Korseveridine (0.18 g) was oxidized with chromium trioxide (0.18 g) in acetic acid (5 ml) as for the oxidation of korseveridinine. This yielded the monoketone korseveridinone with mp 122-124°C (aqueous acetone).

SUMMARY

1. Korseveriline, korseveridine, and the new alkaloid korseveridinine have been isolated from the ether-soluble alkaloids of the epigeal part of *Korolkovia severtzovii* Rgl., collected in Katrantau.

2. On the basis of the results of a study of the IR, NMR, and mass spectra of korseveridinine and its conversion into the known alkaloid korseveridinone, the structure and configuration of korseveridinine have been established as cevan-8(14)-ene-3α,15β-diol.

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THE STRUCTURE OF FLORIPAVIDINE

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The alkaloid floripavidine has been isolated previously [1] from *Papaver floribundum*, and for it the composition $C_{21}H_{29}O_5N$ and the developed formula $C_{17}H_{19}(N{-}CH_3)(OCH_3)\cdot(CH_2O_2)_2$ or $C_{18}H_{21}O_2(N{-}CH_3)\cdot(OCH_3)\cdot(CH_2O_2)$ have been proposed. The composition and properties of floripavidine differed from those of known alkaloids, but it could not be assigned to any definite group. Continuing a study of this base, we have determined its composition more accurately: $C_{24}H_{29}O_6N$.

The IR spectrum of the base shows absorption bands at (cm^{-1}) 3575 and 3430 (hydroxy group), 1595 and 1500 (aromatic ring) and 1000-1200 — a series of strong bands characteristic for glycoalkaloids. In the UV spectra there are maxima at (nm) 229 (inflection), 273, and 310 (log ε 4.37, 4.25, 3.45), which are characteristic for the aporphine alkaloids having no substituents in ring D [2]. In the NMR spectrum taken in deuterochloroform, in the strong-field region there are a three-proton doublet at 1.51 ppm (J = 5 Hz) from a >CH—CH_3 group and two three-proton singlets at 2.27 ppm (N—CH_3) and 3.54 ppm (OCH_3). Aromatic protons appear in the form of a four-proton multiplet in the 6.70-7.25 ppm region and at 8.45 ppm in the form of a broad one-proton doublet. At 5.95 ppm there is a one-proton singlet, and at 4.63 and 4.33 ppm two-proton multiplets. The mass spectrum of the base has contains, in addition to the peak of the molecular ion with m/e 427, strong peaks of ions with m/e

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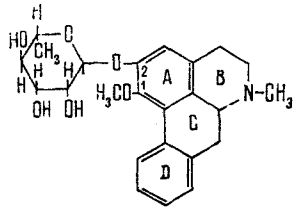
281, 280, 266, 250, and 238. The splitting out of a fragment with 146 amu from the molecular ion of the alkaloid and strong bands at 1000-1200 cm^{-1} in the IR spectrum permitted floripavidine to be assigned to the glycoalkaloids. Hydrolysis of the base with 0.2 N sulfuric acid yielded an aglycone with mp 194-195°C and L-rhamnose, which was identified by TLC, paper chromatography, and GLC. The mass spectrum of the aglycone had the peaks of ions with m/e 281 (M^+), 280, 266, 265, 250, and 238, which are characteristic for the aporphine alkaloids. Its NMR spectrum taken in deuterochloroform showed signals from a N–CH_3 group at 2.48 ppm and from a methoxy group at 3.50 ppm. Aromatic protons appear at 6.60 ppm in the form of a one-proton singlet, at 7.21 ppm in the form of a multiplet, and at 8.20 ppm in the form of a broadened one-proton doublet. The methylene and methine protons appear at 2.50-3.10 ppm. The result of analysis of the mass and NMR spectra, and also the empirical formula ($C_{18}H_{19}O_2H$) of the aglycone show that it is a disubstituted aporphine with a methoxy group at C_1 and a hydroxy group at C_2. This conclusion follows from the presence of the signal of a methoxy group at 3.50 ppm and of a one-proton singlet of an aromatic proton at 6.60 ppm [3]. In actual fact, in its melting point and spectral characteristics the aglycone was identical with N-methylasimilobine [4]. The L-rhamnose in floripavidine is attached to the aglycone by an α-glycosidic bond (Klyn's rule). Consequently, floripavidine is the first glycoalkaloid of the aporphine series and has the structure:



The alkaloid floribundine isolated previously from this plant [1] proved to be identical with N-methylasimilobine.

In a study of the plant *P. bracteatum* collected in the environs of Mineral'nye Vody (Caucasus), from the nonphenolic fraction we isolated a base with mp 240-241°C identical according to TLC and a mixed melting point with floripavidine.

EXPERIMENTAL

The mass spectra were taken on an MKh-1303 instrument fitted with a system for direct introduction into the ion source, the NMR spectrum on a JNM-4H-100/100 MHz instrument with HMDS as internal standard (δ scale), the UV spectra on a Hitachi spectrophotometer, and the IR spectra on a UR-10 instrument (tablets with KBr). Chromatography was performed in a thin layer of KSK silica gel in the benzene–ethanol (4:1) system.

Floripavidine formed transparent prisms with mp 241-242°C (ethanol), $[\alpha]_D$ −156° (c 1.6; methanol).

Hydrolysis of Floripavidine. A mixture of 0.034 g of floripavidine and 3 ml of 0.2 N sulfuric acid was heated in the water bath for 5 h. The acid solution after cooling was neutralized with barium carbonate. The precipitate that deposited was separated off and the filtrate was extracted several times with chloroform. After the solvent has been distilled off, the aglycone was obtained, with mp 194-195°C, $[\alpha]_D$ −220.6° (c 0.25, chloroform). The aqueous layer was evaporated and the residue was identified as L-rhamnose by TLC paper chromatography, and GLC.

SUMMARY

From a study of the physical and chemical properties of the base itself and of the product of its hydrolysis, the structure of floripavidine has been established as N-methylasimilobine-2-O-α-L-rhamnoside.

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