METHYLEVOXINE – A NEW ALKALOID FROM Haplophyllum perforatum

V. I. Akhmedzhanova, I. A. Bessonova, and S. Yu. Yunusov

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We have continued a study of the alkaloids of the epigeal part of the plant Halophyllum perforatum [1]. By chromatographing the combined bases on a column of alumina we have isolated a new alkaloid (I), which crystallizes in the form of colorless needles with mp 55-56°C. The substance is readily soluble in acids, chloroform, and methanol, sparingly soluble in ether, and insoluble in water and alkali.

The IR spectrum of the base shows the absorption bands of active hydrogen at 3450 cm^{-1} and of a furan ring at 3140 and 3170 cm^{-1}. The UV spectrum of the substance [λ_{max} 251, 322, 334 nm (log ε 4.91, 3.78, 3.77)] is close to that of evoxine (II) [2].

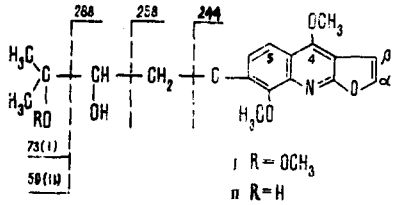
The NMR spectrum (I) (taken in $CDCl_3$, τ scale) shows signals at 2.37 and 3.08 (d, 1 H each, J = 9 Hz, $H_{5,6}$), 2.75 and 3.27 (d, 1 H each, J = 3 Hz, $H_{\alpha,\beta}$), 5.83-6.45 (m, 3 H, CH–O, CH_2–O), 5.82, 6.11, 6.89 (s, 3 H each, 3 OCH_3), and 8.83 ppm [s, 6 H, $C(CH_3)_2$]. All the signals with the exception of the singlet at 6.89 ppm, the chemical shift of which is typical for aliphatic methoxy groups, are present in the spectrum of evoxine [3]. Consequently, we assumed that the base has the structure of evoxine in which one hydroxy group is methylated.

Mass spectra, m/e:

I. 361 (M^+ 48.5%), 288 (5%), 258 (7.5%), 245 (59.5%), 244 (22.2%), 227 (100%), 216 (18.2%), 73 (92.9%).

II. 347 (M^+ 69%), 288 (13%), 258 (10%), 245 (36%), 244 (49%), 227 (100%), 216 (20%), 59 (79%).

The mass spectra of the base isolated and of evoxine contain the same set of ions with the exception of M^+ and $(M - 288)^+$, differing by 14 units. This shows that the methoxy group is present on a tertiary carbon atom. Consequently, the alkaloid has structure (I), and we have called it methylevoxine.



The acetylation of methylevoxine with acetic anhydride in pyridine gave an acetyl derivative (III), mol. wt. 403 (mass spectrometrically), ν_{max} 1745 cm^{-1} ($OCOCH_3$).

The downfield displacement by more than 1 ppm (τ 4.73) in the NMR spectrum of (III) of the signal of the proton geminal to the acetyl group shows the secondary nature of the free hydroxy group.

The positions of the substituents in the furanoquinoline nucleus were confirmed by the formation of haplopine when methylevoxine was fused with alkali.

LITERATURE CITED

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