ALKALOIDS OF *Colchicum szovitsii.*

STRUCTURE OF SZOVITSAMINE

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Colchicum szovitsii Fisch. et Mey. is known as a colchicine-containing plant [1]; however, its alkaloid content has not been investigated in detail. By the usual method [2], we extracted 3 kg of the plant (epigeal and hypogeal parts) in the fruit-bearing period with ethanol. This gave 0.11% of a weak-base fraction and 0.04% of a strong-base fraction. Then the weak-base fraction was separated into alkali-soluble and alkali-insoluble components (yields 0.06 and 0.05%, respectively). The mixtureof alkali-insoluble substances was found to contain colchicine with R_f 0.81 and nontropolone compounds with R_f 0.14, 0.31, and 0.56 [TLC, type KSK silica gel; chloroform—methanol—benzene (10:3:3)]. The substances soluble in alkali consisted of 2-demethylcolchicine (R_f 0.55), 3-demethyl-β-lumicolchicine (R_f 0.72), an unidentified compound with R_f 0.64 [TLC on alumina, chloroform—methanol (24:1)]; 2-dimethylcolchiceine with R_f 0.10, and colchiceine with R_f 0.41 [PC, n-butanol—12% aqueous ammonia (50:50)].

By preparative separation on a thin layer of silica gel of 700 mg of the mixture of alkali-insoluble compounds we isolated 200 mg of a base with the composition $C_{22}H_{27}O_5N$, mp 188-190°C (from ehter), $[\alpha]_D^{20}$ +86° (c 1.4; chloroform) and R_f 0.31, which we have called *szovitsamine* (I). The UV spectrum of the base has absorption maxima at 258 and 287 nm (log ε 4.33, 4.07) which permits it to be assigned to the group of homoaporphine compounds [3]. The NMR spectrum of (I) shows the signals of four methoxy groups (nine-proton singlet at 3.82 ppm and three-proton singlet at 3.50 ppm), a N-methyl group (three-proton singlet at 2.33 ppm), and two benzene-ring protons isolated from one another (one-proton singlets at 6.37 and 6.64 ppm).

By methylating szovitsamine with diazomethane we obtained a O-methyl ether which was identical with di-O-methylfloramultine. This shows that substance (I) has substituents in the C_2, C_3, C_4, C_5, and C_6 positions, one of them being occupied by a hydroxy group and the others by methoxy groups. To determine the positions of the functional groups we started from the PMR and mass spectra. Since in the PMR spectra of the homoaporphine bases the signals of C_3 and C_4 methoxy groups appear in a relatively stronger field than other O-methyl groups [4-6], the three-proton singlet at 3.50 ppm in the spectrum of szovitsamine can be assigned to one of these positions. To answer this question, we analyzed the mass spectrum of szovitsamine, which contained characteristic peaks with m/e 385 (M^+), M – 15, M – 17, M – 31 (100%), and M – 43. According to literature information [4, 7], the maximum peak of the M – 31 ion in the mass spectrum is observed in those homoaporphine alkaloids in which the C_3 position is substituted by a methoxy group. In this case, the C_4 position of the szovitsamine molecule must be substituted by a hydroxy group.

The results given above permit us to put forward for szovitsamine the structure of 4-hydroxy-2,3,5,6-tetramethoxyhomoaporphine:

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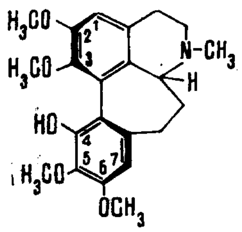

On the basis of the positive sign of the specific rotation and literature information [8, 9], compound (I) corresponds to the absolute R configuration.

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