KORSINAMINE — A NEW ESTER ALKALOID FROM *Korolkowia sewerzowii*

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Continuing the separation of the mixture of alkaloids from the epigeal part of *Korolkowia sewerzowii* Rgl. [1], we have isolated korsine [2-4] and a new alkaloid — korsinamine with mp 155-158°C, $[\alpha]_D$ +68.2°, composition $C_{29}H_{45}NO_4$ (I).

Korsinamine is a tertiary unsaturated base. Its IR spectrum shows absorption bands at (cm^{-1}) 3440 (OH), 2960-2860, 1470, 1446 (CH_3; $-CH_2$), 2790 (trans-quinolizidine), 1738, 1248 (ester C=O), and 1650 (C=C).

The NMR spectrum of (I) has singlets at (ppm) 1.02 (3H, 19-CH_3) and 2.01 (3H, $OCOCH_3$), doublets at 0.80 from the protons of two secondary methyl groups, and a multiplet at 4.94 (H, $\underline{H}C{-}OCOCH_3$). The mass spectrum of korsinamine has the peaks of ions with m/e 110, 111, 137, 149, 167, 170, 178, 181, 220, 222, 234, 400 $(M-71)^+$, 411 $(M-CH_3COOH)^+$, 428 $(M-43)^+$, 429 $(M-42)^+$, $(M-29)^+$, $(M-15)$, 471 M^+ (100%).

By saponifying korsinamine we obtained an amino alcohol with the composition $C_{27}H_{43}NO_3$ (II), mp 236-238°C, identical with korsine (melting point, IR spectrum) [2-4], and acetic acid. The NMR spectrum of (II) has a singlet at 1.0 ppm (3H, 19-CH_3) and doublets at 0.81 ppm (3H, 21-CH_3) and 0.87 ppm (3H, 27-CH_3).

The acetylation of korsinamine gave a diacetyl derivative (III) identical with an authentic sample of triacetylkorsine [3]. The NMR spectrum of (III) had singlets at (ppm) 1.02 (3H, 19-CH_3), 1.95 (3H, $OCOCH_3$), 1.98 (3H, $OCOCH_3$), and 2.01 (3H, $OCOCH_3$), doublets at 0.82 (3H, 21-CH_3) and 0.82 (3H, 27-CH_3), and multiplets at 4.98 (2H, $\underline{H}C{-}OCOCH_3$) and 4.70 (H, $\underline{H}C{-}OCOCH_3$).

The identity of the amino alcohol with korsine and also of diacetylkorsinamine with triacetylkorsine confirmed that korsinamine was a monoacetyl derivative of korsine [4]. It remained to determine the position of the acetoxy group in the korsinamine molecule.

In triacetylkorsine, the signals of the protons geminal to the acetoxy groups are located at 4.65 ppm ($1H_a$, $C_3{-}H$) and 4.96 ppm ($2H_e$, $C_6{-}H$; $C_{23}{-}H$) [4, 5].

In korsinamine, the proton geminal to the acetoxy group appears at 4.94 ppm. Consequently, the acetic acid residue in the korsinamine molecule may be present at C_6 or C_{23}.

A comparison of the chemical shifts of the protons of the secondary and tertiary methyl groups showed that on passing from diacetylkorsinamine to korsine a considerable downfield shift (5 Hz) was observed in the chemical shifts of the protons of the 27-CH_3 groups. From this is may be assumed that in the korsinamine molecule the acetic acid residue is located at C_{23}. This is confirmed by the fact that in the mass spectrum of korsine there is the strong peak of an ion with m/e 128 which is formed by the scheme described previously [3] from ring F and shows the presence of a hydroxy group at C_{23}. In the mass spectra of (I) and (III) the peak of the ion with m/e 128 is absent, and in place of it there is a peak with m/e 170, i.e., the fragment with m/e 128 has been increased by 42 m.u. (acetic acid residue).

According to what has been said above, korsinamine has the structure of 23β-O-acetylkorsine

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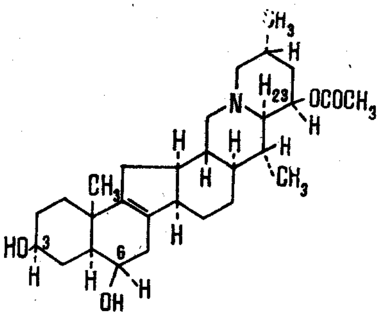

EXPERIMENTAL

For TLC we used KSK silica gel (100 mμ) and the chloroform—methanol (10:0.7) system. The IR spectra were taken in KBr on a UR-20 spectrophotometer the NMR spectra on a JNM-4H-100/100 MHz instrument [(I) in $CDCl_3$; (II) and (III) in $CDCl_3$ + CD_3OD; internal standard HMDS (values given in the δ scale)], and the mass spectra on a MKh-1303 instrument fitted with a glass system for the direct introduction of the sample into the ion source.

Korsine. Previously, in the separation of 35 g of the combined-soluble bases on a column we obtained 29 fractions [1]. The combined fractions 16-24 were treated with methanol, which gave korsine with mp 236-238°C (methanol).

Korsinamine. The residue from the korseveridine mother liquor (13 g) [1] was dissolved in acetone, the solution was passed through a column of silica gel, and the column was washed with acetone—benzene (3:1). The elutate was collected in 60 20-ml fractions.

The material from fractions 42-60 (4.8 g) was dissolved in chloroform and chromatographed on a column of silica gel with elution by chloroform. The eluate was collected in 41 50-ml fractions. The combined fractions 1-6 were rechromatographed on a column of silica gel and eluted with ether—methanol (20:1). The eluate was distilled off and the dry residue was treated with acetone—hexane (1:1). Korsinamine precipitated with 155-158°C, $[\alpha]_D$ +68.2° (c 1.202; chloroform), R_f 0.4; M^+ 471.

Saponification of Korsinamine. A solution of 0.15 g of korsinamine in 5% methanolic caustic potash was heated for 2 h. The methanol was evaporated off in vacuum. Water was added to the residue and the reaction product was extracted with chloroform. After the solvent had been distilled off, the residue was treated with methanol, which led to the deposition of crystals having mp 236-238°C (methanol), $C_{27}H_{43}NO_3$, R_f 0.07, identical with korsine.

In alkaline solution after the separation of korsine, acetic acid was detected by paper chromatography [6].

Acetylation of Korsinamine. A mixture of 0.1 g of korsinamine, 1 ml of pyridine, and 2 ml of acetic anhydride was kept at room temperature for three days. Then the solution was evaporated in vacuum. The residue was dissolved in 5% sulfuric acid. The acid solution was made alkaline with 25% ammonia solution and extracted with chloroform. This gave diacetylkorsinamine having R_f 0.76; M^+ 555.

SUMMARY

1. Korsine and the new alkaloid korsinamine have been isolated from the epigeal part of *Korolkowia sewerzowii* Rgl.

2. On the basis of the results of a study of the IR, NMR, and mass spectra of korsinamine and also of passage to the known alkaloid korsine, the structure of korsinamine has been established as 23β-O-acetylkorsine.

LITERAUTRE CITED

1. K. Samikov, R. Shakirov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 367 (1976).
2. R. N. Nuriddinov, A. I. Saidkhodzhaev, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 61 (1969).
3. R. N. Nuriddinov, A. I. Saidkhodzhaev, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 161(1968).
4. R. N. Nuriddinov, Author's Abstract of Doctoral Dissertation, Tashkent (1970).
5. P. F. Zürcher, Helv. Chim. Acta, 46, 2054 (1963).
6. K. Samikov, R. Shakirov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 790 (1971).