerically, though not dimensionally, equal to k_0 , the 'rotation constant'. This value of specific rotation refers to a wavelength not much greater than 10,000 Å.U., in the infra-red. The longest wavelength for which our observations have been made, Li 6708, is not far removed from this wave-length, and an extrapolation to this value where $\lambda = \sqrt{1 + \lambda_0^2}$ is permissible in view of the linear nature of the dispersion equations. Then the value of the rotation constants may be taken as a measure of the absolute rotatory power of the substances at "corresponding" wavelengths. A comparison may then be made of these constants with the dielectric constants of the solvents.

The values of the absolute rotatory power and the dielectric constant are given in Table I. Only glacial acetic acid and chloroform present anomalous behaviour, whereas the other solvents roughly follow the sequence of their dielectric constants.

CASE OF GLACIAL ACETIC ACID

The anomalous behaviour of camphor carboxylic acid in glacial acetic acid may be explained in the following way: It was found in an earlier investigation² that the specific rotation of camphor carboxylic acid in water

increases with concentration. On the electrolytic dissociation hypothesis, the acid at higher concentrations is less dissociated. If the undissociated acid molecule has a higher specific rotation than the acid ion, the specific rotation would rise with concentration. On the basis of this assumption, the increase in specific rotation of camphor carboxylic acid in water at higher concentrations is explained. In an acid medium, the rotation should be higher due to the suppression of ionisation. Camphor carboxylic acid in glacial acetic acid solution shows the highest rotatory power of all the solvents, in conformity with the above assumption.

PHYSICAL IDENTITY OF ENANTIOMERS

The rotatory powers of *d*- and *l*-forms of camphor carboxylic acid are identical in all the solvents examined, and this lends further support to Pasteur's Principle of Molecular Dissymmetry. Out of 187 observations recorded in this paper, in as many as 151 cases, the difference in the numerical values of the specific rotatory power of the optically active and opposite isomers corresponds to an angle of less than 0.01° in the observed angle of rotation and in 30 cases the corresponding angle lies between 0.01° and 0.02° which is within the limits of experimental error allowed in these measurements. In the remaining six cases this difference corresponds to about 0.03° , mostly for Hg violet line which is difficult to read. All these differences are, however, of the nature of casual experimental errors.

ROTATORY DISPERSION EQUATIONS FOR CAMPHORS AND *l*-BORNEOL

The rotatory dispersion of Camphors in alcoholic solution (conc. 33.5415 gm./100 c.c.) has been recorded by Singh and Mahanti in an earlier paper.¹ The dispersion formula is, however, wrongly recorded. We have re-calculated the two-term Drude equation and find it to be

$$[\alpha] = \frac{21.91}{\lambda^2 - 0.087} - \frac{11.50}{\lambda^2 - 0.037}$$

This gives 2 values for the dominant absorption bands at λ 1924 Å.U. and λ 2950 Å.U. One of these at λ 1924 Å.U. has been identified with λ 1912 Å.U. derived from refractive dispersion equation³ and the other at λ 2950 Å.U. corresponds to λ 2874 Å.U. and λ 2890 Å.U. determined from direct absorption measurements by Baly *et al.*⁴ and Hartley⁵ respectively.

The differences between the calculated and observed values of rotatory power of the *d*- and *l*-camphors are shown in Table XI.

In the same paper by Singh and Mahanti the rotatory dispersion of *l*-Borneol in benzene and ethyl alcohol has been recorded, but no dispersion equations had been worked out. We have now calculated the one-term

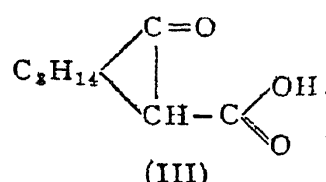
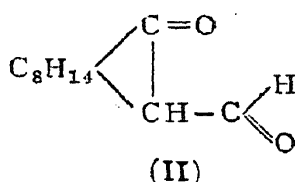
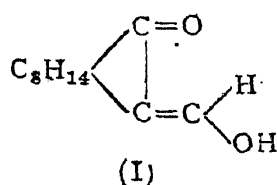
Drude equations which fit the data (Tables XII and XIII). The value of λ_0 the dominant absorption band in alcohol (λ 1940 Å.U.) deduced from the rotatory dispersion equation agrees with that obtained from refractive dispersion data (λ 1962 Å.U.).

CHEMICAL CONSTITUTION AND OPTICAL ROTATORY POWER

The effect of the structure of a molecule on rotatory power is well illustrated by comparing the specific rotation $[\alpha]_{5461}^{35^\circ}$ of the six compounds camphor, borneol, camphor carboxylic acid, iso-nitroso camphor (stable and unstable), camphorquinone and oxymethylenecamphor (Table II). The replacement of a hydrogen atom of the methylene group of camphor (1) by an $-\text{OH}$ group in borneol (2) lowers rotation from 59.6° to 43.45° . In camphor-quinone the methylene group is converted to a keto group producing an ortho diketone in which the two $-\text{C}=\text{O}$ groups are in complete conjugation. This has raised the rotation to a much higher value (165.5°). The introduction of the oximino group $=\text{N}-\text{OH}$ for the two atoms of hydrogen in the methylene group of the camphor molecule as in iso-nitroso camphors, (4) has also brought about a complete conjugation between the keto and the $=\text{N}-\text{OH}$ groups, accompanied by a still larger rise in rotatory power from 59.6° to 241.2° (stable) and to 214.8° (unstable). In the case of camphor carboxylic acid, the conjugation of the keto group with the

$-\text{C}\begin{matrix} \text{O} \\ \diagup \\ \text{OH} \end{matrix}$ group is however broken by two consecutive single bonds, thus $\begin{matrix} \text{C}=\text{O} \\ | \\ \text{CH}-\text{C}=\text{O} \\ | \\ \text{OH} \end{matrix}$. The resulting increase in rotation is accordingly small (59.6° to 72.5°).

Oxymethylene camphor has been represented by formula I



The aldehydic formula II is very similar to that of camphor carboxylic acid III, the only difference being the replacement of $-\text{OH}$ group by a hydrogen atom. On this formulation and on the above-mentioned analogy and comparison of the rotatory power of borneol and camphor, where the replacement of one hydrogen atom for one hydroxy group raises the rotation by about 16° , the value of rotatory power of oxymethylene camphor should be only slightly higher for formula II than that of camphor carboxylic acid, namely 72.5° . But the observed rotatory power of oxymethylene camphor⁶

is the highest of all the compounds given in Table II, namely, 243.35° . This strongly supports formula I for oxymethylene camphor as this shows a complete conjugation between the keto and the ethylenic bonds which is however not the case with formula II. This is in harmony with previous work by one of us⁷ in which oxymethylene camphor was given formula I, but in solution was found to undergo mutarotation with an equilibrium value of $\pm 229.5^\circ$ between the two modifications I and II.

EXPERIMENTAL

Camphorcarboxylic acids, *d*-, *l*-, and *dl*-, were prepared and purified by the method of Bredt.⁸

The rotatory power determinations were carried out in a 2-dcm. jacketed tube at 35°C . The values of the λ_0 calculated from the dispersion formulæ are given in the tables and stated in Å.U.

SUMMARY

1. The rotatory dispersion of *d*- and *l*-camphorcarboxylic acids in 8 solvents is described. The dispersion is simple and obeys the one-term Drude equation.

2. The effect of solvents on the rotatory power is discussed.

3. The effect of constitution on rotatory power of camphorcarboxylic acid is also discussed.

4. The *d*- and *l*-forms give identical rotation within the limits of experimental error and thus support Pasteur's Law of Molecular Dissymmetry.

5. The formula for the complex dispersion of *d*- and *l*-camphors in ethyl alcohol has been recalculated. The simple rotatory dispersion formulæ for *l*-borneol in ethyl alcohol and benzene have also been calculated.

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