STRUCTURE OF SEVEDAMINE

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From the combined chloroform-extracted material of the epigeal part of Korolkowia sewerzowii Regel the new alkaloid sevedamine has been isolated, with mp 256-258°C (acetone) $[\alpha]_D$ +3.6° (c 1.25; ethanol), $C_{27}H_{45}NO_3$. On the basis of the results of a study of the UV, IR, PMR, and mass spectra of sevedamine and also performance of a transition to the known alkaloid korseverilinedione it has been established that sevedamine has the structure and configuration of 3β,6α,14α-trihydroxycevanine.

Continuing the separation of the combined chloroform material extracted from the epigeal part of Korolkowia sewerzowii Regel [1], we have isolated the new alkaloid sevedamine (I) with mp 256-258°C, $C_{27}H_{45}NO_3$.

Alkaloid (I) is a tertiary base and its IR spectrum has absorption bands at 3390, 1060, and 1040 cm^{-1} (hydroxy groups), 2950-2850 and 1460 cm^{-1} ($-CH_3$; $-CH_2-$), and 2770 cm^{-1} (trans-quinolizidine). The fragmentation of (I), giving rise to the peaks of ions with m/z 98, 111 (100%), 112, 124, 125, 138, 149, 162, 164, 178, 179, 218, 232, 373, 400, 402, 413, 414, 416, 431 M^+ is very similar to that of korseveriline [3-5]. The PMR spectrum of sevedamine has a singlet at 0.73 ppm (3 H, 19-CH_3) and a signal from two methyl groups at 0.84 ppm.

The acetylation of sevedamine with acetic anhydride in pyridine gave diacetylsevedamine (II). The IR spectrum of (II) had adsorption bands at 3500 and 1032 cm^{-1} (hydroxy group), 2760 cm^{-1} (trans-quinolizidine), and 1738 and 1245 cm^{-1} (C=O of ester groups). The PMR spectrum of (II) showed signals at 0.79 ppm (3 H, 19-CH_3, 2.00 ppm (6 H, 2 $COOCH_3$), a signal from two methyl groups at 0.84 ppm, and a multiplet with center at 4.63 ppm (2 H, $HC-OCOCH_3$).

When (I) was oxidized with chromium trioxide in acetic acid the diketone sevedaminedione (III) was obtained with mp 215-217°C, composition $C_{27}H_{41}NO_3$, identical with korseverilinedione which we obtained by the oxidation of korseveriline [2, 4, 5].

The identity of sevedaminedione and korseverilinedione showed that sevedamine had the heterocyclic skeleton of cevanine and that the two secondary hydroxy groups were located in the C_3 and C_6 positions and the tertiary hydroxy group at C_{14} [2, 5]. Consequently, sevedamine differs from korseveriline, sevedine and korseveramine only by the configurations of the secondary hydroxy groups and is one of the isomers of these alkaloids. The A/B, B/C, C/D, D/E, and E/F ring linkages in sevedamine are the same as in korseveriline, while the C-21 and C-27 methyl groups are α-orientated [2, 4-6].

A comparison of the chemical shifts of the C-19 methyl groups in compounds (I-III) with those of isodihydroimperialine, diacetylisodihydroimperialine, and imperialone showed that the hydroxy group in (I) at C_3 has the β- and that at C_6 the α-equatorial orientation, which is also shown by the presence in the PMR spectrum of diacetylseverdamine of a multiplet 4.63 ppm from C3α-H and from C6β-H [5, 7-10].

Thus, on the basis of the facts given the structure and configuration of sevedamine have been established as 3β,6α,14α-trihydroxycevamine (I).

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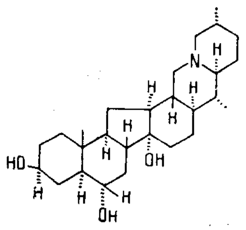

EXPERIMENTAL

For TLC we used KSK silica gel (90 mμ). The solvent system was chloroform—methanol (10:1). IR spectra were taken on a UR-20 spectrometer (KBr tablets), mass spectra on a MKh-1303 instrument, and PMR spectra on JNM-3H-100/100 MHz instrument in $CDCl_3$ ((I)—in $CH_3OD + CDCl_3$), with HMDS as internal standard (δ scale).

Sevedamine. The combined chloroform-extracted material (20 g) from the epigeal part of Korolkowia sewerzowii was chromatographed on a column of alumina with elution by benzene—methanol (10:1) eluate was rechromatographed on a column of silica gel with elution by benzene—acetone (1:1 and 1:2). The benzene—acetone (1:2) eluate, after treatment with acetone, yielded sevedamine $C_{27}H_{45}NO_3$, mp 256-258°C (acetone), $[\alpha]_D$ +3.6° (c 1.25; ethanol), R_f 0.12, M^+ 431 (mass-spectrometrically); severdamine hydrochloride had mp 226-228°C (ethanol—acetone (1:1)).

Diacetylseverdamine (II). A mixture of 0.15 g of sevedamine, 1.5 ml of pyridine, and 2 ml of acetic anhydride was kept at room temprature for 60 h. After the elimination of the pyridine, the residue was dissovled in 5% sulfuric acid, the solution was made alkaline with ammonia and extracted with chloroform, and the solvent was distilled off. This gave amorphous diacetylsevedamine with R_f 0.57.

Mass spectrum: m/z 98, 111 (100%), 112, 124, 138, 139, 150, 162, 164, 166, 178, 180, $(M-60)^+$, $(M-59)^+$, $(M-56)^+$, $(M-43)^+$, $(M-42)^+$, $(M-29)^+$, $(M-18)^+$, $(M-15)^+$, 515 M^+.

Sevedaminedione (III). A solution of 0.17 g of sevedamine in 1.5 ml of acetic acid was mixed with a solution of 0.08 g of chromium trioxide in 1.5 ml of acetic acid with the addition of one drop of water. The mixture was heated in the water bath for 30 min and evaporated in vacuum, and the dry residue was dissolved in water. The acidic solution was made alkaline with ammonia and extracted with chloroform. After the chloroform had been distilled off, the residue in chloroform and chromatographed on alumina. This gave the diketone sevedaminedione with mp 215-217°C (benzene), R_f 0.47. IR spectrum, ν_{max}, cm^{-1}: 3560-3410, 1030 (OH), 2765 (trans-quinolizidine), 1710 (C=O).

The diketone sevedaminedione was shown to be identical with the diketone obtained with the oxidation of korseveriline (mixed melting point and IR spectrum).

SUMMARY

The new alkaloid sevedamine has been isolated from the combined chloroform-extracted material from the epigeal part of Korolkowia sewerzowii Regel. On the basis of a study of its physicochemical properties and passage to the known alkaloid korseverilinedione, the structure and configuration of sevedamine has been established as 3β,6α,14α-dihydroxycevanine.

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