THE STRUCTURE OF GALANTHUSINE

D. M. Tsakadze, A. Abdusamatov,
R. Razakov, and S. Yu. Yunusov

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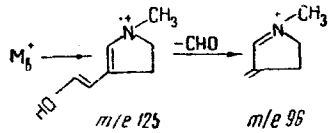
On separating the combined chloroformic alkaloids of Galanthus caucasicus (Bak.) Grossh. [1] by chromatography on a column of alumina, we obtained from the ethereal eluate a new base with mp 118-119°C (acetone), $[\alpha]_D^{30} - 66.6°$ (c 0.42; ethanol), $C_{18}H_{23}NO_5$, mol. wt. 333 (mass spectrometrically), R_f 0.45 in TLC on Al_2O_3 [butan-1-ol–water–acetic acid (20 : 20 : 1)]; hydrobromide with mp 198-200°C (with foaming).

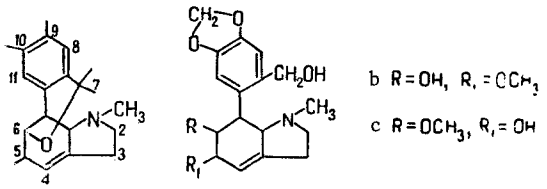
The IR spectrum of the substance has absorption bands at (cm^{-1}) 3400-3200 (OH) and 940 $\left(\begin{matrix}-O\\-O\end{matrix}>CH_2\right)$. UV spectrum: λ_{max} (ethanol) 242, 292 nm (log ε 3.87, 3.77).

In the NMR spectrum of the base, in the weak-field region two one-proton singlets appear at 2.63 and 3.48 ppm (τ scale) corresponding to aromatic protons 8 and 11, respectively. In addition to the aromatic protons, the spectrum clearly shows signals from the protons of a $-O-CH_2-O-$ group at 4.22 ppm and of an olefinic proton at 4.40 ppm corresponding to C-4. An OCH_3 signal is found at 6.44 ppm and that of a $>N-CH_3$ group at 8.42 M.

The mass spectrum of this base has peaks of the molecular ion with m/e 333 and other fragments ($M-H_2O$, $M-CH_3O$, $M-CH_3OH$ and $M-H_2O-CH_3OH$) in the region of high mass numbers. They have a low intensity. The maximum intensity corresponds to the peak of a fragmentary ion with m/e 125. An ion with m/e 96 also has a high intensity. Such a pattern is characteristic for the mass spectra of alkaloids of the type of lycorenine [2].



The presence in the mass spectrum of the base of the peak of a fragment with m/e 125 shows that there is a hydroxy group in position 5 of the lycorenine skeleton (a), as is the case for the hippeastrine molecule. In addition, the mass spectrum of this base, both with respect to the m/e value of the molecular ion and with respect to the nature of the spectrum in the region of high mass numbers, is similar to that of tetrahydroungerine (b).



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The M − 32 peak in the mass spectrum and also the signals of protons at τ 6.44 ppm in the NMR spectrum show that the molecule contains an alicyclic methoxy group. The mass and NMR spectra exclude positions 2, 3, and 5 for it. Consequently the methoxy group is present in position 6.

On the basis of the facts given, we propose for galanthusine structure c as the most probable.

LITERATURE CITED

1. D. M. Tsakadze, A. Abdusamatov, and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 5, 331, 1969.
2. R. Razakov, Kh. A. Abduazimov, N. S. Vul'fson, and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 3, 23, 1967.