The Electronic Spectra of Psoralens in Their Ground and Triplet Excited States

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Synopsis. The first absorption band in psoralens arises from the coumarin moiety, and its location, intensity and polarization are strongly dependent on 5- and 8-substitution. The first two absorption bands in psoralen, angelicin, and methylpsoralens are polarized nearly parallel (angle between them $\Delta\theta \leq 20°$), while methoxypsoralens display wider polarization angles.

Psoralens are photobiologically reactive agents which undergo photocycloaddition to nucleic acids upon irradiation with near UV light.[1] The UV spectra of psoralen and coumarin have already been analyzed by linear dichroism and fluorescence polarization.[2,3] We now extend the spectral analysis to other psoralens.

The T-T absorption spectra of psoralens have been measured.[4,5] In this paper, we attempt to assign the broad absorption bands of psoralen in terms of MO predictions.

Experimental

Absorption spectra were recorded on a Cary 118C spectrophotometer, using a specially built adaptor for the liquid N_2 dewars. Concentrations of all compounds were kept at approximately 50 μM (1 M=1 mol/dm^3). The polarized luminescence excitation spectra were recorded on a single photon counting spectrofluorometer (at a spectral resolution of ≈1 nm) by using a pair of Glan-Thompson polarizers under photoselection conditions.[6,7]

Results and Discussion

From the low temperature spectra shown in Figs. 1 and 2, it can be seen that the first absorption band (331 nm for psoralen; Ps) is the most sensitive to perturbation of the furocoumarin system by substitution. 5- and 8-Methoxy substituents exert the strongest perturbation, as the three resolved band system of Ps (Fig. 1) nearly converges into a two band system for 8-MOP and 5-MOP (Fig. 2). While other psoralens show relatively small variations in polarization degree over the first and second absorption bands, 8- and 5-MOP's display polarization differences of *ca.* 0.4 and 0.3, respectively (Fig. 2). This suggests that the angle ($\Delta\theta$) between the two transition moments for the first and second absorption bands is greater (40—50°) than that in other psoralens.

The above noted difference in polarization arises from the fact that the methoxy substitution at position 5 or 8 realigns the transition vector for the first absorption band from the C_3-C_5 axis orientation in Ps to the C_5-C_8 axis orientation in the methoxypsoralens. The polarization of the first band in iPs remains along the long molecular axis (Fig. 1), and is nearly parallel to the polarization direction of the second band, consistent with relatively small differenee in polarization values over the two bands (yielding $\Delta\theta=20°\pm10°$).**

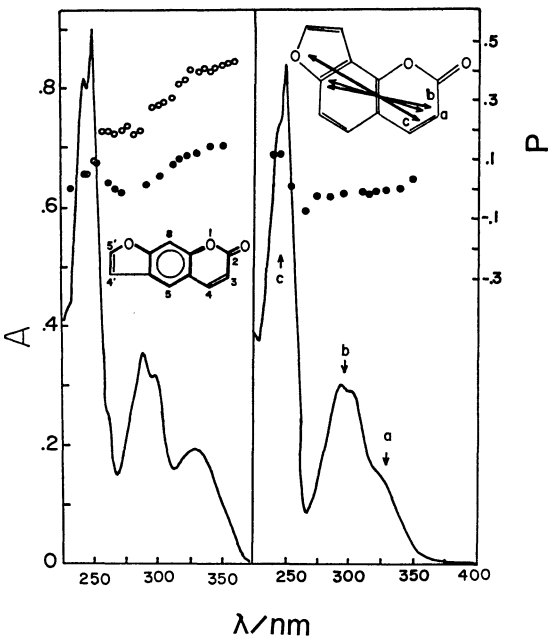

Fig. 1. The absorption spectra of psoralen (left panel) and isopsoralen (right panel) in ethanol at 77 K. Fluorescence excitation polarization (open circle) for psoralen was monitored with respect to emission at 410 nm. Phosphorescence excitation polarization (solid circle) for psoralen and angelicin monitored with respect to the 0-0 phosphorescence at 455 nm. The inset (right panel) shows transition moment directions for the three bands (a, b, c).

In coumarin, the first band is polarized along the long axis, while the second is polarized along the C_2-C_6 axis, with $\Delta\theta=10°\pm5°$.[2] MO calculations are in agreement with the nearly parallel, long axis polarization for the first two bands. For example, MO calculations predict that the first two bands of 7-hydroxycoumarin (λ calculated at 317 and 290 nm) are polarized along the long molecular axis.

Since psoralen is isoelectronic with anthracene, it is reasonable to assign the first and second bands as L_b and L_a origin. The third band in psoralens, which likely contains contribution from a fourth transition,[2] can then be assigned as B_a and/or B_b. It is clear that the first band arises from the coumarin moiety, since the hydrogenation at the pyrone 3,4-C=C bond results in a benzofuran-like spectrum (Fig. 3). The spectral genealogy of psoralens with coumarins is predictable in view of the fact that the first absorption band in both Ps and coumarin is long-axis polarized.[2] In this regard, it is significant that *o*-coumaric acid [3-(2-hydroxyphenyl)propionic acid] (λ_{max}≈336 nm) displays an absorption spectrum closely resembling that of coumarin or Ps (Fig. 3), although the two bands

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** Fluorescence polarization data (not shown) for angelicin (iPs) are similar to those for Ps shown in Fig. 1.

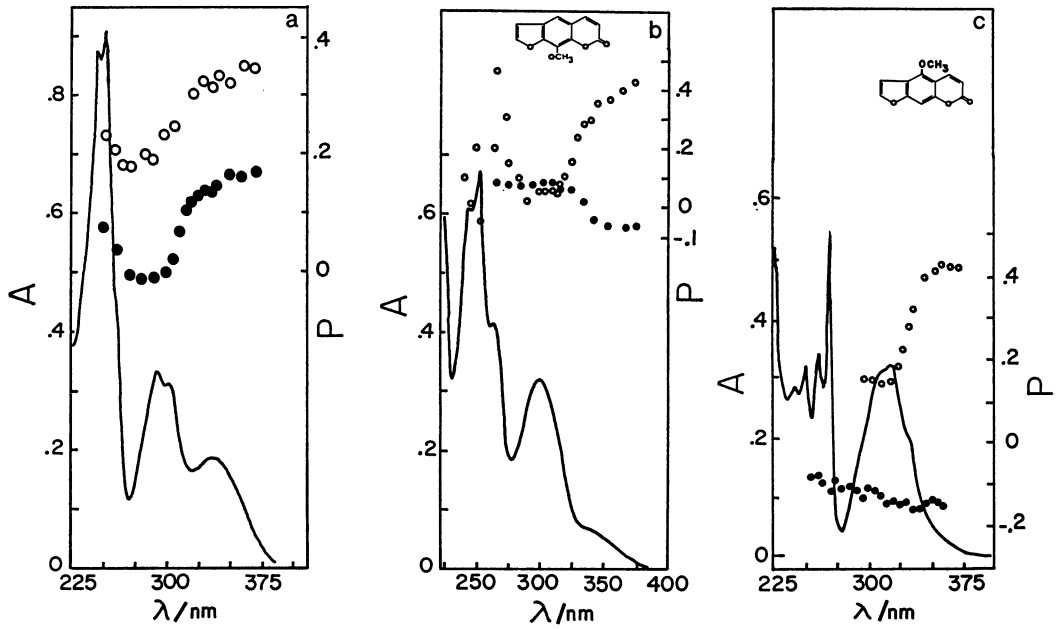

Fig. 2. The absorption spectra of (a) 4,5′,8-trimethylpsoralen, (b) 8-MOP, and (c) 5-MOP in ethanol at 77 K. Fluorescence (open circle) and phosphorescence (solid circle) excitation polarizations were monitored with respect to fluorescence at 415, 435, and 435 nm, respectively, and phosphorescence at 478, 458, and 466 nm, respectively.

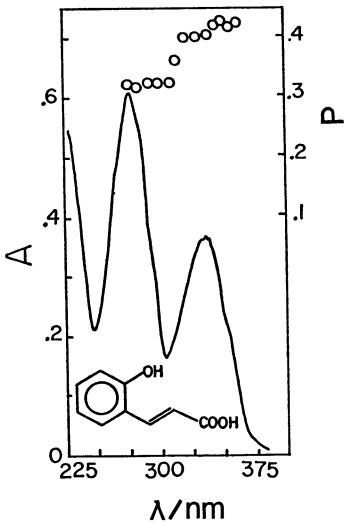

Fig. 3. The absorption spectrum of *o*-coumaric acid in ethanol at 77 K. Fluorescence excitation polarization (open circle) was monitored with respect to fluorescence at 375 nm.

collapse into one overlapping band in *p*-coumaric acid [3-(4-hydroxyphenyl)propionic acid] ($\lambda_{max}\approx318$ nm). Polarization directions for the two bands in *o*-coumaric acid are also nearly parallel, as the fluorescence polarization values differ by only *ca.* 0.1 (Fig. 3).

The phosphorescence of coumarins and psoralens is substantially out-of-plane polarized, particularly 0-0 phosphorescence.[6] This is confirmed by the polarized phosphorescence excitation spectra in Figs. 1 and 2, further suggesting that the first absorption band is largely due to an in-plane polarized $\pi\rightarrow\pi^*$ transition in psoralens and coumarins. However, the phosphorescence polarization over the first absorption band of Ps and trimethyl Ps is not negative (Fig. 1), suggesting that n, π^* perturbations (*e.g.*, vibronic and spin-orbit couplings)[6] are stronger in these molecules than in the others. This may be attributed to the close proximity of the first π, π^* and n, π states in the former.

From MO data calculated (not shown), we tentatively assign the observed T-T absorption maximum at 428 nm to either the $T_1\rightarrow T_9$ or T_8. We further predict that a strong absorption occurs in the near UV region, as suggested by the MO calculation (*i.e.*, $T_1\rightarrow T_{10}$ transition at 324 nm with $f=0.7274$). In coumarin, the intense T-T band is predicted at 283 nm with $f=0.7154$. However, the reported spectrum covers from 300—500 nm, with a broad maximum at 400—460 nm,[8,9] extending to 600 nm.[10] The most intense transitions predicted in this region from MO calculations are at 370 and 319 nm, corresponding to $T_1\rightarrow T_7$ ($f=0.0355$) and $T_1\rightarrow T_8$ ($f=0.0626$), respectively.

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