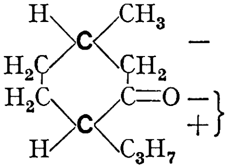
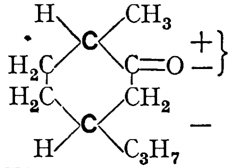
157. *The Rotatory Dispersion of Organic Compounds. Part XXVII. Menthone and Carvomenthone.*

By T. M. Lowry and R. E. Lishmund.

Menthone (I) and carvomenthone (II), purified in Prof. Read's laboratory at St. Andrews, were investigated in order to ascertain whether they would exhibit the same anomaly as camphor (Kuhn and Gore, *Z. physikal. Chem.*, 1931, *B*, **12**, 389) and camphor-β-sulphonic acid (Lowry and French, J., 1932, 2654), *viz.*, a circular dichroism limited to the long-wave-length side of the ketonic absorption band, which was thus shown to be unexpectedly composite.



(I.) *l*-Menthone.



(II.) *l*-Carvomenthone.

Since the two ketones are both liquid, they cannot be purified as rigorously as camphor; hence, the *l*-menthone may contain a little *d*-*iso*menthone and a trace of menthol, and the carvomenthone may contain the *cis*- as well as the *trans*-ketone. There is, however, no reason to think that these impurities would have any marked effect on the general course of the anomalies of rotatory dispersion in the region of absorption. We therefore regard as trustworthy the conclusion that the maximum of circular dichroism of carvomenthone is displaced in the same direction as in camphor and to almost exactly the same extent, *viz.*, 110 Å.U. in the direction of longer wave-lengths.

Measurements of the rotatory dispersion of each ketone were carried right through the absorption band, and the complete loop of anomalous rotatory dispersion was plotted. The induced rotation of the ketonic radical of carvomenthone is, as is usual, opposite in sign to the fixed rotation of the asymmetric carbon atoms; but it is noteworthy that the partial rotation of the ketonic band of menthone is of the same sign as the residual rotation. Since we are still entitled to expect that the induced activity of the ketonic radical will be of opposite sign to that of the asymmetric carbon atom to which it owes its activity, this effect may be attributed (as in the α-halogeno-derivatives of camphor, J., 1925, **127**, 1264) to a high-frequency rotation of opposite sign, associated with another (and in this case a more remote) asymmetric carbon atom. If this attribution is accepted, the signs of the different radicals are as indicated alongside the preceding formulæ. It will be seen that opposite signs are attributed to the asymmetric carbon atoms in menthone and in carvomenthone; but this does not necessarily imply a reversal of configuration, since this effect might easily result from the handing over of the carbonyl radical from one asymmetric carbon atom to the other.

Absorption Spectra.—The molecular extinction coefficients in alcohol and in *cyclo*hexane are plotted in Figs. 1 and 2, and the principal constants of the curves are shown in Table I.

Table I.

Absorption Spectra of Menthone and Carvomenthone.

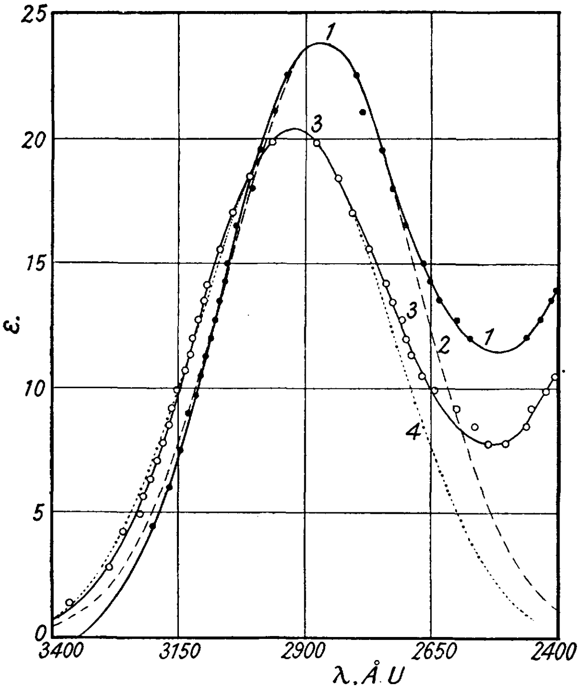
Compound.	Solvent.	Maximum.		Width,	Strength,
		ε.	λ_0.	λ'.	$f \times 10^4$.
Menthone	EtOH	23·8	2867	443	8·3
,,	C_6H_{12}	20·3	2920	448	7·2
Carvomenthone (sample *a*)	EtOH	22·3	2841	351	6·2
,, (,, *b*)	,,	22·3	2840	360	—
,, (,, *b*)	C_6H_{12}	19·5	2886	454	7·1

The absorption spectra of the two isomerides, in spite of their similarity of structure, show definite points of contrast, since the maximum extinction coefficient, and the strength, *f* (which depends on the total area of the band), are slightly greater for menthone than for carvomenthone. This difference, however, is less than that produced by changes of solvent. Thus, the alcoholic solutions are more absorbent by about $\frac{1}{6}$ than those in *cyclo*hexane, in spite of the fact that the formation of an alcoholate would tend to eliminate the ketonic absorption band.

The curve for carvomenthone in alcohol is remarkable for the complete absence of general absorption at wave-lengths down to 2540 Å.U. This feature is due to the exceptional optical purity of sample (*a*); but, since the sample (*b*) used for the measurements of rotatory dispersion (α_D — 11·20, $n = 1{\cdot}4552$) gave the same wave-length and intensity of maximum absorption, and the same half-width (so that the two absorption bands were identical up to and a little beyond the maximum), we think it unlikely that the unknown impurity, to which the general absorption of sample (*b*) must be attributed, would affect the curve of anomalous rotatory dispersion in the region covered by the absorption band.

FIG. 1.

Molecular extinction coefficients of menthone.



1. In alcohol (obs.).
2. ,, ,, (calc. from Lowry and Hudson's equation).
3. In *cyclo*hexane (obs.).
4. ,, ,, (calc., as above).

The absorption curve for the alcoholic solution of carvomenthone which showed no general absorption is very nearly symmetrical on a scale of wave-lengths, like those of the xanthates studied by Lowry and Hudson (*Phil. Trans.*, 1933, *A*, **232**, 117), and can be expressed to a close approximation by the equation $\varepsilon = \varepsilon_{\text{max.}} e^{-(\lambda - \lambda_0)^2/\theta}$ ($\theta = \lambda'/1{\cdot}6651$) which they devised to express the form of absorption curves of this type. The same equation was used to calculate the theoretical values for the other three curves; but, since only one arm was fully developed, in consequence of overlapping by the general absorption on the side of shorter wave-lengths, the symmetry of the curves was not so well established.

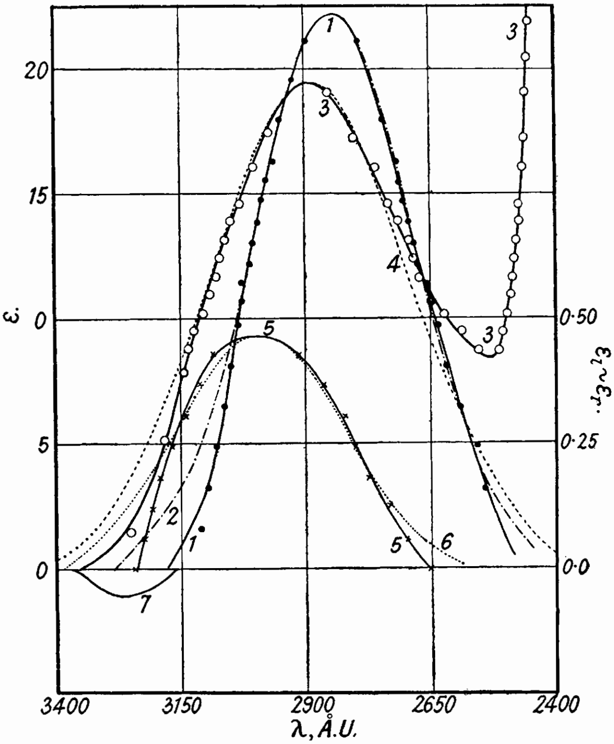
Circular Dichroism.—The circular dichroism of menthone was too small for accurate measurement, but the values for solutions of carvomenthone in *cyclo*hexane are included in

Fig. 2. The maximum of circular dichroism at 2995 Å.U. is displaced by about 110 Å.U. from the maximum of absorption at 2886 Å.U., exactly as in the case of camphor, where it is displaced from 3020 to 2910 Å.U.

The theoretical curve was calculated by means of Lowry and Hudson's equation (*loc. cit.*), the following parameters being used: $\lambda_0 = 2995$ Å.U.; $(\varepsilon_l \sim \varepsilon_r)_{\text{max.}} = 0{\cdot}4675$; $\lambda' = 382{\cdot}1$ Å.U.; $\theta = 229{\cdot}5$ Å.U. The agreement is good on the side of shorter wavelengths, but the experimental data fall off much more rapidly on the side of longer wavelengths. This anomaly can be attributed to a weak circular dichroism of opposite sign, *e.g.*, $\lambda_{\text{max.}} = 3260$ Å.U.; $(\varepsilon_l \sim \varepsilon_r)_{\text{max.}} = 0{\cdot}054$; $\lambda' = 125$ Å.U., similar to that postulated by Hudson, Wolfrom, and Lowry in penta-acetyl μ-glucose (J., **1933**, 1179) and correlated by them with a subsidiary aldehydic absorption band observed by Schou (*Compt. rend.*, 1926, **182**, 965). A weak band of opposite sign in this position is also required in order to eliminate a loop in the residual curve of rotatory dispersion, after allowing for the partial rotation of the principal band.

FIG. 2.

Absorption and circular dichroism of carvomenthone.



1. In alcohol (obs.).
2. ,, ,, (calc., as above).
3. In *cyclo*hexane (obs.).
4. ,, ,, (calc., as above).
5. Circular dichroism (obs.).
6. ,, ,, (calc., as above).
7. ,, ,, (subsidiary component).

Rotatory Dispersion.—The rotatory dispersions of menthone and carvomenthone in the region of absorption are tabulated in Tables II and III and plotted in Figs. 3 and 4, and show the following anomalies:

	Negative maximum.	Reversal.	Positive maximum.
Menthone	$[M] = -242°$ at 3025 Å.U.	None.	$-72°$ at 2712 Å.U.
Carvomenthone	$[M] = -868°$ at 3195 Å.U.	3021 Å.U.	$+1170°$ at 2770 Å.U.

TABLE II.

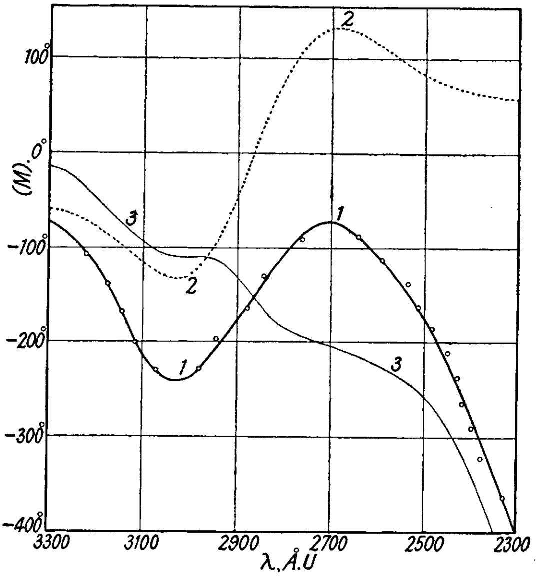
Anomalous Rotatory Dispersion of Menthone at 20° in cyclo*Hexane.*

$c = 0{\cdot}00788$ g./c.c.; $l = 1$ cm.

α (obs.).	[*M*].	λ, Å.U.	α (obs.).	[*M*].	λ, Å.U.	α (obs.).	[*M*].	λ, Å.U.	α (obs.).	[*M*].	λ, Å.U.
0·05°	− 78°	3266	0·175°	−230°	3068	0·075°	− 92°	2762	0·2°	−211°	2450
0·075	−108	3220	0·175	−228	2981	0·075	−89·5	2642	0·225	−237·5	2431
0·1	−139	3175	0·15	−197	2944	0·1	−113	2591	0·25	−265	2420
0·125	−169·5	3144	0·125	−164	2878	0·125	−138·5	2537	0·275	−290·5	2399
0·15	−201	3117	0·1	−130	2844	0·15	−163·5	2517	0·3	−323	2379
						0·175	−185	2485	0·35	−364	2333

FIG. 3.

Rotatory dispersion of menthone.



1. Total rotation (obs.).
2. Partial rotation of >CO group (calc.).
3. Residual rotation (Curve 1 minus Curve 2).

TABLE III.

Anomalous Rotatory Dispersion of Carvomenthone at 20° in cyclo*Hexane.*

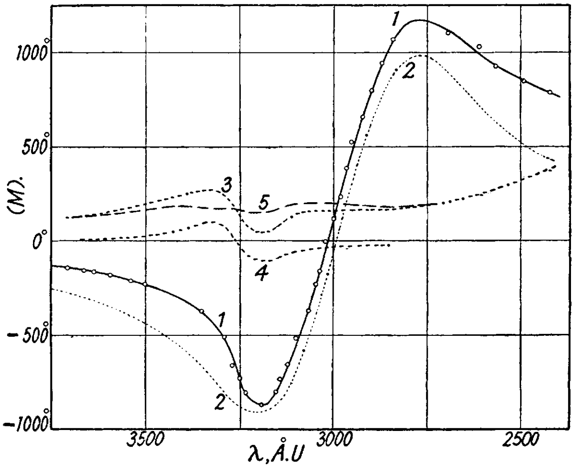
(a) $c = 3{\cdot}23$ g./100 c.c.; $l = 4$ dm.; (b) $c = 1{\cdot}081$ g./100 c.c.; $l = 1$ cm.; (c) $c = 0{\cdot}572$ g./100 c.c.; $l = 1$ cm.

(a).			(b).			(c).		
α (obs.).	[*M*].	λ, Å.U.	α (obs.).	[*M*].	λ, Å.U.	α (obs.).	[*M*].	λ, Å.U.
18°	−208·5°	3541	−0·1°	−156°	3640	0°	0°	3021
15·5	−180	3594	−0·15	−226	3500	0·1	261	2981
13	−150·5	3664	−0·25	−370	3352	0·15	390	2966
12	−139·5	3707	−0·35	−512	3291	0·2	528	2952
10·5	−122	3770	−0·45	−654	3271	0·25	662	2929
9	−104·5	3850	−0·5	−725	3248	0·3	795	2900
8	− 93	3903	−0·55	−796	3235	0·35	940	2873
7	− 82	3982	−0·6	−868	3193	0·4	1070	2843
6·25	− 73	4067	−0·55	−796	3153	0·4	1103	2696
5·5	− 64	4154·5	−0·5	−725	3143	0·35	1030	2612
4	− 47·5	4353	−0·45	−654	3123	0·3	929	2570
3	− 36	4575	−0·35	−512	3100	0·25	850	2492
2	− 24	4940	−0·25	−370	3067	0·2	789	2425
			−0·15	−226	3048			
			−0·1	−156	3037			

It is noteworthy that the curve for menthone, in which the negative anomalous rotation of the carbonyl group is superposed on a negative residual rotation, does not cross the axis, so that the second maximum becomes a minimum. The anomalous partial rotation (calculated from Lowry and Hudson's equation with an arbitrary factor) is exceptionally weak, since the observed range between the two " maxima " is only 170°, as compared with about 2040° for carvomenthone and over 7000° for a solution of camphor in *cyclo*hexane. On the other hand, the residual rotation is exceptionally large, and rises so steeply (from — 14° at 3300 Å.U. to — 400° at 2350 Å.U.) as to indicate the near approach to a highly active absorption band of shorter wave-length. The ripples on the curve are not of any importance, since they may be due merely to the limitations of the theoretical equation.

FIG. 4.

Rotatory dispersion of carvomenthone.



1. Total rotation (obs.).
2. Partial rotation of >CO group (calc.).
3. Residual rotation (Curve 1 minus Curve 2).
4. Subsidiary partial rotation.
5. Residual rotation corrected (Curve 3 minus Curve 4).

The anomalous partial rotation of the ketonic band in carvomenthone was calculated from the circular dichroism by means of Lowry and Hudson's equation; but the residual partial rotation of high frequency showed a ripple, which was eliminated (as in the case of penta-acetyl μ-glucose) by postulating a subsidiary band of opposite sign, giving rise to a small partial rotation with a reversal of sign at 3260 Å.U.

SUMMARY.

(*a*) The maximum of circular dichroism of carvomenthone is displaced by 110 Å.U. in the direction of longer wave-lengths from the maximum of absorption, exactly as in the case of camphor.

(*b*) Menthone and carvomenthone exhibit anomalous rotatory dispersion in the region of absorption. In the latter, a negative anomalous rotation, with a range of about 2000°, is superposed on a positive residual rotation of high frequency; but in the former, a negative anomalous rotation with a range of less than 200° is superposed on a negative residual rotation, which rises steeply with decreasing wave-length, and is evidently composite in character.

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UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, April 3rd,* 1935.]