GLYCOPERINE – A NEW ALKALOID FROM *Haplophyllum perforatum*

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From the total alkaloids of the epigeal part of H. perforatum collected by K. Taizhonov in the Dzhungarian Ala-Tau in the vegetation period of the plant, we have isolated a base (I) with the composition $C_{19}H_{21}NO_8$, mp 224-225°C (methanol); mol. wt. 391 (mass spectrometry); $[\alpha]_D$ −66.3° (c 2.32; pyridine), which we have called glycoperine.

The alkaloid dissolves readily in acid, less readily in hot water, and sparingly in the usual organic solvents, and it is insoluble in alkali.

The IR spectrum of glycoperine has a broad maximum at 3340 cm^{-1} (OH groups). The UV spectrum of (I) [λ_{max} 250, 322.5 nm (log ε 3.90; 3.96), λ_{min} 275 (log ε 3.12)] is typical for alkaloids of the 7,8-methylenedioxydictamnine series [1]. The alkaloid gives a weak molecular peak with m/e 391 (3.4%) and strong peaks with m/e 245 (100%), 227 (48.6%), and 216 (10.3%).

When glycoperine was fused with alkali, haplopine, identified by comparison with an authentic sample [2], was isolated. Thus, we have established that the main nucleus of glycoperine is 4,8-dimethoxyfuroquinoline to which a $C_6H_{11}O_4$ residue is attached through an oxygen atom in position 7.

The acetylation of (I) with acetic anhydride in pyridine gave a triacetyl derivative (II) with mp 181-182°C (benzene–petroleum ether), $[\alpha]_D$ −76.2° (c 2.57; ethanol); mol. wt. 517 (mass spectrometry); ν_{max} 1750 cm^{-1}. The presence in the mass spectrum of (II) of intense ions with m/e 273 (41.5%) and 111 (64%), which are characteristic for acetyl derivatives of 6-deoxypyranoses, permitted the assumption that glycoperine is a glycosidic alkaloid [3]. In the NMR spectrum of (II) ($CDCl_3$, τ scale) the signals of the protons from the furoquinoline nucleus appeared clearly at 2.07, 2.79 and 2.44, and 3.00 ppm (two pairs of doublets, J = 9 and 3 Hz, respectively, $H_{5,6}$ and $H_{\alpha,\beta}$), at 5.63 and 5.89 ppm (two singlets, 3H each, 2 OCH_3). Multiplets at 4.44, 4.86, and 5.75 (3H, 1H, and 1H, respectively, anomeric proton and 3 >CH–OAc), three three-proton singlets at 7.85, 7.95, and 7.99 ppm (3 $OCOCH_3$), and a doublet at 8.85 ppm (3H, J = 6.5 Hz, >CH–CH_3) are due to the protons of a sugar residue.

The hydrolysis of glycoperine with 0.5% sulfuric acid gave haplopine and L-rhamnose, which was identified by TLC, paper chromatography, and the production of the p-nitrophenylhydrazone. The presence of L-rhamnose in glycoperine was also confirmed by the results of the GLC of the trimethylsilyl derivative of the methyl glycoside [4].

Thus, glycoperine (I) is the first glycoalkaloid of the furoquinoline series and has the following structure:

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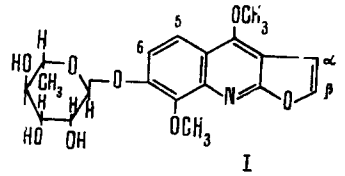

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The value of M_D calculated according to Klyne shows that the L-rhamnose is attached to the haplopine by an α-glycosidic bond.

The partial synthesis of the acetyl derivative of glycoperine has been performed by the condensation of 2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl chloride with haplopine. The synthetic product was identical with (II) according to TLC, melting point, and mass, IR, and NMR spectra.

LITERATURE CITED

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