

### 190. *The Rotatory Dispersion and Circular Dichroism of Santonide and Parasantonide in the Ultra-violet.*

By STOTHERD MITCHELL and KONRAD SCHWARZWALD.

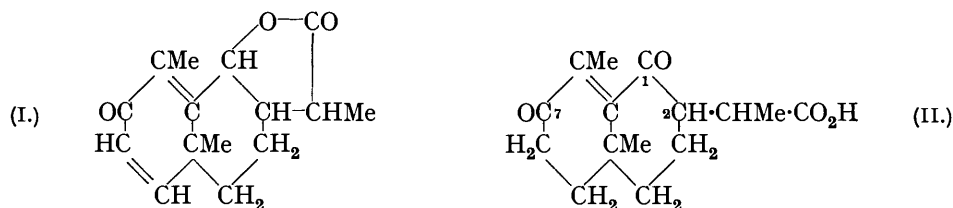
Both santonide and parasantonide show the Cotton effect associated with a strong ketonic band which in alcoholic solution has its head at about 3000 Å. For santonide  $\epsilon_{\text{max.}} = 1000$  and for parasantonide  $\epsilon_{\text{max.}} = 1170$ , but despite these large values it has been possible to take rotation readings right through the band in each case. The specific rotation of santonide reaches  $+25,500^\circ$  on the long-wave side of the band, and  $-31,000^\circ$  on the other side. For parasantonide the corresponding values are even larger, being  $+32,000^\circ$  and  $-35,000^\circ$ , respectively. The latter values are remarkable, as they are about ten times the normal, and about three times the value ( $+11,000^\circ$ ) obtained by Kuhn and Biller (*Z. physikal. Chem.*, 1935, B, 29, 23) for the dimethylamide of methoxyphenylacetic acid, which has the largest specific rotation hitherto measured in homogeneous solution.

The maxima of circular dichroism ( $\epsilon_l - \epsilon_r$ ) are also abnormally large, but the anisotropy factors  $(\epsilon_l - \epsilon_r)/\epsilon$  have normal values which average 0.030 and 0.038 for santonide and parasantonide, respectively.

NASINI (*Atti R. Accad. Lincei*, 1881, 3A, 13, 129) investigated visually the rotatory dispersion of a number of santonine derivatives. Of these, santonide and parasantonide were considered remarkable at the time, for their specific rotations in alcohol and chloroform had values lying between  $2000^\circ$  and  $3000^\circ$  for violet light. Recent work on the Cotton effect has made us familiar with specific rotations of the order of  $3000^\circ$  in the neighbourhood of absorption bands, and so we thought it probable that an extension of the rotatory dispersion curves of santonide and parasantonide into the near ultra-violet might furnish further examples of this interesting effect.

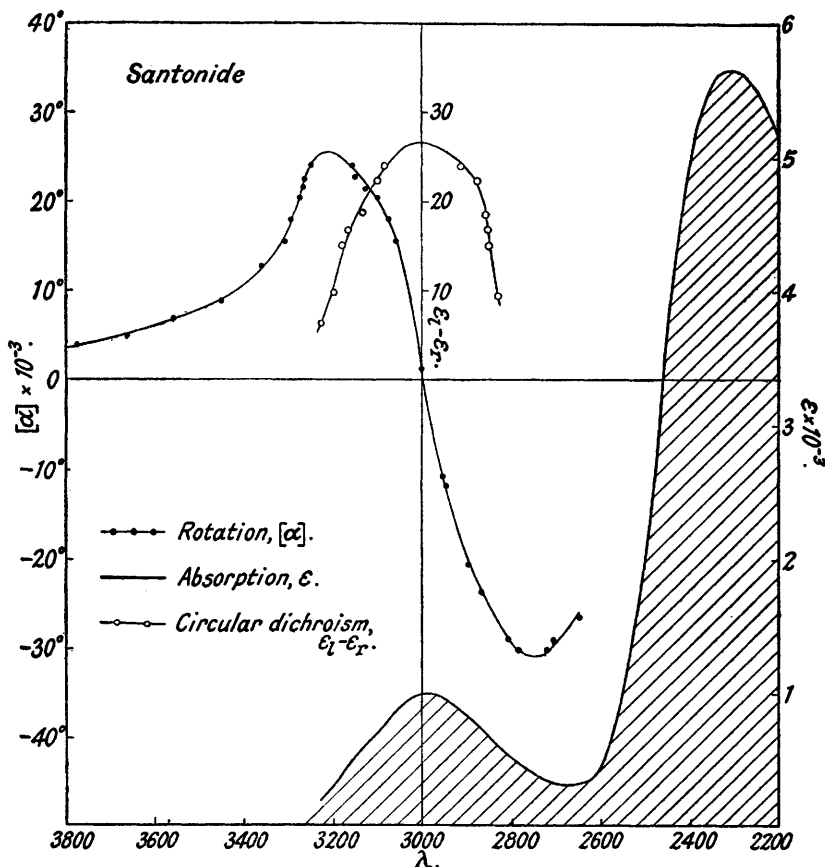
According to Clemo, Haworth, and Walton (J., 1930, 1110), santonine has the structure (I). The lactone ring is readily opened by warming with dilute alkali solution, but after prolonged boiling santononic acid (II) can be isolated (cf. Cannizzaro and Sestini, *Gazzetta*,

1873, 3, 241; Abkin and Medvedev, *J. Gen. Chem. Russia*, 1934, 4, 1407; *A*, 1935, 755). Santonide is prepared from (II) by refluxing with acetic acid, distilling off the latter, and



heating the residue to 180°. For parasantonide the procedure is similar, but the final heating is carried out at 260–300° (Cannizzaro and Valente, *Gazzetta*, 1878, 8, 315).

FIG. 1.

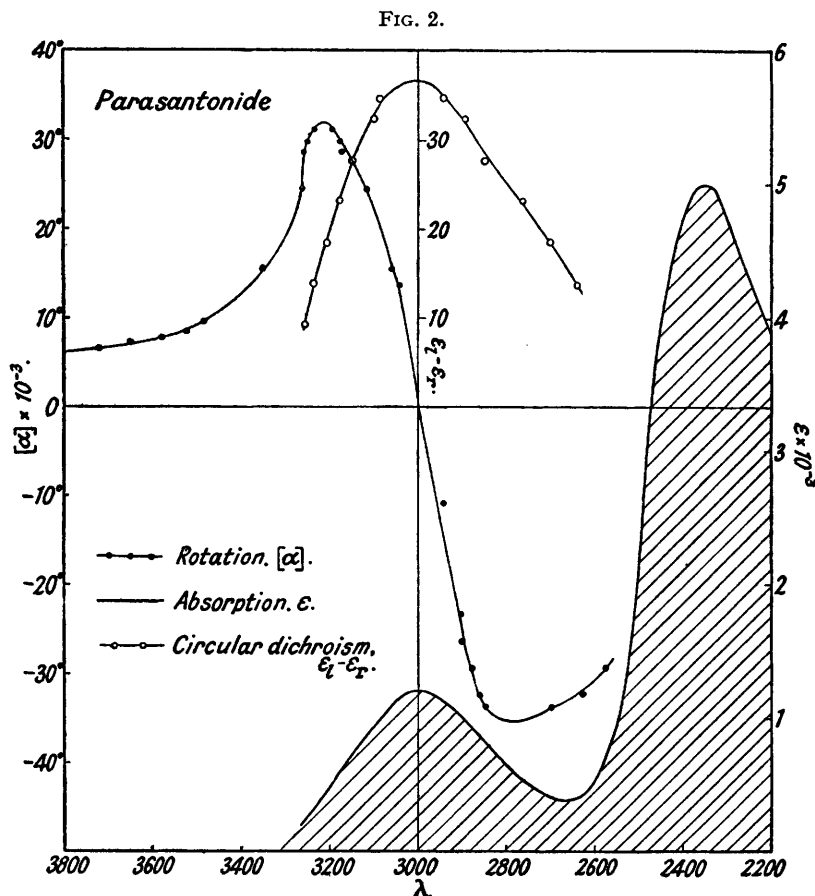


Santonide (m. p. 127·5°) and parasantonide (m. p. 110·5°) are isomeric keto-lactones ( $C_{15}H_{18}O_3$ ) whose structure has not yet been fully established, but it seems probable that the lactone ring in these compounds is formed, not between the carbon atoms 1 and 2 as in santonine, but between the carbon atoms 7 and 2.

*Absorption Spectra.*—We examined the absorption spectra of santonide and parasantonide with a Hilger sector spectrophotometer, using alcohol as solvent and 1-cm. tubes. In each case two absorption bands were found. Fig. 1 shows the molecular extinction coefficient,  $\epsilon$ , plotted against wave-length,  $\lambda$ , for santonide. For the smaller band a solution containing 0·0340 g./100 c.c. was used, and for the larger band 0·0069 g./100 c.c. For the parasantonide (Fig. 2) the concentrations were 0·0323 and 0·0057 g./100 c.c., respectively. The first band is weaker in santonide, and the second in parasantonide.

There is little doubt that the first band in each case is a ketonic band. The second one appears to be due to the lactone ring, as it is not found in parasantonide acid (produced by opening the lactone ring of parasantonide). Further, the ketonic band in parasantonide is much stronger than in this acid (for which  $\epsilon_{\max.} \approx 40$ ), so that we must attribute this increase in strength, and the remarkable optical properties associated with it, to the influence of the lactone ring. In santonide also this ring must be regarded as the dominating factor.

*Rotatory Dispersion.*—We have been able to obtain rotatory dispersion data for both santonide and parasantonide right through the first band, but in each case the second band is too intense to permit of readings being taken beyond about 2600 Å. Our measure-



ments were made with the ultra-violet polarimeter previously described (Mitchell and Gordon, J., 1936, 853).

Carnelutti and Nasini (*Gazzetta*, 1880, 10, 529) observed that when a solution of parasantonide in chloroform was exposed to sunlight for some time the rotation gradually diminished. We found that this also occurred when alcoholic solutions of santonide and parasantonide were irradiated with light from our iron arc. As long exposures (up to 1 hour) were necessary when examining the rotations in the neighbourhood of the negative maxima, we used a tube through which fresh solution was allowed to flow slowly.

The rotation data are in Table I, and in the diagrams the specific rotation,  $[\alpha]$ , is plotted against wave-length,  $\lambda$ . The points of interest in the curves may be summarised as follows:

	Positive maximum.	Reversal.	Negative maximum.
Santonide $[\alpha]$	$+25,500^\circ$ at 3210 Å.	3000 Å.	$-31,000^\circ$ at 2750 Å.
Parasantonide $[\alpha]$	$+32,000^\circ$ at 3210 Å.	3000 Å.	$-35,000^\circ$ at 2750 Å.

*Circular Dichroism.*—For measuring ellipticities, a fused-silica Fresnel rhomb was inserted after the polariser of the ultra-violet polarimeter, and different settings were given to the polariser. The complete data are in Table II. The values of  $\epsilon$  shown in col. 4 of each part of the table were read off from the absorption curves for the required wave-lengths. The last column in each case contains the anisotropy factor,\* ( $\epsilon_l - \epsilon_r$ )/ $\epsilon$ .

In the middle of a simple band this factor remains practically constant, but the values in Table II are not constant. The maximum at  $\lambda = 3178$  for santonide indicates the presence of a subsidiary band which is just detectable from the absorption curve but is more evident from the circular dichroism curve (Fig. 1). The case of parasantonide is more complicated. The high values of the anisotropy factor for the longer wave-lengths suggest a subsidiary band similar to that of santonide. In addition, the maximum between  $\lambda = 2762$  and  $2706$  [Table II (ii), col. 5] points to the presence of another component with which is associated a considerable broadening of the circular dichroism curve on the short-wave side (Fig. 2) and of the negative loop of the rotatory dispersion curve.

In view of the complex nature of the circular dichroism curves we have not included any calculation of the rotatory dispersion curves from the circular dichroism data.

TABLE I.

(i) *Rotatory Dispersion of Santonide in Alcohol.*Solutions: (a) 0.4030; (b) 0.0416; (c) 0.0340 g./100 c.c.;  $l = 1$  cm.;  $t = 17^\circ$ .

$\lambda$ .	a.	[ $\alpha$ ].	$\lambda$ .	a.	[ $\alpha$ ].	$\lambda$ .	a.	[ $\alpha$ ].
Solution (a).								
3924	+1.20°	+ 2,978°	3660	+2.00°	+ 4,963°	3451	+3.60°	+ 8,933°
3776	+1.60	+ 3,970	3555	+2.80	+ 6,949	3360	+5.20	+12,900
Solution (b).								
3307	+0.65	+15,630	3158	+1.00	+24,040	3000	+0.05	+ 1,230
3292	+0.75	+18,030	3148	+0.95	+22,830	2957	-0.45	-10,820
3274	+0.85	+20,430	3126	+0.90	+21,630	2807	-1.20	-28,850
3263	+0.90	+21,630	3100	+0.85	+20,430	2782	-1.25	-30,050
3262	+0.95	+22,830	3075	+0.75	+18,030	2719	-1.25	-30,050
3248	+1.00	+24,040	3059	+0.65	+15,630	2706	-1.20	-28,850
Solution (c).								
2945	-0.40	-11,770	2864	-0.80	-23,540	2644	-0.90	-26,470
2895	-0.70	-20,590						

(ii) *Rotatory Dispersion of Parasantonide in Alcohol.*Solutions: (d) 0.3232; (e) 0.0453; (f) 0.0324 g./100 c.c.;  $l = 1$  cm.;  $t = 17^\circ$ .

$\lambda$ .	a.	[ $\alpha$ ].	$\lambda$ .	a.	[ $\alpha$ ].	$\lambda$ .	a.	[ $\alpha$ ].
Solution (d).								
4062	+1.30	+ 4,022	3719	+2.10	+ 6,497	3521	+2.70	+ 8,354
4034	+1.50	+ 4,641	3647	+2.30	+ 7,116	3485	+3.10	+ 9,592
3920	+1.70	+ 5,260	3575	+2.50	+ 7,734			
Solution (e).								
3350	+0.70	+15,550	3234	+1.40	+31,090	3172	+1.30	+28,870
3262	+1.10	+24,430	3193	+1.40	+31,090	3117	+1.10	+24,430
3257	+1.30	+28,870	3178	+1.35	+29,980	3059	+0.70	+15,550
3248	+1.35	+29,980						
Solution (f).								
3042	+0.45	+13,890	2878	-0.95	-29,320	2699	-1.10	-33,950
2941	-0.35	-10,800	2859	-1.05	-32,400	2631	-1.05	-32,400
2902	-0.75	-23,150	2846	-1.10	-33,950	2575	-0.95	-29,320
2899	-0.85	-26,230						

\* The name "anisotropy factor" was introduced by Kuhn and Braun (*Z. physikal. Chem.*, 1930, B, 8, 445). Lowry and Hudson (*Phil. Trans.*, 1933, A, 232, 117) objected to it and called the ratio the "dissymmetry factor." Later, Kuhn and Biller (*Z. physikal. Chem.*, 1935, B, 29, 9), while admitting that their term was not an ideal name, showed that it is preferable to Lowry and Hudson's.

TABLE II.

(i) *Circular Dichroism of Santonide in Alcohol.*Concn., 0.0416 g./100 c.c.;  $l = 1$  cm.;  $t = 17^\circ$ .

$\lambda$ .	Ellip- ticity.	$\epsilon_1 - \epsilon_2$ .	$\epsilon$ .	$(\epsilon_1 - \epsilon_2)/\epsilon$ .	$\lambda$ .	Ellip- ticity.	$\epsilon_1 - \epsilon_2$ .	$\epsilon$ .	$(\epsilon_1 - \epsilon_2)/\epsilon$ .
3222	0.35°	6.3	200	0.032	2912	1.35°	24.2	861	0.028
3197	0.55	9.9	310	0.032	2874	1.25	22.4	760	0.030
3178	0.85	15.2	405	0.038	2859	1.05	18.8	705	0.027
3162	0.95	17.0	472	0.035	2852	0.95	17.0	680	0.025
3134	1.05	18.8	565	0.033	2846	0.85	15.2	660	0.023
3100	1.25	22.4	670	0.033	2828	0.55	9.9	590	0.017
3083	1.35	24.2	755	0.032					

(ii) *Circular Dichroism of Parasantonide in Alcohol.*Concn., 0.0323 g./100 c.c.;  $l = 1$  cm.;  $t = 17^\circ$ .

3257	0.40	9.2	—	—	2941	1.50	34.6	1140	0.030
3234	0.60	13.9	280	0.050	2892	1.40	32.3	975	0.033
3205	0.80	18.5	410	0.045	2846	1.20	27.7	820	0.034
3175	1.00	23.1	610	0.038	2762	1.00	23.1	560	0.041
3148	1.20	27.7	735	0.038	2706	0.80	18.5	439	0.042
3100	1.40	32.3	885	0.037	2642	0.60	13.9	382	0.036
3091	1.50	34.6	935	0.037					

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UNIVERSITY OF GLASGOW.

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