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STRUCTURE AND CONFIGURATION OF KORSININE

R. N. Nuriddinov, A. I. Saidkhodzhaev, and S. Yu. Yunusov

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The combined alkaloids isolated by extraction from the bulbs of Korolkowia sewerzowii [1] (collected in the Chatkal valley) were eluted from a column (h = 70, d = 15 cm) of alumina (1 : 50) with benzene, a mixture of benzene and chloroform (9 : 1), a mixture of chloroform and benzene (9 : 1), and chloroform. By separating the fractions of the mixture of bases with respect to their basicity and their solubility in organic solvents, we isolated korsine (1), korsevine (2), korseveriline (3), korseverine (4), and a new base—korsinine (I) with mp 164–165° C (from acetone), $[\alpha]_D$ +105° (c 0.77; methanol), composition $C_{27}H_{43}O_2N$. Its IR spectrum: ν_{max} 3410 and 1015–1070 cm^{-1} (OH), 2780 cm^{-1} (trans-quinolizidine), 2920–2870 and 1450 cm^{-1} ($C-CH_3$), and 1650 cm^{-1} (C=C). The alkaloid gives a hydrochloride with mp 238–239° C. The hydrogenation of korsinine in the presence of a Pt catalyst gave dihydrokorsinine (II) with mp 226–228° C (acetone—water), the IR spectrum of which lacked the absorption band of a double bond. When korsinine was oxidized with chromic acid, the diketone korsininedione was formed. The UV spectrum of the diketone—λ_{max} 252, 303 mμ (log ε 2.6, 2.19)—is characteristic for diketones.

The action on korsinine of acetic anhydride in the presence of pyridine gave diacetylkorsinine (III). The IR spectrum of (III) had bands at 1025, 1240, and 1730 cm^{-1} and lacked the absorption bands of hydroxy groups. Thus, the two hydroxy groups in korsinine are secondary. Korsinine was unchanged by treatment with periodic acid.

The mass spectrum of korsinine has peaks of ions with m/e 97, 98, 111, 112, 395 (M-18), 398 (M-15), and 413 (M^+). The figures for the NMR spectra of (I), (II), and (III) are given in the table.

Chemical Shifts, τ

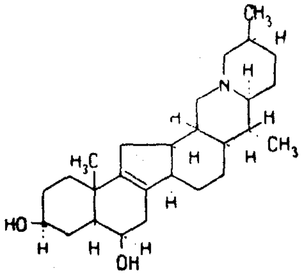
Substance	(s), 3H $C-19\ CH_3$	(d), 3H $C-21\ CH_3$	(d), 3H, $C-27\ CH_3$	(s), 6H $OCOCH_3$	(m), H, 3α—H	(m), H, 6α—H
(I)	9.01	9.14	8.96	—	—	—
(II)	9.04	9.14	8.97	—	—	—
(III)	9.01	9.12	8.97	8.04	5.38	5.05

Note: s—singlet, d—doublet, m—multiplet

A consideration of the features of the mass and NMR spectra of korsinine and its derivatives permits the heterocyclic skeleton of imperialine (5) to be proposed for korsinine. The absence from the NMR spectrum of korsinine of a signal from an olefinic proton and the displacement of the signal from the C-19 methyl group to a stronger field when korsinine was converted into the dihydro compound shows that the double bond in korsinine is in position C_8-C_9.

The presence in the IR spectra of korsinine and diacetylkorsinine of absorption bands at 1052 and 1025 cm^{-1}, respectively, shows that one hydroxy group of the alkaloid is located at C_3 and has the β-orientation. This is confirmed by the multiplet at 5.38 τ from the 3α-H in the NMR spectrum of diacetylkorsinine (6).

The positions C_7 and C_{11} are excluded for the secondary hydroxy group by the UV spectrum of the diketone of korsinine, since it is not an α,β-unsaturated ketone. By comparing the values of the chemical shifts from the C-19 methyl groups in (I), (II), and (III) and in the conversion products of imperialine (7), a position at C_6 and the β-orientation may be proposed for the second hydroxy group, and this is verified by the presence in the NMR spectrum of diacetylkorsinine of a multiplet at 5.05 τ from the 6α-H. From the chemical shifts, the 21-methyl group has the α-orientation and the 27-methyl group the β-orientation. Thus, korsinine has the following most probable structure and configuration:



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Institute of the Chemistry of Plant Substances, AS UzSSR

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ALKALOID CONTENT OF SOME PLANTS OF THE FAMILY LABIATAE

T. P. Pulatova

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We have studied 30 species of plants of the family Labiatae growing in Uzbekistan for their alkaloid content; 15 of them gave a positive reaction for alkaloids. As a result of the quantitative determination and isolation of nitrogen bases by the chromatographic method (on a column of neutral alumina), we obtained two fractions. The first fraction (elution of the bases with 10–20% solutions of ethanol in chloroform), consisted of stachydrine and the second (elution with 20–40% solutions of ethanol in chloroform), consisted of liquid bases.

The amounts (%) of stachydrine were: in Marrubium alternidens Rech., 1.16; in Sideritis montana L., 0.82; in Eremostachys speciosa Rupr., 0.35; in Lamium album L. (white deadnettle), 2.01; in Leonurus turkestanicus V. Krecz et Rupr., 1.5; in Lagochilus setulosus Vved., 1.3; in L. Pubesceus Vved., 0.71; in L. inebrians Bge., 0.52; in L. platycalyx Schrenk., 1.45; in Stachys betoniciflora Rupr., 0.74; in S. hissarica Rgl., 0.47; and in Scutellaria immaculata Nevsci ex Juz, traces.

The amount of liquid bases in these plants varied from 0.14 to 3.29%, apart from Lagochilus platycalyx Schrenk., where they were absent.

In the qualitative investigation of the bases isolated by the method of descending chromatography on paper of type FN-3 (medium speed) a base was found with R_f 0.33 in system 1 [1-butanol—acetic acid—water (4 : 1 : 5)] and R_f 0.88 in system 2 (15% acetic acid). This base was shown to be identical with an authentic sample of stachydrine. A base with R_f 0.22 was shown chromatographically to be identical with choline. The latter was found in six plants.

A base with R_f 0.37 in system 1 was found in all the plants except L. platycalyx and one with R_f 0.43 in system 1 in six plants.

Characteristic of Lagochilus Bge. from the section Inermus is a base with R_f 0.9 (system 1) and 0.8 (system 2)—a white crystalline substance readily soluble in methanol, ethanol, and acetone, and sparingly soluble in water, not fluorescing in UV light, mp 105° C. The study of this base is continuing.

Thus, in an investigation of plants of the family Labiatae we have found stachydrine, choline, and unknown bases.

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Tashkent Pharmaceutical Institute