THE STRUCTURE OF SEVEDINE

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We have previously [1] reported the isolation from the combined bases of the epigeal part of Korolkowia sewerzowii Regel of an alkaloid with mp 212-214°C, $[\alpha]_D$ −17.2°, with the composition $C_{27}H_{45}NO_3$. The base proved to be new and we have called it sevedine (I).

The IR spectrum of the alkaloid shows characteristic absorption frequencies at (cm^{-1}) 3375, 1035 (OH), 2983-2865, 1470, 1450 ($-CH_3$; $-CH_2-$), and 2775 (trans-quinolizidine). The NMR spectrum of (I) shows a singlet at 0.94 ppm (3 H, $19-CH_3$) and poorly resolved doublets from the protons of two secondary methyl groups. The mass spectrum of sevedine has the peaks of ions with m/e 98, 111 (100%), 112, 124, 125, 138, 139, 150, 162, 164, 166, 178, 179, 360, 375, 398, 402 $(M-29)^+$, 413 $(M-18)^+$, 416 $(M-15)^+$, 431 $(M)^+$, which are characteristic for C-nor-D-homosteroid alkaloids of the cevine group [2-5].

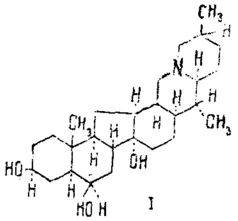
The acetylation of sevedine with acetic anhydride in pyridine yielded diacetylsevedine (II) the IR spectrum of which showed the absorption bands of an ester carbonyl (1740, 1250 cm^{-1}) and of a hydroxy group (3480, 1035 cm^{-1}).

The NMR spectrum of diacetylsevedine showed singlets at 0.94 ppm (3 H, $19-CH_3$) and 2.00 ppm (6 H, two $COOCH_3$), a doublet at 0.81 ppm (6 H, $21-CH_3$ and $27-CH_3$), and multiplets with their centers at 4.68 ppm (H, $\underline{H}C-OCOCH_3$) and 4.97 ppm (H, $\underline{H}C-OCOCH_3$). Consequently, sevedine contains two secondary and one tertiary hydroxy groups.

The oxidation of (I) with chromium trioxide in acetic acid yielded a diketone – sevedinedione (III) – with mp 215-217°C, composition $C_{27}H_{41}NO_3$, identical with korseverilinedione which we obtained by the oxidation of korseveriline [4, 5]. The NMR spectrum of (III) has a singlet of 0.87 ppm (3 H, $19-CH_3$) and a doublet at 0.81 ppm (6 H, $21-CH_3$ and $27-CH_3$).

The identity of sevedinedione and korseverilinedione shows that sevedine has the heterocyclic skeleton of cevanine, and the two secondary hydroxy groups are present in the C_3 and C_6 positions and the tertiary hydroxy group at C_{14} [4, 5]. Thus, sevedine differs from korseveriline by the configurations of the secondary hydroxy groups, and the A/B, B/C, C/D, D/E, and E/F ring linkages in sevedine are the same as in korseveriline, and the tertiary hydroxy group and the C-21 and C-27 methyl groups are α-oriented [6-8].

A comparison of the chemical shifts of the C-19 methyl groups in (II) with those of korsinine, severtzidine, and dihydroimperialine shows that the hydroxy group at C_3 has the β-equatorial and that C_6 the β-axial orientation, which is also shown by the presence in the NMR spectrum of diacetylsevedine of a multiplet at 4.68 ppm from C-3αH and one at 4.97 ppm from the C-6αH [9-15].



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On the basis of these facts, it may be concluded that sevedine is the diastereomer of korseveriline at C_3 and has the structure of 3β,6β,14α-trihydroxy(27α-methyl)cevanine (I).

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EXPERIMENTAL

For thin-layer chromatography (TLC) we used KSK silica gel (100 mμ) and the chloroform–methanol (10 : 1) solvent system; the revealing agent was Dragendorff's solution. The IR spectra were recorded on a UR-20 double-beam spectrophotometer (molded tablets with KBr), the mass spectra on an MKh-1303 mass spectrometer, and the NMR spectra on a JNM-4H-100 MHz instrument in deuterochloroform (compound (I) in $CDCl_3 + CD_3OD$) with HMDS as internal standard (δ scale).

Sevedine has mp 212-214°C (from acetone) [1], $[\alpha]_D$ −17.2° (c 1.22; chloroform), $C_{27}H_{45}NO_3$, M^+ 431, R_f 0.06.

Diacetylsevedine. A mixture of 0.23 g of sevedine, 2 ml of pyridine, and 3 ml of acetic anhydride was kept at room temperature for three days. Then it was evaporated in vacuum and the residue was dissolved in 5% sulfuric acid. The acid solution was made alkaline with ammonia and was extracted with chloroform. The solvent was distilled off and the residue was purified by recrystallization from a mixture of acetone and petroleum ether. The melting point of the diacetylsevedine was 202-204°C [from acetone–petroleum ether (1:5)], R_f 0.42.

IR spectrum, cm^{-1}: 3480 (OH), 2960-2863, 1465, 1488 ($-CH_3$, $-CH_2-$), 1740, 1250 (C=O, ester), 2770 (trans-quinolizidine).

Sevedinedione. A solution of 0.24 g of sevedine in 3 ml of acetic acid was mixed with 0.15 g of chromium trioxide in 3 ml of 80% acetic acid. The mixture was heated on the water bath for 30 min and was then evaporated in vacuum; the residue was dissolved in water, and the solution was made alkaline with ammonia and was extracted with chloroform. The residue after the solvent had been driven off was dried in vacuum, dissolved in benzene, and chromatographed on alumina. The benzene eluates after concentration yielded crystals with mp 215-217°C (from benzene) identical with an authentic sample of korseveridinedione according to R_f values, mixed melting point, and IR, NMR, and mass spectra; M^+ 427, R_f 0.23.

IR spectrum, cm^{-1}: 3450 (OH), 2960-2860, 1465, 1420 (CH_3-, $-CH_2-$), 1715 (C=O), 2770 (trans-quinolizidine).

SUMMARY

From the epigeal part of Korolkowia sewerzowii Regel we have isolated a new base with mp 212-214°C, which has been called sevedine, and for which, on the basis of a study of IR, NMR, and mass spectra, and also its conversion into korseverilinedione, the structure of 3β,6β,14α-trihydroxy(27α-methyl)cevanine has been established.

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