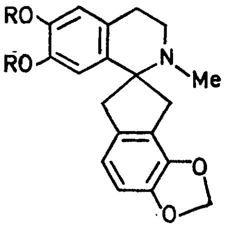
Absolute Configuration of Some Spirobenzylisoquinoline Alkaloids

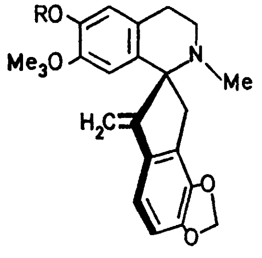
By M. SHAMMA* and J. L. MONIOT
(*Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania* 16802)
R. H. F. MANSKE
(*Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada*)
and WAN KIT CHAN and KOJI NAKANISHI
(*Department of Chemistry, Columbia University, New York*)

Summary The absolute configuration of ochotensine (**2**), ochotensimine (**3**), ochrobirine (**4**) and fumariline (**5**) has been established using the aromatic chirality method.

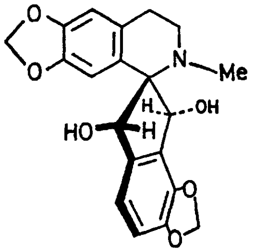
SEVERAL spirobenzylisoquinoline alkaloids are presently known, and they all share in common the nucleus (**1**).[1] Application of the aromatic chirality method[2] has now allowed the assignment of absolute configuration to some of these compounds.



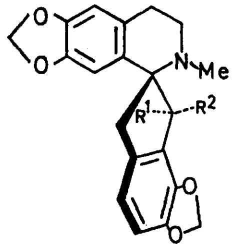
(1)



(2) R=H
(3) R=Me$_3$



(4)



(5) R^1;R^2=O
(6) R^1=OH, R^2=H

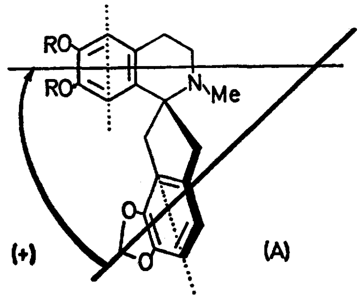


FIGURE. *Positive chirality of (+)-ochotensine, (+)-ochrobirine, and dihydrofumariline.*

The c.d. spectrum of ochotensine (**2**)[3] showed Davydov split extrema centred at 278 nm, corresponding to the $L_b \leftarrow A$ band, with a positive first Cotton effect (Table). The chirality between the two long-axis polarized transition moments is, therefore, also positive. (+)-Ochotensimine (**3**) has been related chemically to ochotensine (**2**), so these two bases possess the absolute configuration indicated.

(+)-Ochorobirine (**4**) and dihydrofumariline (**6**), the latter being the $LiAlH_4$ reduction product of the naturally occurring ketonic spirobenzylisoquinoline (+)-fumariline (**5**), also exhibited a Davydov split centred at 288 nm in each case, corresponding again to the $L_b \leftarrow A$ band, and with a positive first Cotton effect (Table).

The positive chirality of (+)-ochotensine, (+)-ochrobirine, and dihydrofumariline, and, by extension, (+)-

TABLE

Spectroscopic data for some spirobenzylisoquinolines

	λ_{max}/nm	log ϵ	c.d./nm	$\Delta\epsilon$	
(+)-Ochotensine [EtOH–dioxan (1:1)]	284	4·04	293 249	+ 2·1 − 2·2	Davydov split
	228sh*	4·36	230*	+10·2	
(+)-Ochrobirine (EtOH)	291	3·87	298 280	+14·9 − 4·0	Davydov split
	239*	3·91	240*	+ 9·0	
	201	4·91	—	—	
Dihydrofumariline (EtOH)	291	3·68	297 280	+ 7·3 − 2·9	Davydov split
	239sh*	3·76	240*	+ 3·8	

* The u.v. maxima at *ca.* 239 nm correspond to $L_a \leftarrow A$ transitions, as depicted by the dotted lines in (A). In the present case these $L_a \leftarrow A$ transitions run in roughly parallel directions and hence do not give rise to split Cotton effects.

line, means that all these spirobenzylisoquinolines the same absolute configuration, with the 9,10-methylenedioxy-group of ring D situated below the mean plane of the molecule as shown.

This research was supported by grants from the National Institutes of Health (to M.S. and K.N.).

(*Received*, 10*th January* 1972; *Com.* 039.)

---

[1] For a review on the spirobenzylisoquinoline alkaloids see M. Shamma in 'The Alkaloids', vol. **13**, ed. R. H. F. Manske, Academic Press, New York, 1971, p. 165. Other recently characterized spirobenzylisoquinolines have been described by M. Castillo, J. K. Saunders, D. B. MacLean, N. M. Mollov, and G. I. Yakimov, *Canad. J. Chem.*, 1971, **49**, 139, and by D. A. Fesenko and M. E. Perelson, *Khim. prirod. Soedinenii.*, 1971, **7**, 166.

[2] N. Harada and K. Nakanishi, *J. Amer. Chem. Soc.*, 1969, **91**, 3989; N. Harada, K. Nakanishi, and S. Tatsuoka, *ibid.*, p. 5896; M. Shamma, J. L. Moniot, W. K. Chan, and K. Nakanishi, *Tetrahedron Letters*, 1971, 3425, 4207. *Cf.* also, S. F. Mason, K. Shofield, R. J. Wells, J. S. Whitehurst, and G. W. Vane, *Tetrahedron Letters*, 1967, 137.

[3] S. McLean, M.-S. Lin, A. C. MacDonald, and J. Trotter, *Tetrahedron Letters*, 1966, 185.