ORIPAVIDINE – A NEW ALKALOID FROM Papaver orientale

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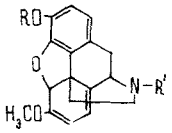
From the phenolic fraction of the combined alkaloids of Papaver orientale L. collected in Nakhichevan (Azerbaidshan SSR) in the flowering/fruit-bearing period we have isolated a new base which we have called oripavidine (I) $[\alpha]_D$ −90° (c 0.27; methanol). Oripavidine decomposes at temperatures above 250°C. The alkaloid is readily soluble in methanol, ethanol, and alkalis, and sparingly soluble in ether, benzene, chloroform, pyridine, and hexane. The UV spectrum: [$\lambda_{max}^{ethanol}$ 207, 228, 286 nm (log ε 4.45, 4.07, 3.84)] was identical with that of oripavine. The IR spectrum showed absorption bands at 1605 cm^{-1} (aromatic ring) and 3430 cm^{-1} (active hydrogen). In the NMR spectrum of the base taken in CD_3OD there were a three-proton singlet at 3.53 ppm from a methoxy group, one-proton doublets at 4.09, 5.10, and 5.68 ppm (J = 8 Hz), and a one-proton singlet at 5.29 ppm. In the region of aromatic protons there are two one-proton doublets at 6.45 and 6.56 ppm (J = 8 Hz, ortho aromatic protons). Methylene protons appear at 1.5-3.5 ppm. The CD curve was close to that of oripavine.

The facts given enable oripavidine to be assigned to the alkaloids of the morphinan group [1]. When the base was methylated with formaldehyde, followed by reduction with sodium tetrahydroborate [2], the N-methyl derivative (II) was obtained. When chromatographed in a thin layer of silica gel in various solvent systems, (II) showed the same R_f values as oripavine, and they were both colored yellowish green by iodine vapor, this color changing to brown on standing in the air. Because of the small amount of the product obtained it could not be crystallized. When (II) was methylated with diazomethane, a product identical according to TLC and its mass spectrum [m/e 311 (M^+) 296, 255, 155.5] with thebaine.

Thus, oripavidine has the structure of N-demethyloripavine



Ovipavidine R = R′ = H
Ovipavine R = H; R′ = CH_3
Thebaine R = R′ = CH_3

LITERATURE CITED

1. R. H. F. Manske, The Alkaloids, Academic Press, New York, Vol. XII (1970), p. 364.
2. T. Macao and K. Mutsuo, J. Pharm. Soc. Jpn., 85, 77 (1965).

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