

FLUORESCENCE LIFETIMES OF SOME RAUWOLFIA ALKALOIDS

J. HIDALGO, D. GONZALEZ ARJONA, E. ROLDAN and M. SANCHEZ
Departamento de Fisicoquímica Aplicada, Facultad de Farmacia,
c/ Tramontana s/n, 41012 Sevilla, Spain.

ABSTRACT

The natural fluorescence lifetimes of the following Rauwolfia alkaloids, Reserpine, Rescinnamine, Corynanthine, Yohimbine, --- Ajmalicine, Serpentine and Ajmaline, have been calculated from a modified form of the Strickler-Berg equation. The actual lifetimes were derived from the quantum yields and the calculated natural lifetimes.

INTRODUCTION

Rauwolfia alkaloids have long attracted interest because of their pharmacological properties (ref. 1) as antihypertensive, tranquilizer and sedative agents. Moreover, a Rauwolfia alkaloid, the Serpentine, inhibits selectively Cancer cell DNA synthesis in vitro (ref. 2,3).

The most important parameters which characterize the fluorescence emission of a molecule are the lifetime τ and the quantum yield, Q . These parameters are often related with the natural fluorescence lifetimes τ_0 , by the formule $\tau = Q \cdot \tau_0$.

As part of a program in which the spectrofluorimetric characteristics and the stability of various indole alkaloids are being investigated the fluorescence natural lifetimes τ_0 in ethanol, of seven Rauwolfia alkaloids were calculated by using a modified form of the Stricker-Berg equation (ref.4), proposed by Birks and Dyson (ref.5). From these values and the quantum yields, Q , previously measured (ref.6,7), the actual lifetimes τ have been calculated.

METHOD AND RESULTS

The natural or radiative lifetimes τ_0 , are related theoretically, to the absorption band area (ref.7). Stricker and Berg (ref.4) have developed a theory and proposed an equation which is applicable to polyatomic molecules under certain conditions. Birks and Dyson -- (ref.5) have derived a modified form of Stricker-Berg equation.

Their final result is

$$\frac{1}{\tau_o} = 2.880 \times 10^{-9} \frac{n_f^3}{n_a} \langle \bar{\nu}_f^{-3} \rangle_{av.}^{-1} \int \epsilon(\bar{\nu}) d\bar{\nu} / \bar{\nu} \quad (1)$$

where

$$\langle \bar{\nu}_f^{-3} \rangle_{av.}^{-1} = \int F(\bar{\nu}) d\bar{\nu} / \int F(\bar{\nu}) \bar{\nu}^{-3} d\bar{\nu} \quad (2)$$

$F(\bar{\nu})$ is the fluorescence intensity in units of relative numbers of quanta at each frequency, n_f is the mean refractive index of the solvent over the fluorescence band, n_a the mean value over the -- absorption band and $\epsilon(\bar{\nu})$ is the molar absorption coefficient.

Absorption spectra were taken on a Perkin-Elmer Lambda 5 spectrophotometer. Fluorescence spectra were recorded on a Perkin-Elmer -- 650-40 spectrophotofluorometer. A Perkin-Elmer Data Processor 650-0178 was used to obtain the corrected spectra. The wavelengths of excitation and emission were calibrated against the Xenon line -- emission spectrum. The sensitivity and stability were checked by using the Raman band of distilled water. The corrected excitation and emission spectra were recorded in relative quantum per unit wavelength interval versus wavelength. Rhodamine B was the standard employed for quantum counter.

The integrals were calculated by using the Simpson's method applied to specific bands. Previously the spectra were deconvoluted in individual bands by a least-square program, assuming a long-normal shape (ref.8). In figure 1 as an example, the deconvoluted UV spectrum of Reserpine is shown.

The relative indice values, n_f and n_a in equation 1, for ethanol were taken from "International Critical Tables" (ref.9).

The experimental results and calculated values are shown in Table 1. Columns 3 and 4 list the values of the integrals in equation 1. The Table 1 contains also the values for the quinine sulphate in 1 N sulphuric acid. The τ_o calculated natural fluorescence lifetime, 27.4 ns, agrees well with the literature value (ref.5).

ACKNOWLEDGMENT

We gratefully acknowledge financial support from the "Comisión Asesora de Investigación y Técnica".

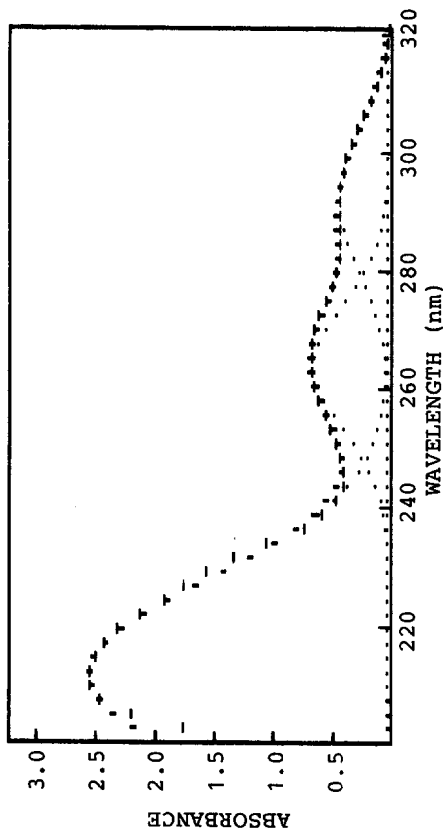


Fig. 1. Deconvolution of UV spectrum of Reserpine:-----, experimental spectrum;...., log-normal curves;||||, addition of log-normal curves.

TABLE 1.- Summary of the calculation of lifetimes

(1) Compound	(2) Solvent	(3) $10^{-3} \int \epsilon(\nu) d\nu/\bar{\nu}$	(4) $10^{13} \langle \nu_f^{-3} \rangle_{av.}$	(5) n_a	(6) n_f	(7) τ_0 (ns)	(8) Q^a	(9) τ (ns) calc.
Reserpine	Ethanol	1.07	0.48	1.39	1.38	8.2	0.05	0.4
Rescinnamine	Ethanol	4.92	0.77	1.39	1.37	2.9	0.005	0.02
Yohimbine	Ethanol	1.06	0.46	1.40	1.38	8.1	0.40	3.2
Corynanthine	Ethanol	1.07	0.46	1.40	1.38	8.0	0.34	2.7
Ajmalicine	Ethanol	0.66	0.44	1.40	1.38	12.5	0.02	0.3
Serpentine	Ethanol	0.57	0.95	1.38	1.37	31.0	0.63	19.5
Ajmaline	Ethanol	0.27	0.48	1.39	1.38	33.1	0.10	3.2
Quinine	aq. NH_2SO_4	0.77	1.09	1.34	1.34	27.4	0.546	15.0

^aReference 6

REFERENCES

- 1 J.S. Glasby, *Encyclopedia of the Alkaloids*, Plenum Press, New York and London, 1975.
- 2 M. Beljanski and M.S. Beljanski, *Expl. Cell. Biol.*, 50(1982)79
- 3 M. Beljanski and M.S. Beljanski, *IRCS Med. Sci.*, 12(1984)587.
- 4 S.J. Strickler and R.A. Berg, *J. Chem. Phys.*, 37(1962)814.
- 5 J.B. Birks and D.J. Dyson, *Proc. Roy. Soc.*, A275(1963)135.
- 6 J. Hidalgo, P.P. Tejada, M.A. Muñoz, A. Maestre, M. Balón and M. Sánchez, *Pharm. Acta Helv.*, in press.
- 7 T. Förster, *Fluoreszenz Organischer Verbindungen*, Vandenhoeck and Ruprecht, Göttinger, 1951.
- 8 C.M. Harris, R.J. Johnson and D.E. Metzler, *Biochim. Biophys. Acta*, 421(1976)181.
- 9 *International Critical Tables*, McGraw Hill Book Company Inc., New York, Vol VII, 1926.