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ALKALOIDS OF Korolkowia sewerzowii. STRUCTURE OF KORSELIDINE

K. Samikov, R. Shakirov, and S. Yu. Yunusov

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Two new alkaloids have been isolated from the combined alkaloids of the epigeal part of <u>Korolkowia sewerzowii</u> Regel.: a base with mp 272-274°C (methanol) and the alkaloid korselidine. As a result of a study of the chemical and physical properties of the alkaloid itself and of the products of its transformation, the structure and partial configuration of 3β , 6β , 20β -trihydroxy- 27α -methylcevanine has been established for korselidine.

Continuing an investigation of the alkaloids of the epigeal part of <u>Korolkowia sewer-zowii</u> [1], on the separation of the mother liquor from korseveridine with a citrate-phosphate buffer solution a base with mp 272-274°C was isolated and also the new alkaloid korselidine with the composition $C_{27}H_{45}NO_3$ (I), the structure of which is considered in the present paper.

The IR spectra of (I) showed absorption bands at (cm^{-1}) 3450 (hydroxy groups), 3000-2810, 1450 (-CH₃; -CH₂-) and 2765 (trans-quinolizidine). The mass-spectrometric fragmentation of korselidine took place similarly to that of dihydroimperialine: m/z 98, 111, 112 (100%), 113, 124, 125, 149, 150, 154, 386, 387, 412, 414, 416, 430, 431 M⁺. The PMR spectrum of (I) contained the singlets at (ppm) 0.95 (3H, 19-CH₃) and 1.02 (3H, 21-CH₃), a doublet at 0.80 (3H, 27-CH₃), and multiplets at 3.41 and 3.73 (2H, H-C-OH).

The acetylation of (I) with acetic anhydride in pyridine gave diacetylkorselidine (II), M^+ 515. The IR spectrum of (II) contained absorption bands at (cm⁻¹) 3500 (OH), 2780 (transquinolizidine), and 1740-1250 (ester C=O). In the PMR spectrum of (II) there were singlets at (ppm) 0.93 (3H, 19-CH₃), 1.05 (3H, 21-CH₃), and 1.95 (6H, OCO-CH₃), a doublet at 0.78 (3H, 27-CH₃), and multiplets at 4.68 and 4.93 (2H, CH-OCOCH₃).

When korselidine was oxidized with chromium trioxide, the diketone korselidinedione (III) was isolated the IR spectrum of which showed absorption bands of a carbonyl group at 1710 cm^{-1} and of a hydroxy group at 3450 cm^{-1} .

On the basis of the facts given above it could be assumed that korselidine had a cevanine skeleton with one tertiary and two secondary hydroxy groups. A comparison of the values of the chemical shifts (CSs) of the signals from the 19-CH₃ protons in (I-III) with those of severtzidine [1], sevedine [2], and dihydroimperialine [3-5] showed that secondary hydroxy groups were present in rings A and B, being β -equatorial at the C₃ position and β -axial at the C₆ position. This was confirmed by the presence in the PMR spectrum of diacetylkorselidine of a multiplet at 4.68 ppm from C-3 α H and 4.93 ppm for C-6 α H [6, 7].

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Judging from the values of the CSs of the protons of the secondary and tertiary methyl groups in korselidine the A/B and B/C are trans-linked, the $21-CH_3$ and $27-CH_3$ groups have the α -orientation, and the tertiary hydroxy group at C_{20} , the β -orientation [8]. The presence of a Bohlmann band [9] in the IR spectrum of korselidine indicated the trans-linkage of rings E/F.

Thus, korselidine has the structure and partial configuration of 3β , 6β , 20β -trihydroxy-27 α -methylcevanine (I).



EXPERIMENTAL

IR spectra (KBr) were taken on a UR-20 instrument, PMR spectra on a JNM-4H-100/100 MHz instrument ((I) in $\text{CDCl}_3 + \text{CD}_3\text{OD}$, and (II) and (III) in CDCl_3 , with HMDS as internal standard; values given in the δ scale), and mass spectra on a MKh-1310 instrument. TLC was performed on Al_2O_3 with the solvent system chloroform-methanol (10:0.5), the spots being revealed with the Dragendorff reagent.

Isolation of a Base with mp 272-274°C and Korselidine. The mother liquor from korseveridine (17 g) [1] was dissolved in benzene and separated according to basicity by citrate-phosphate buffer solutions with pH 8-3 (pH interval of one unit). The fractions at pH 6.0 and 5.0 were combined (1.66 g) and were treated with methanol. This gave a base with mp 272-274°C (methanol), $R_f 0.42$, $[\alpha]_D$ -75° (c 0.12; ethanol). The mother liquor from this base was combined with the fraction at pH 4.0 (5 g) and chromatographed on a column of silica gel with elution by ether and by chloroform-methanol (20:1). The first 600 ml of the ethereal eluate yielded korselidine with mp 276-278°C (acetone), $[\alpha]_D$ -53° (c 0.3; ethanol).

<u>Diacetylkorselidine</u>. A mixture of 0.07 g of korselidine, 1 ml of pyridine, and 1 ml of acetic anhydride was kept at room temperature for three days and was then evaporated in vacuum. The residue was dissolved in 5% sulfuric acid, the acid solution was made alkaline with ammonia, and the reaction product was extracted with chloroform. This gave diacetylkorselidine with R_f 0.85. Mass spectrum: m/z 98, 111, 112 (100%), 124, 149, 150, 154, 156, 394, 412, 470, 471, 472, 515 M⁺.

<u>Korselidinedione.</u> A mixture of 0.08 g of korselidine in 2 ml of pyridine and 0.04 g of chromium trioxide in 2 ml of pyridine with one drop of water was heated in the water bath for 3 h and was then evaporated in vacuum. The residue was dissolved in 10 ml of 5% sulfuric acid, and the acid solution was made alkaline with ammonia. The reaction product was extracted with chloroform and the extract was washed several times with water. The residue after the chloroform had been distilled off yielded korselidinedione with R_f 0.80. PMR spectrum of (III): singlets at 0.88 ppm (3H, 19-CH₃) and 1.01 ppm (3H, 21-CH₃), and a doublet at 0.79 ppm (3H, 27-CH₃). Mass spectrum: m/z 98, 111, 112 (100%), 124, 149, 150, 154, 156, 382, 398, 408, 410, 412, 416, 427 M⁺.

SUMMARY

A base with mp 272-274°C and the alkaloid korselidine have been isolated from the total alkaloids of the epigeal part of <u>Korolkowia sewerzowii</u> Regel. As a result of the study of the chemical and physical properties of the alkaloid itself and of the products of its transformation, the structure and partial configuration of korselidine has been established as $3\beta, 6\beta, 20\beta$ -trihydroxy- 27α -methylcevanine.

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PHYTOCHEMICAL INVESTIGATION OF Datura innoxia

S. F. Aripova and S. Yu. Yunusov

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The alkaloids in the various organs of the plant Datura innoxia cultivated in the Darmina sovkhoz [collective farm], Chimkent province, Kazakh SSR, have been studied. Ten individual bases and two terpenoids were isolated. The percentages of the main alkaloids have been determined. It has been shown that the epigeal part of the plant can be used to obtain scopolamine hydrobromide.

The high physiological activity of the tropane alkaloids from plants of the genus Datura, family Solanaceae, is generally known. Thus, scopolamine hydrobromide - the main alkaloid of plants of this genus - is widely used in psychiatry, surgery, neurology, and opthalmic practice and as an antiemetic and tranquilizer for sea and air sickness as a component of Aeron tablets. Datura leaves are components of powders (Astmatal) and cigarettes (Astmatin) used in bronchial asthma [1].

Scopolamine hydrobromide is obtained from the seeds of D. innoxia cultivated in the Darmina sovkhoz [collective farm] (Chimkent province, Kazakh SSR) of Lekrasprom SSSR (All-Union Combine for the Production, Preparation, and Processing of Medicinal Plants of the USSR Ministry of the Medical Industry). In order to determine the possibility of using other organs of the plant for industrial purposes and to study its alkaloid composition, we have investigated the leaves, stems, and roots (in the budding and flowering period) and also the seeds (in the fruit-bearing period). The total alkaloids were extracted with chloroform from raw material previously wetted with dilute ammonia solution. After the appropriate working up, the following amounts of total alkaloids (% on the raw material) were obtained: from the leaves, 0.31; from the stems, 0.29; from the roots, 0.28; from the seeds, 0.28.

In all cases the main alkaloids were hyoscyamine and hyoscine, which were obtained in the form of perchlorates. Their proportions in the total were (%): in the seeds, 71.4; in the leaves, 55.2; in the stems, 56.3; in the roots, 50.0. The mother liquors from the perchlorates were separated on a column of alumina with elution successively by hexane, ethyl acetate, chloroform, and chloroform-methanol (0.5, 1, 5, and 10%).

As a result of the separation of the total alkaloids of the epigeal part and the seeds, 10 individual bases were isolated: hyoscine, hyoscyamine, apohyoscine, apoatropine, tropine, pseudotropine, 3,6-dihydroxytropane, oscine(scopoline), and bases 9 and 10.

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