Preliminary information on the analysis of the products of the hydrolysis of the methylated glycoside has enabled us to show that it contains three monomethyl sugars, which indicates an unusually high degree of branching of the carbohydrate components of saponaside D.

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THE STRUCTURE OF CLEMATOSIDE A'

V. Ya. Chirva and V. P. Konyukhov

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In the present paper we report the determination of the structure of a compound that we have found in Clematis manshurica Rupr. [1-3]—clematoside A' [mp 176-179° C, $[\alpha]_D^{20}$ −31° (c 5; CH_3OH); acetate with mp 149-151° C, $[\alpha]_D^{20}$ −1.9° (c 5; CH_3OH)], which is a pentaoside of oleanolic acid.

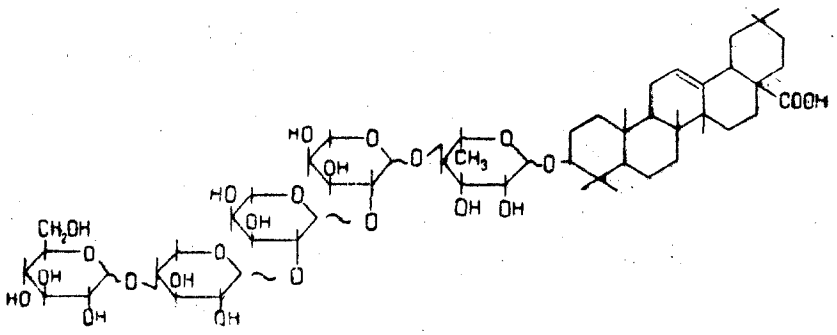
The saponin was isolated by chromatography on silica gel by the method described previously [1, 3]. When clematoside A' was subjected to acid hydrolysis, glucose, xylose, arabinose, and rhamnose (1 : 1 : 2 : 1) were identified in the carbohydrate fraction. The monosaccharides were determined quantitatively by the paper chromatography of the hydrolysate of the glycoside and the subsequent photocolorimetric determination of the optical density of the eluates of the spots obtained on the chromatograms.

The molecular weight of the saponin (1170) was determined from the yield of genin. Hydrolysis of the glycoside after its treatment with diazomethane permitted the isolation of methyl oleanolate, which shows the absence of a carbohydrate chain from the carboxy group of the aglycone. This was also confirmed by the treatment of clematoside A' with alkali, which left the saponin unchanged.

The chromatographic behavior, IR spectra, and specific rotation, of clematoside A' was identical with that of the glycoside obtained by the alkaline hydrolysis of clematoside A. A similar comparison of their acetates showed that the latter were identical.

When methylated clematoside A' ($[\alpha]_D^{20}$ −14°) was decomposed, 1 mole each of 2,3,4,6-tetra-O-methyl-D-glucose, 2,3-di-O-methyl-D-xylose, and 2,3-di-O-methyl-L-rhamnose and 2 moles of 3,4-di-O-methyl-L-arabinose were identified by gas-liquid chromatography. This was also confirmed by paper and thin-layer chromatography. The methylated monosaccharides proved to be identical with the methylated sugars of the glycoside erythrodiol obtained from methylated clematoside A after its decomposition with lithium aluminum hydride. The results of methylation agree with those of the periodate oxidation of clematoside A'.

Thus, the carbohydrate moiety of clematoside A' is attached to the hydroxy group at C_3 of the aglycone and is identical with the corresponding carbohydrate chain of clematoside A. There is no doubt that clematoside A' is a biogenetic precursor of the saponins found in the Manchurian ground clematis.



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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: