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STRUCTURE OF GLAUFININE

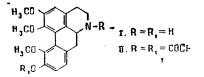
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Continuing a study of the alkaloid composition of <u>Glaucium fimbrilligerum</u> [1, 2], from the epigeal part of the plant collected at Talas (Kirghiz SSR) in the flowering period we have isolated a new amorphous base with the composition $C_{19}H_{21}NO_4$ having $[\alpha]_D$ +165° (c, 0.4; methanol), which we have called glaufinine (I). The UV spectrum of (I) has three absorption maxima, at 222, 270, and 309 nm (log ε 4.35, 3.82, 3.43). The mass spectrum of (I) showed the peaks of ions with m/z 327 (M⁺), 326, 312, 310, 298, 296, and 163.5 (M²⁺). In the PMR spectrum (CDCl₃, δ scale) there were the signals of three methoxy groups at (ppm) 3.62 (OCH₃) and 3.80 (2 OCH₃) and of three aromatic protons in the form of a one-proton singlet at 6.63 and a two-proton singlet at 6.75. At 2.30-3.70 there was a multiplet corresponding to methylene and methine protons. The presence in the mass spectrum of the base of the peak of the (M - 29)⁺·ion, and also the absence of the signal of the protons of a N-methyl group from the PMR spectrum showed the secondary nature of the nitrogen atom [3]. On the basis of the facts given above, glaufinine was assigned to the noraporphine alkaloids of the type of corydine [3] with three methoxy and one hydroxy groups.

When (I) was acetylated with acetic anhydride in pyridine, the N,O-diacetyl derivative (II) was obtained. The PMR spectrum of (II) showed the signals of two acetoxy groups, at 2.10 and 2.17 ppm, of three methoxy groups at 3.34, 3.76, and 3.78 ppm, and of three aromatic protons in the form of one siglet at 6.61 ppm and two doublets with J = 8 Hz at 6.80 and 7.06 ppm. The methylene and methine protons gave signals in the form of multiplets in the 2.00 - 3.70 ppm region.

The hydroxy group in glaufinine must be located at C_{10} , since in the PMR spectrum of (II) the signal of the aromatic proton at C_9 is shifted downfield (7.06 ppm) and the signal of one methoxy group is shifted upfield ($C_{11} - OCH_3$, 3.34 ppm) as compared with those for (I), while the chemical shifts of the other aromatic protons and of the methoxy groups have changed only slightly.

Consequently, glaufinine has the structure (I):



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