397. *The Rotatory Dispersive Power of Organic Compounds. Part XX. Rotatory Dispersion and Circular Dichroism of Camphor-β-sulphonic Acid in the Region of Absorption.*

By T. MARTIN LOWRY and (MISS) HELEN S. FRENCH.

THE rotatory dispersion of camphor in the region of absorption (Lowry and Gore, *Proc. Roy. Soc.*, 1932, *A*, **135**, 13) shows the following maxima :

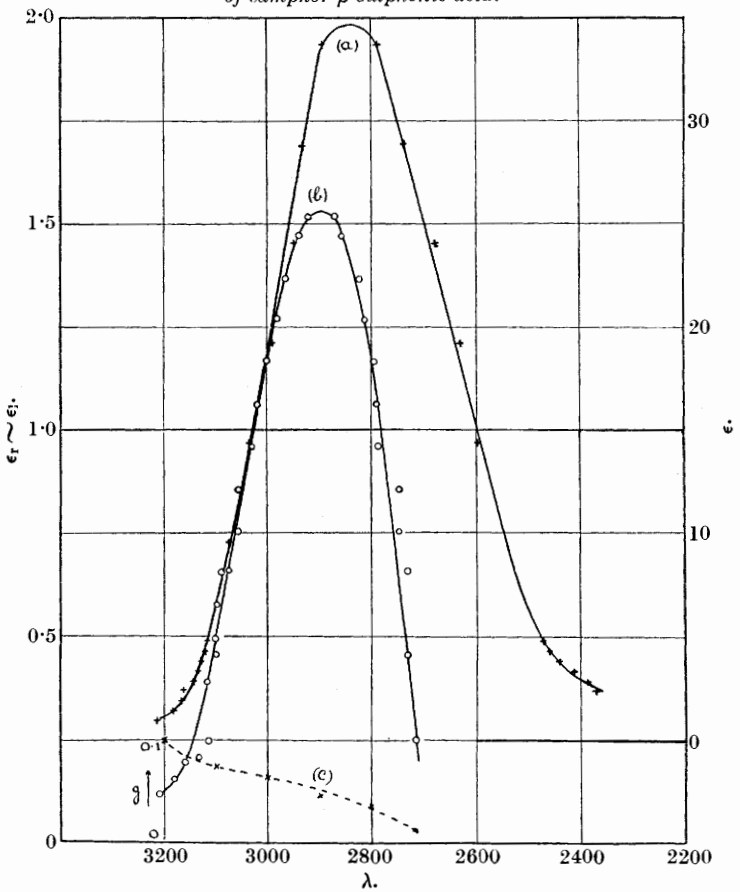
Camphor vapour at 180°.	*Solution in* cyclo*hexane at* 20°.
[α] = + 2000° at 3200 Å.U.	[α] = + 2600° at 3200 Å.U.
− 1860° at 2800 Å.U.	− 2100° at 2720 Å.U.

The positive maximum is exceptionally sharp, but the negative maximum is of the usual smoothly-rounded form. Solutions of camphor in hexane (Kuhn and Gore, *Z. physikal. Chem.*, 1931, **12**, 389) also show the anomaly that the optical activity of the ketonic band, instead of being distributed uniformly throughout the region of selective absorption, is concentrated in the part of the band nearest to the visible spectrum. Thus the circular dichroism reaches a maximum at about 3020 Å.U., whereas the maximum of ordinary

absorption is not reached until the wave-length has fallen to a value 2910 Å.U., beyond which the circular dichroism soon becomes negligible. The familiar ketonic band is therefore shown, by measurements of circular dichroism, to be composite in character,

FIG. 1.

(a) *Molecular extinction-coefficients,* (b) *circular dichroism,* (c) *optical anisotropy of camphor-β-sulphonic acid.*



including a weak component of longer wave-length, which is strongly dichroic towards circularly polarised light, and a strong component of shorter wave-length which is almost entirely inactive.

The present experiments show that precisely similar phenomena appear in aqueous solutions of camphor-β-sulphonic acid. Thus, the curve of rotatory dispersion rises rapidly to a positive maximum $[\alpha] = 2000°$ at 3090 Å.U., and falls to a negative maximum $[\alpha] =$

— 2450° at 2690 Å.U., with a reversal of sign at 2950 Å.U. The ordinary absorption rises to a maximum, $\varepsilon = 35$ at 2840 Å.U., but the circular dichroism (measured with a Fresnel rhomb of silica instead of with a water rhomb) has already reached a maximum, $\varepsilon_r \sim \varepsilon_l = 1{\cdot}535$, at 2900 Å.U. The steepness of the curve of circular dichroism on the side of shorter wave-lengths suggested that the selective absorption at higher frequencies might perhaps cover a weak circular dichroism of opposite sign (like the second absorption band of the xanthates), but no negative values could be detected in the present experiments. The "optical anisotropy" $g = (\varepsilon_r \sim \varepsilon_l)/\varepsilon$, which in normal cases is proportional to the frequency, falls towards a zero value at about 2700 Å.U., since the circular dichroism disappears at this wave-length.

Rotatory Dispersion of Camphor-β-sulphonic Acid in Aqueous Solutions at 20° (Photographic Readings).

$l = 10$ cm.; $c = 0{\cdot}11854$—$0{\cdot}0004742$ g./c.c.

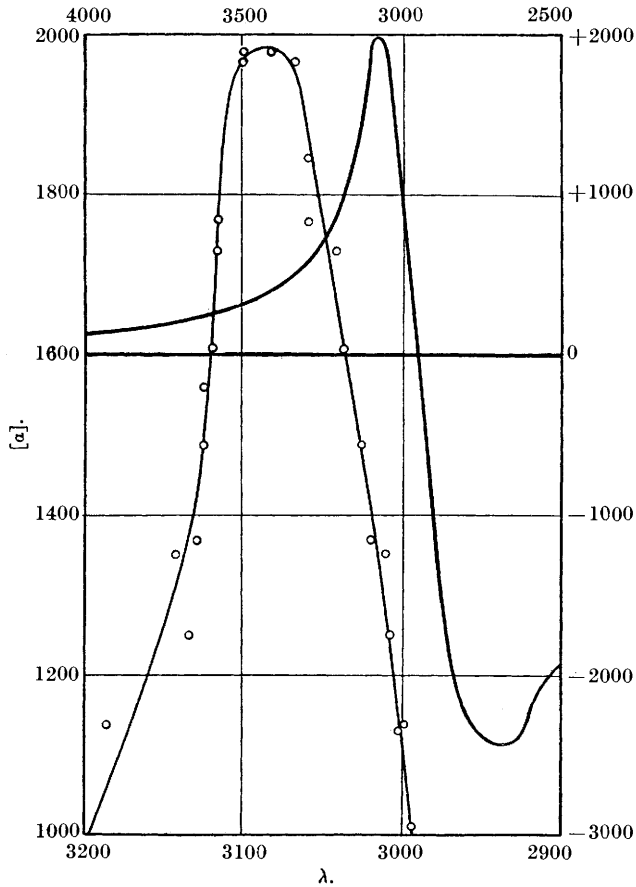
(*a*) Positive rotations.						(*b*) Negative rotations.	
[*a*].	λ.	[*a*].	λ.	[*a*].	λ.	[*a*].	λ.
82·97°	4176	479·3°	3352	837·0°	3222	126·53°	2941
84·35	*2950*	483·7	3348	928·0	*2994*	337·4	2937
99·86	4045	506·0	*2973*	1005·0	3203	365·6	2912
116·73	3966	521·6	3324	1010·3	*2994*	506·1	2929
118·08	*2965*	530·1	3317	1130·3	*3003*	548·2	2923
142·04	3872	539·7	3317	1138·3	3185	646·9	2923
158·87	3805	547·0	3315		*2999*	787·3	2912
167·34	3788	563·9	3306	1250·6	3134	928·0	2907
184·20	3758	583·8	3298		*3008*	1068·5	2904
201·05	3695	589·1	3306	1349·6	3143	1772·8	2846
202·40	*2941*	597·4	3298		*3011*	1912·5	*2490*
209·5	3680	605·7	3292	1371·0	3129	1990·0	*2529*
226·35	3640	622·7	3292		*3021*	2053·0	2844
243·2	3603	639·6	3287	1491·0	3126		*2563*
251·65	3595	656·4	3280		*3026*	2074·5	2864
268·55	3565	668·1	3254	1560·4	3126		*2598*
285·4	3530	673·3	3271		*3045*	2159·0	*2599*
293·8	3530	689·3	3248	1611·4	3119	2193·5	2795
295·2	*2960*	690·3	3268		*3037*		*2586*
310·65	3490	707·0	3266	1732·0	3117	2334·0	2762
327·6	3485	710·3	3244		*3042*		*2631*
344·4	3466	717·0	*2984*	1771·4	3117	2412·0	2756
361·25	3447	724·0	3258		*3059*		*2631*
378·2	3445	731·3	3236	1851·9	3101	2474·6	—
395·0	3424	740·8	3254		*3059*		
412·0	3413	752·5	3233	1972	3101		
419·0	3407	790·3	3228		*3067*		
445·5	3397	794·7	3228	1982	3100		
462·5	3380	815·7	3226		*3084*		

(i) The *molecular extinction coefficients*, ε, for 4-cm. columns of concentrations 0·0519 and 0·00519*M* at room temperature are shown in Fig. 1. (ii) The *circular dichroism*, $\varepsilon_r \sim \varepsilon_l$, of 1-cm. columns of

0·3737, 0·1495, and 0·0299*M* concentrations at room temperature, and the *optical anisotropy*, $g = (\varepsilon_r \sim \varepsilon_l)/\varepsilon$, are plotted in the same diagram. (iii) Values for the *optical rotatory power* of camphor-sulphonic acid, in the region of complete transparency, have already been recorded by Richards and Lowry (J., 1925, **127**, 1503). A

FIG. 2.

Rotatory dispersion of camphor-β-sulphonic acid. (The maximum is shown on a larger scale, see left-hand and bottom legends.)



new series of photographic readings for more dilute solutions is se out in detail in the table, where the wave-lengths of the lines of th iron arc corresponding to a given rotation are recorded, the numbe in italics being those of lines on the short wave-length side of maximum. These data are plotted in Fig. 2 as a complete curve c rotatory dispersion from 4000 to 2500 Å.U.; the specific rotatior

over the range 3200—3000 Å.U., which includes the positive maximum, are also shown on a larger scale in the same diagram. As in the case of camphor, this maximum could be drawn with a narrow steep-sided peak, but this is probably an accidental sequel to the discontinuity of the spectrum of the iron arc, as a result of which two or three successive extinctions may be assigned to the same line.

Summary.

Aqueous solutions of camphor-β-sulphonic acid show a maximum absorption $\varepsilon = 35$ at 2840 Å.U., and a maximum circular dichroism $\varepsilon_r \sim \varepsilon_l = 1{\cdot}535$ at 2900 Å.U. The rotatory dispersion shows a positive maximum $[\alpha] = 2000°$ at 3090 Å.U., a reversal of sign at 2950 Å.U., and a negative maximum $[\alpha] = -2450°$ at 2690 Å.U.

LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE UNIVERSITY. [*Received, July 13th,* 1932.]