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STRUCTURE OF KORSEVERILINONE

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From the combined ether-extracted material of the epigeal part of *Korolkowia sewerzowii* a new base has been isolated — korseverilinone with mp 222-223°C $[\alpha]_D$ $-18.8°$, $C_{27}H_{42}NO_3$. On the basis of the results of a study of the IR, PMR, and mass spectra of korseverilinone and also its conversion into the known alkaloid korseveriline it has been established that korseverilinone has the structure of 3α, 14α-dihydroxycevanin-6-one.

Continuing a study of the epigeal part of *Korolkowoa sewerzowii* Rgl., gathered in the Fergana Province [1, 2], from the combined ether-extracted material we have isolated by column chromatography a new alkaloid — korseverilinone with mp 222-223°C $[\alpha]_D - 18.8°$, $C_{27}H_{43}NO_3$ (I).

Korseverilinone is a saturated tertiary base the IR spectrum of which exhibits absorption bands at (cm^{-1}) 3450 (OH), 2955-2860 and 1465 (CH_3-; $-CH_2-$), 2775 (trans-quinolizine), and 1710 (C=O). The mass spectrum of (I) has the peaks of ions with m/z 98, 111 (100%), 112, 124, 125, 149, 164, 166, 373, 396, 400, $(M-18)^+$, $(M-17)^+$, $(M-15)^+$, 429 M^+, which are characteristic for the C-nor-D-homosteroid alkaloids of the cevine group [3-5]. The PMR spectrum of (I) shows: a three-proton singlet at 0.66 ppm (19-CH_3), unresolved signals from the protons of secondary C-methyl groups in the form of singlets at 0.83 ppm (21-CH_3 and 27-CH_3), and a multiplet at 4.08 ppm (HC-OH).

The acetylation of (I) gave monoacetylkorseverilinone (II) in the IR spectrum of which absorption bands appear at (cm^{-1}) 3450, 1025 (OH), 2770 (trans-quinolizine), 1740, 1250 (ester C=O), and 1715 (C=O).

The PMR spectrum of (II) contained signals from the protons of C-methyl groups at 0.67 ppm (19-CH_3), and 0.83 ppm (21-CH_3 and 27-CH_3), a three-proton singlet from an acetoxy group at 1.96 ppm ($-OCOCH_3$), and a multiplet at 5.05 ppm (H, HC$-OCOCH_3$).

The reduction of (I) with sodium tetrahydroborate formed dihydrokorseverilinone (III), identical with korseveriline (mixed melting point, IR spectrum, R_f) [3]. The oxidation of (I) with chromium trioxide in acetic acid gave a diketone identical with korseverilinedione [3]. The identity of dihydrokorseverilinone with korseveriline and of the diketone with korseverilinedione shows that korseverilinone is a monoketone of korseveriline [3].

It remained to determine the position of the carbonyl group in the korseverilinone molecule. In the PMR spectrum of diacetylkorseveriline the multiplet at 4.86 ppm from the protons germinal to the acetoxy groups relates to $C_6\alpha$-H and that at 5.03 ppm to $C_3\beta$-H [3].

In acetylkorseverilinone, the proton geminal to the acetoxy group gives a signal at 5.05 ppm. Consequently, in the korseverilinone molecule the hydroxy group is present at C_3 and the carbonyl group at C_6. This is confirmed by the 23-Hz difference in the chemical shifts of the 19-CH_3 group between diacetylkorseverilinone and acetylkorseverilinone [3, 6]. According to these results, korseverilinone has the structure and configuration of 3α, 14α-dihydroxycevanin-6-one (I).

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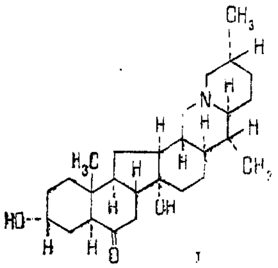

I

EXPERIMENTAL

IR spectra (KBr) were recorded on a UR-20 spectrometer, PMR spectra on a JNM-4H-100/100 MHz instrument (in $CDCl_3$) with HMDS as internal standard (the values are given in the δ scale), and mass spectra on a MKh-1303 instrument fitted with a glass system for direct introduction into the ion source. For TLC, Al_2O_3 was used with the chloroform—methanol (10 : 0.1) system.

Isolation of Korseverilinone. The combined ether-extracted alkaloids (60 g) were chromatographed on a column of silica gel (KSK, 250 μ, 130 × 4 cm). Elution was carried out with benzene and with benzene—methanol (100 : 0.5; 100 : 1, 100 : 3; 10 : 1; 10 : 3; 10 : 5, 10 : 8; 1 : 1; and 1 : 2).

Similar fractions, as found by TLC, were combined, giving 14 combined fractions. The fourth combined fraction (0.26 g), when rechromatographed on a column of Al_2O_3 (with chloroform as eluent) yielded korseverilinone with mp 222-223°C (acetone), $[\alpha]_D - 18.8°$ (c 0.478; chloroform), R_f 0.25.

Acetylkorseverilinone. A mixture consisting of 35 mg of korseverilinone, 1.5 ml of pyridine, and 2 ml of acetic anhydride was kept at room temperature for 2 days. After elimination of the pyridine, the residue was dissolved in 5% sulfuric acid, the solution was made alkaline with ammonia, the alkaloids were extracted with chloroform, and the solvent was distilled off. This gave amorphous monoacetylkorseverilinone with R_f 0.93.

Mass spectrum: m/z 98, 111 (100%), 112, 114, 125, 149, 150, 164, 166, 178, 410, 411, 412 $(M - 43)^+$, $(M - 42)^+$, $(M - 29)^+$, $(M - 15)^+$, 471 M^+.

Dihydrokorseverilinone. A solution of 56 mg of korseverilinone in 10 ml of methanol was treated with 200 mg of sodium tetrahydroborate for 30 min. The reaction mixture was kept at room temperature for 30 min. The solvent was distilled off, and the residue was decomposed with water and extracted with $CHCl_3$. Treatment of the dry extract with acetone yielded dihydrokorseverilinone with mp 239-241°C, R_f 0.13, M^+ 431, identical with korseveriline.

Oxidation of Korseverilinone. Korseverilinone (27 mg) was treated with 2 ml of 80% acetic acid and 20 mg of chromium trioxide. The reaction was performed in a similar manner to the oxidation of korseveriline [3]. This gave a diketone identical with korseverilinedione, R_f 0.47.

SUMMARY

1. A new alkaloid, korseverilinone, has been isolated from the epigeal part of *Korolkowia sewerzowii* Rgl. collected in the Fergana Province.

2. On the basis of the results of a study of IR, PMR, and mass spectra of korseverilinone and also of a passage to the known alkaloid korseveriline, it has been established that korseverilinone has the structure of 3α,14α-dihydroxycevanin-6-one.

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