STRUCTURE OF SZOVITSIDINE

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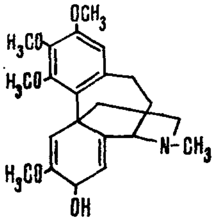
Continuing an investigation of the alkaloids of Colchicum szovitsii Fisch [1], we have separated the strong-base fraction into phenolic and nonphenolic substances (0.03% and 0.01%, respectively). The mixture of phenolic substances consisted of compounds with R_f 0.03, 0.45, and 0.80, and that of the nonphenolic substances of compounds with R_f 0.01, 0.22, and 0.34 [TLC on type KSK silica gel in the chloroform–methanol–benzene (10 : 4 : 1) system].

By preparative TLC on silica gel of the mixture of substances we have succeeded in isolating individual bases with R_f 0.22 and 0.45. The structure of the first of them has been established, and we have called it szovitsidine.

Szovitsidine, with the composition $C_{22}H_{29}O_5N$, has an absorption maximum in its UV spectrum at 280 nm, and in its mass spectrum the peaks of the strongest ions with m/e 387 (M^+, 100%), 372, 356, 344, 316, and 149. On the basis of the facts presented, szovitsidine can be assigned to compounds of the homomorphinandienone series [2-5]. The PMR spectrum of szovitsidine shows the signals of one N-methyl group (three-proton singlet at 2.32 ppm), four methoxy groups (three-proton singlets at 3.52, 3.74, 3.83, and 3.86 ppm), and three aromatic protons (at 6.50, 6.40, and 6.26 ppm). Consequently, it may be assumed that szovitsidine is one of the reduced forms of O-methylandrocymbine. The absence from the IR spectrum of the base of the absorption band of a carbonyl group excludes the structure of 5,6- and 8,15-dihydro-O-methylandrocymbines for it. Thus, the most probable structure for szovitsidine is 2,3,4,6-tetramethoxyhomomorphinandienol:



The presence in this compound of a secondary alcoholic hydroxy group in place of the carbonyl group characteristic for the known homomorphinandienones was confirmed by the IR spectrum of O-acetylszovitsidine, in which the absorption band of the carbonyl of an ester group appeared (1760 cm^{-1}).

We have also studied the base with R_f 0.56 isolated previously. It has the composition $C_{21}H_{27}O_5N$, mp 176-178°C (from ether and hexane), $[\alpha]_D$ $-140°$ (c 0.71; chloroform), mol. wt. 385 (mass spectrometrically). The UV spectrum has maxima at 238 and 280 nm (log ε 4.26 and 3.70). The IR spectrum of the base shows absorption bands of a carbonyl group conjugated with a double bond (1670, 1642, and 1610 cm^{-1}) and of the C=C bonds of an aromatic ring (1600 cm^{-1}). The NMR spectrum shows the presence in the alkaloid of an N-methyl group (2.32 ppm), and of three aromatic protons (one-proton singlets at 6.74, 6.27, and 6.22 ppm). The mass-spectrometric decomposition of the base formed ions with m/e 385 (M^+, 100%), 370 (M^+-15), 356 (M^+-29), 354 (M^+-31), and 342 (M^+-43). According to these spectral characteristics, the base with R_f 0.56 is identical with the known (−)-O-methylandrocymbine [6]. It must be mentioned that the information in the literature on the physical constants of O-methylandrocymbine is contradictory [3, 6, 7].

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