Phytochemistry, 1981, Vol. 20, pp. 347–348. © Pergamon Press Ltd. Printed in England. 0031–9422/81/0201–0347 $02.00/0

ISOORIDINE, A NEW ALKALOID FROM *PAPAVER OREOPHILUM*

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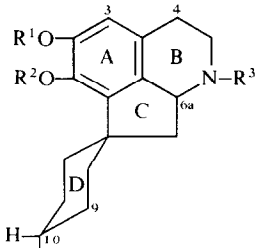
(*Received* 18 *April* 1980)

Key Word Index—*Papaver oreophilum*; Papaveraceae; proaporphine alkaloids; ^{1}H NMR, ^{13}C NMR and CD spectral data.

Studies of the alkaloids from *Papaver oreophilum* Rupr. [1] have led to the isolation of the proaporphine alkaloid oridine (Syn. oreoline) (**1**) [2–4] and, in addition, of an alkaloid mp 166–168°. An alkaloid with the same mp had been isolated earlier [5] and was named 'oridine 2'. The TLC and the UV spectrum of this compound are identical with those of oridine (**1**). The bands at 289 nm of both substances in 0.1 M NaOH exhibit a bathochromic shift of 11 nm. The mass spectra of these substances have a M^+ at *m/e* 289 and major fragments at *m/e* 288 and 260. The ^{1}H NMR spectra display a singlet for a OMe group and a multiplet for a OCH proton. They differ, however, in the methine and methylene envelope and in the chemical shift of the aromatic proton at C-3 ($\Delta\delta$ 0.12 ppm in DMSO-d_6, $\Delta\delta$ 0.04 ppm in $CDCl_3$–CD_3OD, 1:1). The ^{13}C NMR spectra are not identical but the distribution of the carbon atoms of the individual types are similar; consequently, these two substances are isomers. They may differ in the orientation of the secondary OH at C-10 or in the B/C ring fusion, and in the position of the OMe group on ring A, respectively. In these two alkaloids the axial orientation of the OH at C-10 is indicated by *ca* the same width of the multiplets of the OCH protons. The chemical shifts of the corresponding carbon atoms differ only by 0.1 ppm (the difference between the axial C and the equatorial C is assumed to be 4–6 ppm [6]). The small difference between the chemical shifts of the carbon atoms C-6a (57.7 and 57.3 ppm) and the fact that these two alkaloids have the same CD spectra are contradictory to the assumption that they differ in the B/C ring fusion. Methylation of oridine (**1**) and of the alkaloid mp 166–168 with CH_2N_2 in MeOH yields the same *O,N*-dimethyl derivative **2** (mmp, UV, IR and ^{1}H NMR spectra). Thus the new alkaloid isooridine (**3**) differs from **1** in the position of the OH and OMe groups at C-1 and C-2. This alternative is supported by the different chemical shift of the proton at C-3 and other aromatic carbon atoms.



1 R^1 = Me, R^2 = R^3 = H
2 R^1 = R^2 = R^3 = Me
3 R^1 = R^3 = H, R^2 = Me

EXPERIMENTAL

Mps were determined on a Kofler block and are uncorr. For spectral measurements, the studied compounds were dried at 60°/13 Pa to a constant wt. IR spectra were recorded in KBr discs, ^{1}H NMR spectra (CW) and (FT) at 60 MHz and ^{13}C NMR spectra (FT) at 15.036 MHz.

The plant material was grown in the Experimental Botanical Garden, Medical Faculty, University J. E. Purkyně, Brno, and harvested when the fruit was still immature. The material was dried at room temp., ground and extracted with MeOH. The aerial parts (5 kg) and the roots (1.68 kg) were examined separately. After removal of MeOH by dist., the residue was dissolved in 0.2 M HOAc, filtered and the filtrate worked up in the usual manner [7] to afford the alkaloidal fractions A, B, E, I. On crystallization from $CHCl_3$ and recrystallization from MeOH, the bases of the portion E (aerial part—9.05 g; roots 16.7 g) gave 2.26 g and 4.69 g of oridine (**1**) and 0.11 g and 0.62 g of isooridine (**3**), respectively.

Oridine (**1**). Mp 235–237°, $[\alpha]_D^{20}$ − 82.4° ± 3° (*c* 0.34, MeOH). UV λ_{max} (log ε), EtOH: 235 *sh* (3.89) and 289 nm (3.51); 0.1 M ethanolic NaOH: 255 (3.96) and 300 nm (3.74). IR: 3380 and 3200 cm^{-1} (ν O–H and N–H). CD λ_{max} ($\Delta\varepsilon$), EtOH: 211 (−8.76), 237 (−2.15) and 286 nm (−0.43). MS: *m/e* 289, 288, 260. ^{1}H NMR ($CDCl_3$ + CD_3OD, int. TMS), δ: 3.84*s* (3H), 4.05*mt* ($W_{1/2}$ = 7 Hz, 1H), 6.49*s* (1H); DMSO-d_6, int. TMS): 3.75*s* (3H), 6.48*s* (1H). ^{13}C NMR (DMSO-d_6, off resonance multiplicity), δ: 26.8*t*, 27.4*t*, 29.5*t*, 30.3*t*, 30.8*t*, 44.1*t*, 45.6*t*, 48.3*s*, 57.3*q*, 57.7*d*, 64.3*d*, 110.3*d*, 122.4*s*, 134.1*s*, 136.2*s*, 141.8*s*, 148.5*s*.

O,N-*Dimethyloridine* (**2**). Mp 181–184°. MS: *m/e* 317, 275, 257, 205. ^{1}H NMR ($CDCl_3$, int. TMS), δ: 1.26–3.29*mt*, 2.37*s* (3H), 3.81*s* (3H), 3.84*s* (3H), 4.09*mt* (1H), 6.53*s* (1H).

Isooridine (**3**). Mp 166–168°, $[\alpha]_D^{20}$ − 57.3° ± 3° (*c* 0.55, MeOH). The UV, MS and CD spectra of **3** were in good agreement with those of **1**. ^{1}H NMR ($CDCl_3$ + CD_3OD, int. TMS), δ: 3.86*s* (3H), 4.06*mt* ($W_{1/2}$ = 7.5 Hz, 1H), 6.53*s* (1H); (DMSO-d_6, int. TMS): 3.78*s* (3H), 6.60*s* (1H). ^{13}C NMR (DMSO-d_6, off resonance multiplicity), δ: 25.2*t*, 27.3*t*, 30.1*t*, 30.5*t*, 31.2*t*, 42.2*t*, 44.6*t*, 48.6*s*, 57.0*q*, 57.3*d*, 64.2*d*, 110.2*d*, 121.4*s*, 132.3*s*, 134.2*s*, 142.2*s*, 149.3*s*.

REFERENCES

1. Věžník, F., Táborská, E. and Slavík, J. (1980) *Collect. Czech. Chem. Commun.* (in press).
2. Šantavý, F. and Maturová, M. (1967) *Planta Med.* **15,** 311.
3. Mann, I. and Pfeifer, S. (1967) *Pharmazie* **22,** 124.
4. Tscholombitko, V. A., Mnatsakanjan, V. A. and Salnikova, L. V. (1978) *Khim. Prir. Soedin.* 270.
5. Maturová, M., Pavlásková, D. and Šantavý, F. (1966) *Planta Med.* **14,** 22.
6. Casagrande, C., Canonica, L. and Severini, R. G. (1975) *J. Chem. Soc. Perkin* 1, 1659.
7. Slavíková, L. and Slavík, J. (1966) *Collect. Czech. Chem. Commun.* **31,** 3362.