133. *On the Suitability of Parasantonide for Asymmetric Photolysis.*

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Parasantonide has been photolysed (in alcoholic solution) with mercury lines lying within each of its two ultra-violet absorption bands, and quantum efficiencies of 0·85 (for $\lambda = 3132$—2895 A.) and 0·40 (for $\lambda = 2650$—2537 A.) have been obtained. From these results and from absorption and rotatory-dispersion measurements made with irradiated solutions, it is concluded that racemic parasantonide would fulfil the conditions necessary for asymmetric photochemical work with wave-lengths in the neighbourhood of 3000 A.

THE keto-lactones known as santonide and parasantonide have similar absorption curves with well-defined maxima in the ultra-violet at about 3000 A. and 2350 A., respectively. Mitchell

and Schwarzwald (*J.*, 1939, 889) investigated the Cotton phenomena associated in each case with the first maximum and found normal anisotropy factors but exceptionally large specific rotations, those of parasantonide being the largest hitherto recorded. In the course of these experiments, a decrease in rotation was observed when solutions of both substances were exposed to ultra-violet light, so it was thought that they might be useful for the study of asymmetric photolysis if available in the racemic form. The *r*-santonin required for preparing them in this form appeared to be inaccessible at the time, but the recent work of Paranjape, Phalnikar, Bhide, and Nargund (*Rasayanam*, 1943, 1, 233) has indicated the possibility of obtaining it by synthesis. Before embarking on synthetic work, however, we have carried out some further experiments with *d*-parasantonide in order to determine to what extent it satisfies the photochemical conditions necessary for asymmetric photolysis, which may be summarised as (1) a quantum efficiency ≈ 1 with the absence of chain and dark reactions, and (2) destruction (by the light) of the asymmetric centre producing the Cotton effect.

Preliminary Experiments.—Alcoholic solutions of parasantonide were first exposed in fused-silica tubes to the full radiation from a mercury-vapour lamp. During irradiation there was no evolution of gas, nor was there any absorption of atmospheric oxygen. The change in rotation (α_D) with time of irradiation was then studied, and the results are given in Table I, where c denotes the original concentration of parasantonide in g./100 ml. of alcoholic solution, and the other symbols have their usual significance. When wave-lengths below 2800 A. (*i.e.*, beyond the first band) were cut off by placing a sheet of mica in front of the reaction tube the final rotation remained positive, but when wave-lengths within the first band were removed with a chlorine filter the residual rotation became negative.

TABLE I.

α_D *for solutions during irradiation.*

With mica inserted : $c = 3.040$ g./100 ml.; $l = 0.75$ dm.; $t = 17°$.

α_D	$+18.79°$	$+10.72°$	$+6.78°$	$+3.18°$	$+2.04°$	$+1.68°$
Time (hours)	0	10.5	18.5	33.5	48	62.5
α_D	$+1.54°$	$+1.48°$	$+1.44°$	$+1.30°$	$+1.28°$	$+1.28°$
Time	77	92	106.5	135.5	150	165

With chlorine filter inserted : $c = 1.740$ g./100 ml.; $l = 0.75$ dm.; $t = 17°$.

α_D	$+10.96°$	$+8.58°$	$+6.73°$	$+3.70°$	$+1.68°$	$+0.30°$
Time (hours)	0	8	16	32	46	57
α_D	$-0.52°$	$-1.92°$	$-2.60°$	$-3.02°$	$-3.18°$	$-3.18°$
Time	65	89	109	133	149	165

Periods of irradiation up to about 16 hours were employed in these experiments. The solutions were then left in the dark overnight and sometimes for longer periods. Absence of dark reactions was established by frequently repeating readings before restarting the irradiation.

Quantum Efficiencies.—Measurements of γ were made with groups of mercury lines within each of the two absorption bands of parasantonide. With layers of solution 1 cm. thick and of the same concentrations as given in Table I, complete absorption was achieved by using a nickel–cobalt filter together with mica for $\lambda = 3132$—2895 A. and the chlorine filter for $\lambda = 2650$—2537 A. The amounts of photochemical decomposition were determined polarimetrically, and energy measurements were made with a large-surface Moll thermopile and galvanometer calibrated against a Hefner candle in the usual way (cf. Gerlach, *Physikal. Z.*, 1913, 14, 577). The results are set out in Table II, where λ is the approximate optical centre of the wave-band used for irradiation, c is the initial concentration of parasantonide in g./100 ml. of alcoholic solution, α is the initial rotation, α_n the rotation after exposure for time t_n, and α_∞ the final rotation after prolonged exposure, all rotations being measured at room temperature (17°) with sodium light (5893 A.) and $l = 0.75$ dm.

Let α_p be the rotation due to unchanged parasantonide after time t_n; then

$$\alpha_p = \alpha(\alpha_n - \alpha_\infty)/(\alpha - \alpha_\infty)$$

Hence, concentration of parasantonide after time $t_n = 100\alpha_p/l[\alpha] = c_n$ (in g./100 ml. solution); and number of g.-mols. decomposed $= (c - c_n) \times v/100M$, where v = volume of cell (7.24 ml.) and M is the molecular weight of parasantonide (246). The quantum efficiency γ is given by $\gamma = [(\text{g.-mols. decomposed})/(\text{cals. absorbed})] \times [(2.847 \times 10^8)/\lambda]$. The second value for γ (0.40) although smaller than the first (0.85) is still appreciable and, in order to avoid loss of parasantonide, it will be advisable to cut off the shorter wave-lengths when experiments with

TABLE II.

λ, A.	t_n mins.	c.	a.	a_n.	a_∞.	c_n.	G.-mols. decomposed.	Cals. absorbed.	γ.
3000	660	3·040	18·79°	17·08°	1·28°	2·744	$8·651 \times 10^{-5}$	9·69	0·85
2550	1110	1·740	10·96	10·02	−3·18	1·624	$3·396 \times 10^{-5}$	9·42	0·40

circularly polarised light are carried out. This precaution will also prevent any circular dichroism which may be associated with the second band from being effective.

FIG. 1.
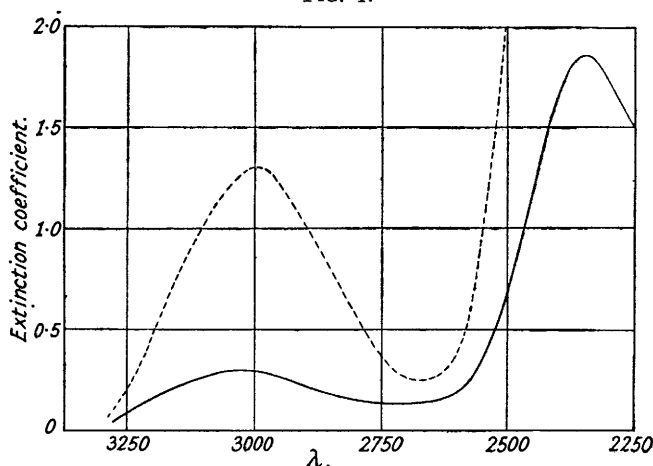
Absorption and Rotatory Dispersion Measurements.—Absorption and rotatory-dispersion curves were next constructed in order to study the effect of irradiation (by wave-lengths in the neighbourhood of 3000 A.) on the absorbing centre with which the Cotton effect in parasantonide is associated. Since we were unsuccessful in our attempts to isolate the products of photolysis in a crystalline state. we used irradiated solutions for this work.

Fig. 1 shows absorption curves drawn from readings taken with a Spekker ultra-violet spectrophotometer using 1-cm. cells. The broken curve was obtained with a non-irradiated

FIG. 2.
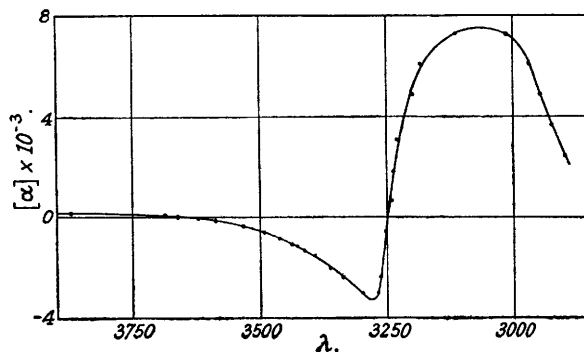
solution of parasantonide containing 0·03 g./100 ml. The solution after prolonged irradiation through mica (Table I) was diluted to correspond with this concentration and gave the continuous curve. It will be seen that the first band (max. 3000 A.), although much weakened, has not been completely destroyed by irradiation. The second band with its head at 2350 A. (not shown in the broken curve) is also present in a modified form.

Rotatory-dispersion measurements were made at room temperature (17°) with alcoholic solutions which had been irradiated through mica until α_D had become constant. Visual readings were taken with a Hilger polarimeter illuminated with light from a 100-c.p. Pointolite lamp after it had passed through a Zeiss–Winkel monochromator. For the photographic

readings we used the ultra-violet polarimeter described by Mitchell and Gordon (*J.*, 1936, 855) but substituted a Bellingham and Stanley polariser (half-shadow angle 6°) for the one previously employed. Table III contains the results. Specific rotations have been calculated (assuming the concentration *c* to be that of parasantonide before irradiation) to facilitate comparison with the values for non-irradiated parasantonide obtained by Mitchell and Schwarzwald (*loc. cit.*). In Fig. 2 [α] is plotted against λ.

TABLE III.

Rotatory-dispersion data for solutions after prolonged irradiation through mica.

Solutions : (a) $c = 1.650$; (b) $c = 0.165$; (c) $c = 0.0825$ g./100 ml.

Solution (a) : $l = 0.75$ dm.

Visual readings :

λ.	α.	[α].	λ.	α.	[α].
7000	+0·41°	+ 33·1°	5500	+0·77°	+ 62·2°
6500	+0·52	+ 42·0	5000	+0·94	+ 76·0
5900	+0·64	+ 51·7	4750	+1·10	+ 88·9

Photographic readings :

λ.	α.	[α].	λ.	α.	[α].
3870	+0·80	+ 64·6	3620	−1·00	− 80·8
3685	+0·40	+ 32·3	3585	−2·00	− 161·6
3660	0·00	0·0	3530	−4·00	− 323·2

Solution (a) : $l = 0.1$ dm.

3490	−1·00	− 606·0	3410	−2·20	−1333
3460	−1·40	− 848·3	3390	−2·60	−1576
3435	−1·80	−1091	3360	−3·40	−2061

Solution (b) : $l = 0.1$ dm.

3320	−0·40	−2425	3250	−0·10	− 606·0
3295	−0·50	−3031	3240	+0·10	+ 606·0
3265	−0·50	−3031	3235	+0·30	+1819
3260	−0·40	−2425	3230	+0·50	+3031

Solution (c) : $l = 0.1$ dm.

3195	+0·40	+4849	2965	+0·50	+6060
3170	+0·50	+6060	2945	+0·40	+4849
3110	+0·60	+7273	2925	+0·30	+3637
3010	+0·60	+7273	2900	+0·20	+2425

Significance of the Results.—The results obtained by irradiation with wave-lengths within the first band (max. 3000 A.) allow us to conclude that racemic parasantonide would be suitable for asymmetric photochemical work. Absence of any chain reaction is shown by $\gamma = 0.85$, and this value is sufficiently close to unity to make asymmetric photolysis a practical proposition, particularly as there is no dark reaction. Some loss of light would be caused, however, by the residual absorption (Fig. 1) which would act as an internal filter. The fall in rotation (α_D) from 18·79° to 1·28° (Table I) suggests that the Cotton effect associated with the first band in parasantonide has been destroyed by the irradiation. This is confirmed by the rotatory dispersion curve (Fig. 2). A " reversed " Cotton effect is now present in which the curve crosses the axis of zero rotation at 3250 A., not at 3000 A. as in parasantonide. Some negative ellipticity has also been detected in the neighbourhood of 3250 A.

EXPERIMENTAL.

Preparation of Parasantonide.—Santonin was first converted into santonic acid as described by Abkin and Medvedev (*J. Gen. Chem. Russia*, 1934, **4**, 1407; *A.*, 1935, 755). Cannizzaro and Valente's method (*Gazzetta*, 1878, **8**, 315) of preparing parasantonide from santonic acid was slightly modified. Santonic acid (10 g.) was refluxed with glacial acetic acid (50 ml.) for 5 hours. The solution was then treated in 5 portions, the first of which was transferred to a small distilling flask with the side arm fitting directly into a receiver, and the acetic acid was removed under reduced pressure. The apparatus was then filled with nitrogen and the flask heated slowly to between 260° and 300° on a metal-bath, with nitrogen bubbling through the viscous mass, which partly distilled. On reducing the pressure, a further amount of material passed into the receiver. The entire distillate was dissolved in ether, washed with dilute sodium carbonate solution, and dried (Na₂SO₄). This procedure was repeated for the other four portions, and the combined amounts of impure parasantonide obtained on distilling off the ether were crystallised from ether–light petroleum, and finally from light petroleum alone; m. p. 110°

Apparatus.—For all the irradiation experiments we used a Hewittic vacuum mercury-vapour lamp running at 4·5 amps. In determining γ with wave-lengths within the first band the infra-red, visible, and ultra-violet radiation down to 3200 A. were absorbed by a filter (215 g. of NiSO₄,7H₂O and 60 g.

of $CoSO_4,7H_2O$ in 600 ml. of aqueous solution) contained in a 500-ml. fused-silica flask. The filter also acted as a condensing lens and suitable stops were arranged to eliminate stray light. A sheet of mica (0·05 mm. thick) for cutting off the ultra-violet below 2800 A. was placed just behind the final stop (5·5 × 0·5 cm.), and in front of it the reaction cell was fixed. This cell consisted of a fused-silica tube of square section (7·5 × 1 × 1 cm.) with a side tube for filling. A small piece of glass tubing about 1 cm. long was inserted for stirring, and glass ends of good optical quality were cemented in position. For measurements within the second band ($\lambda = 2650$—2537 A.) the apparatus was similar to that described above, but a chlorine filter was substituted for the mica plate. The chlorine was contained (at atmospheric pressure) in a fused silica cell, 8 cm. in diameter and 3 cm. thick (cf. Bowen, *J.*, 1935, 76).

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