STRUCTURE OF KORSEVERIDININE

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Continuing an investigation of the alkaloids of the epigeal part of *Korolkovia severtzovii* Rgl. [1], by separating the combined ether-soluble alkaloids we have isolated korseveriline, korseveridine [2, 3], and a new alkaloid korseveridinine, with the composition $C_{27}H_{43}NO_2$ (I).

The IR spectrum of (I) showed absorption bands at (cm^{-1}) 3380 and 3150 (OH), 2990-2820 ($-CH_3$, $-CH_2-$), and 2778 (trans-quinolizidine), and the fingerprint region of the spectrum of (I) was similar to that of korseveridine [3]. The NMR spectrum of (I) had the following resonance signals: singlet at 0.78 ppm (19-CH_3) and doublets at 0.81 ppm (21-CH_3) and 0.86 ppm (27-CH_3).

The NMR spectrum of (I) shows no signal from an olefinic proton, but in a weak sulfuric acid solution korseveridinine instantaneously decolorized a solution of potassium permanganate, which showed the presence of a double bond. The double bond in korseveridinine, like that in korseveridine, is not hydrogenated in acetic acid in the presence of platinum black [3]. The mass spectrum of (I) shows the peaks of ions with m/e 98, 111 (100%), 112, 124, 149, 150, 162, 164, 178, 179, 195, 203, 356 (M–29), (M–18), (M–15), 413 M^+, which are characteristic for C-nor-D-homosteroid alkaloids of the cevine group [4, 5].

Acetylation of korseveridinine with acetic anhydride in pyridine yielded diacetylkorseveridinine (II), the IR spectrum of which showed absorption bands at 1738, 1250, and 1230 cm^{-1} (ester C=O). The NMR spectrum of (II) contained signals from the protons of 19-CH_3, 21-CH_3, and 27-CH_3 groups (0.74, 0.79, 0.84 ppm) of the methyls of two acetyl groups (1.93 and 2.01 ppm), and of protons geminal to acetoxy groups at 5.05 and 4.80 ppm).

When korseveridinine was oxidized with chromium trioxide in acetic acid in the presence of pyridine we succeeded in isolating from the reaction products a monoketone derivative of korseveridinine with mp 122-124°C (III), which proved to be identical with an authentic sample of korseveridinone [3] obtained by the oxidation of korseveridine under the same conditions (according to R_f values, mixed melting point, and IR and mass spectra).

The identity of (III) with korseveridinone confirmed the fact that korseveridinine has the heterocyclic skeleton of cevanine and that two secondary hydroxy groups are present at C_3 and C_{15} (the latter being β-oriented) and there is a double bond between C_8 and C_{14}.

Thus, korseveridinine differs from korseveridine by the configuration of the hydroxy groups at C_3, and the linkage of rings A/B, D/E, and E/F in korseveridinine is the same as in korseveridine and the 21-CH_3 and 27-CH_3 groups have the α-equatorial orientations [6, 7].

In the NMR spectrum of (II), a multiplet from protons geminal to acetoxy groups at 4.80 and 5.05 ppm shows that the acetoxy group at C_3 has the α- and that at C_{15} the β-axial orientation and, consequently, in korseveridinine the hydroxy group at C_3 has the α- and that at C_{15} the β-axial orientation [8, 9].

On the basis of the facts presented above, it may be concluded that korseveridinine has the most probable structure and configuration of cevan-8(14)-ene-3α,15β-diol (I):

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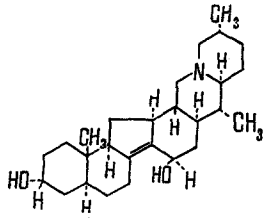

EXPERIMENTAL

The IR spectra (KBr) were taken on a UR-20 spectrophotometer, the NMR spectra on a JNM-4H-100/100 MHz instrument [(I) in $CDCl_3$ + CD_3OD, and (II) in $CDCl_3$] with HMDS as internal standard (the values are given in the δ scale), and the mass spectra on an MKh-1303 instrument fitted with a glass system for direct introduction into the ion source.

For TLC we used KSK silica gel (100 μ) and the following solvent systems: 1) ethyl acetate–chloroform–methanol (15:10:3) and 2) chloroform–methanol (10:0.7). The revealing agent was Dragendorff's solution.

Isolation of the Combined Alkaloids. The dry comminuted epigeal part of *K. sewertzovii* collected on April 24, 1975 in Katrantau, Kirghiz SSR, (54 kg) was moistened with an 8% solution of ammonia, and the alkaloids were exhaustively extracted with chloroform 12 times. The alkaloids were isolated from the concentrated chloroform extract with 10% sulfuric acid. The sulfuric acid solution was made alkaline with ammonia and the mixture of bases was extracted with ether (279.7 g) and chloroform (213.5 g). The total yield of alkaloids was 493.2 g (0.91% of the weight of the dry plant).

Korseveriline. The combined ether-soluble alkaloids (279.7 g) were treated with acetone, which led to the precipitation of 77.5 g of a mixture of crystals with mp 229-241°C. The mixture was dissolved in chloroform and separated according to basic strengths into 19 fractions by extraction with 34-ml portions of 1% sulfuric acid. Fractions 1-3 were combined and, after treatment with methanol, korseveriline was obtained with mp 240-242°C.

Korseveridine and Korseveridinine. Fractions 16 and 17 were also combined (5.31 g), chromatographed on a column of alumina, and eluted with chloroform and chloroform–methanol (10:0.5). The chloroform–methanol eluate yielded korseveridine with mp 290-292°C (methanol), R_f 0.27 (system 1). The chloroform eluate (1.18 g) was rechromatographed on a column of silica gel, and elution was carried out with chloroform and chloroform–methanol (10:0.5). The last chloroform–methanol (10:0.5) eluates yielded 0.98 g of korseveridinine with mp 282-284°C (methanol), $[\alpha]_D$ −39.5° (c 0.582; chloroform–methanol (1:1)); R_f 0.21 (system 1); $C_{27}H_{43}NO_2$; M^+ 413.

Diacetylkorseveridinine. A mixture of 0.18 g of korseveridinine, 6 ml of acetic anhydride, and 3 ml of pyridine was kept at room temperature for three days. Then the solution was evaporated in vacuum and the residue was dissolved in 5% sulfuric acid. The acid solution was made alkaline with ammonia and extracted with chloroform, giving amorphous diacetylkorseveridinine with R_f 0.74 (system 2); M^+ 497.

Oxidation of Korseveridinine and of Korseveridine. A solution of 0.22 g of chromium trioxide in 5 ml of 80% acetic acid was added together with four drops of pyridine to a solution of 0.24 g of korseveridinine in 4 ml of acetic acid. The mixture was heated on the water bath for 40 min and evaporated in vacuum, the residue was dissolved in water, and the solution was made alkaline with ammonia and extracted with chloroform. The oxidation product was chromatographed on a column of alumina and was eluted with chloroform–methanol (10:0.2). This gave a monoketone derivative of korseveridinine with mp 122-124°C (aqueous acetone); R_f 0.31 (system 1).

IR spectrum, ν_{max}, cm^{-1}: 3460 (OH), 2950-2860, 1465-1430 (–CH_3, –CH_2–); 1713 (C=O) and 2770 cm^{-1} (trans-quinolizidine).

Mass spectrum: m/e 98, 111, 112, 124, 149, 162, 164, 178, (M–29), (M–15), 411 M^+.

The monoketone derivative of korseveridinine was shown to be identical with the monoketone obtained by oxidizing korseveridine (mixed melting point and IR spectrum).

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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