Fluorescence Spectrum of the Retinylic Cation

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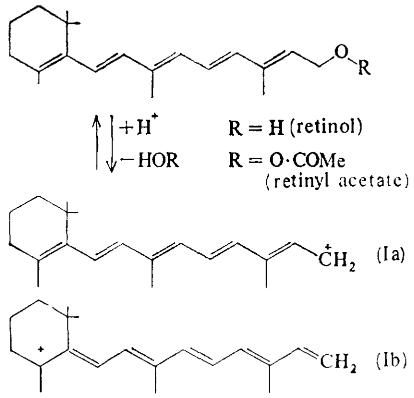
ELECTRONIC absorption spectra and the λ_{max} values of many carbonium ions have been determined.[1] Here we present the first fluorescence spectrum of such an ion.

Previously,[2] we showed that when either retinol or retinyl acetate was placed in a true acid environment, it gave rise to the retinylic cation. This cation is pentaenylic and its structure is shown in (Ia, Ib). Certain alcohol–acid solvent systems give rise to cations of substantial stability. For example, when the retinylic cation is allowed to form in 2-propanol–sulphuric acid at −78°, it is stable for more than an hour. Such stability allowed us to examine the ion for fluorescence. The Table shows the absorption and fluorescence maxima of retinol, retinyl acetate, and the retinylic cation. The ion exhibits a λ_{max} of 603 mμ in 2-propanol–sulphuric acid. The sample, as a viscous glass, was excited at 550 mμ (the half-peak height of the absorption band on the short wavelength side) and scanned above 550 mμ. This wavelength was used in order to enhance the separation of the excitation and emitted light. Fluorescence values have been corrected for the non-linearity of the photomultiplier tube of the spectrofluorometer.



The spectral information is presented more effectively in the Figure where the absorption and corrected emission bands are placed on a wave number plot. In the graph, the fluorescence spectrum has been normalized with respect to the absorbance. Inspection of the plot shows a difference between the absorption and fluorescence maxima of about 9000 cm.$^{-1}$ (25·7 kcal./mol.) for the polyene and 1300 cm.$^{-1}$ (3·7 kcal./mol.) for the carbonium ion. This represents a large vibrational relaxation value consistent with a highly flexible molecule. The polyene which has an alternating double and single bond structure would be expected

TABLE

Absorption and fluorescence maxima of retinylic cation at low temperatures in 2-propanol–sulphuric acid

	Absorption (mμ)		Emission (mμ)	
	Polyene	Cation	Polyene	Cation
all-*trans*-Retinol	326 (−48°)	603 (−48°)	498 (R.T.) 492 (−50°) 469 (liq. N_2)	640 (−78°)
all-*trans*-Retinyl acetate	328 (−49°)	603 (−49°)	484 (−50°)	650 (−78°)

[a] Excitation at 325 mμ; [b] Excitation at 550 mμ with Aminco-Bowman Spectrophotofluorometer.

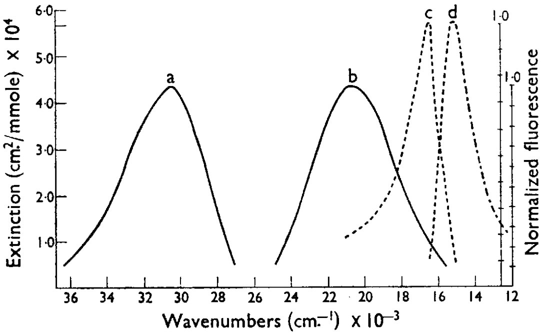


FIGURE. *Absorption and fluorescence spectra of neutral and acidified all-*trans*-retinyl acetate in 2-propanol: (a), retinyl acetate absorption; (b), retinyl acetate fluorescence; (c), retinylic cation absorption; (d), retinylic cation fluorescence.*

to exhibit a large amount of vibrational relaxation. On the other hand, the retinylic cation has a small vibrational relaxation indicating absorption and emission states which are highly similar, a condition expected from a highly inflexible molecule. As pointed out by the authors,[2] the carbonium ion, because of its high degree of resonance stabilization, would have a non-alternating bond structure which would impart rigidity about the former single bonds as well as the former double bonds.

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