ALKALOIDS OF Korolkowia sewertzovii. STRUCTURE OF SEVKORINE

K. Samikov, R. Shakirov,

D. U. Abdullaeva, and S. Yu. Yunusov

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The plant *Korolkowia sewertzovii* Rgl., growing in Katrantau, Kirghiz SSR, has not been studied previously. From the epigeal part collected in the flowering stage, by chloroform extraction we isolated 1.68% of total alkaloids, and from the hypogeal part 1.55%. When the combined ether-soluble basis was separated on a column of alumina, in chloroform-methanol eluate it yielded korseveriline (I) [1, 2]. The sparingly soluble fraction of the combined material was passed through a column of silica gel, and the alkaloids were eluted with benzene-ethanol (4:1). The last fractions yielded a base with mp 236-238°C, $[\alpha]_D$ -41.1° (c 1.011; CH₃OH), composition C₃₄H₅₇NO₇ (II), M⁺ 591, which was identical with sevkorine (melting point, $[\alpha]_D$ IR spectrum) [3]; however, the composition of the base (II) differed from that previously proposed for sevkorine.

The sevkorine was hydrolyzed with 10% hydrochloric acid in the presence of ethanol (1:1), and from the hydrolysis products by chromatography on a column of alumina we isolated D-glucose (paper chromatography) and bases with mp 135-136°C (acetone), $C_{28}H_{43}N$ (III); 178-180°C (acetone), $C_{28}N_{45}NO$ (IV); 241-243°C (acetone), and $[\alpha]_D$ -43.2° (c 0.11, C_2H_5OH), $C_{28}H_{47}NO_2$ (V). The alkaloid isolated in greatest amount was (V) which we have called sevkoridinine. The bases (III) and (IV) proved to be identical with anhydrosevkoridine and sevkoridine [3], respectively. The IR spectrum of (V) has v_{max} (cm⁻¹) 3410, 3135 (OH), 2800 (N-CH₃), 1670 (C=C). With digitinon, sevkoridinine gives a digitonide, which shows the presence of a 3 β -OH group in it [4]. In the mass spectrum of (V) there are the main peaks of ions with m/e 112 (100%), 125, 138, 149, 164, 178, 358, 400 (M - 29)⁺, 411 (M - 15), and 429 (M⁺) which are characteristic for typical steroid alkaloids of the edpetilidine series [5, 6]. The NMR spectrum of (V) showed singlets at (ppm) 0.98 (3H, 19-CH₃), 0.54 (3H, 18-CH₃), 2.12 (3H, N-CH₃), a doublet at 0.81 (3H, 21-CH₃), and a multiplet with its center at 5.35 (2H, olefinic proton) (CDCl₃ + CD₃OD, δ scale).

Sevkoridinine forms an 0.0'-diacetyl derivative with mp 179-181°C (VI), M⁺ 513, in the IR spectrum of which there is no absorption band of an OH group, while the absorption bands of ester carbonyls appear at 1745 and 1250 cm⁻¹.

The NMR spectrum of (VI) shows resonance singlets at (ppm) 1.99 and 2.01 (6 H, OCOCH₃), and multiplets at 4.62 ($H_{(a)}$, HC-OCOCH₃), and 4.89 ($H_{(e)}$, HC-OCOCH₃) from protons geminal to acetoxy groups [6].

When compound (V) was heated with 5% sulfuric acid, the dehydration of the molecule took place, with the formation of the anhydro compounds (III) and (IV) [3]. Consequently, in (II) the aglycone moiety is (V), and not (IV) as was previously found erroneously.

Sevkoridinine has the same composition as edpetilidine (VII) $[6,\ 7]$ and the same Rf values. Their IR, NMR, and mass spectra are similar, but not identical. The difference in melting points for (V) and (VII) is $28\,^{\circ}\text{C}$, and their specific rotations differ in sign.

A comparative study of the chemical shifts of the protons from $19-CH_3$ and $18-CH_3$ in the NMR spectra of (V) and (VI) with those of (VII) and of diacetyledpetilidine [6] and also the passage from (V) to (IV) have shown that (V) and (VII) have the same heterocyclic skeleton and linkage of rings A, B, C, and D. A double bond is present between C_{15} and C_{16} , and there

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are β -oriented hydroxy groups at C₃ and C₆. However, in the NMR spectrum of (V) [0.98 ppm (19-CH₃) 0.57 ppm (18-CH₃), 0.81 ppm (21-CH₃) (in CDCl₃ + CD₃OD)], the signal from the 18-CH₃ proton is shifted upfield by 3 Hz as compared with that of (VII).

The facts given show that (V) is a diastereoisomer of (VII) at the C_{20} or C_{22} asymmetric center, the configurations of these centers having been determined for neither of these alkaloids. In the molecule of (II), according to biogenetic considerations, the D-glucose residue is attached at carbon atom 3 [8]. The results of a determination of molecular rotation differences between (II) and (V) according to Klyne's rule [9] have shown that in the (II) molecule the D-glucose is attached to the (V) by a β -glycosidic bond.

On the basis of what has been said, it may be concluded that sevkorine has the structure and partial configuration of 3β -O-D-glucopyranosylsevkoridinine (II).

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AN INVESTIGATION OF THE ALKALOIDS OF Reseda luteola

M. M. Tadzhibaev, K.L. Lutfullin,

V. M. Malikov, and S. Yu. Yunusov

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Ten species of plants of the genus Reseda grow on the territory of the USSR [1], and none of them have been investigated for their alkaloid content [2]. The present paper gives preliminary information on a study of the alkaloids of R. luteola. The plant was collected in the flowering period in the Samarkand oblast by U. Rakhmankulov. The comminuted raw material (17 kg) was extracted with a 1% solution of sulfuric acid. The extract was passed through KU-1 and KU-2 cation-exchange resins. The alkaloids were desorbed with a 1% ethanolic solution of ammonia. The ammoniacal ethanolic solution was concentrated under vacuum, and the alkaloids were extracted successively with petroleum ether, diethyl ether, and chloroform. This gave 55.64 g of total alkaloids. By chromatographing the combined ethersoluble alkaloids in a column of silica gel (1:20) we isolated two new bases, which we have called resedine (5.5 g) and resedinine (3.5 g).

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