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STRUCTURE OF THE ALKALOID SCHOBERINE

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The structure of an alkaloid of a new type, schoberine, isolated from plants of the genus *Nitraria* has been established by the x-ray structural method as perhydro-1,10-propano-4a,8a-diazaphenanthrene. Its chemical and spectral properties have been studied.

Schoberine (I) was first isolated from the plant *Nitraria schoberi* L. [1, 2] and then from *Nitraria sibirica* Pall. (family Zygophyllaceae) [3]. Structure (Ia) [1] (Fig. 1) of the type of the *Ormosia* alkaloids (see, for example, [4]) was suggested for it. However, a detailed analysis of the spectral characteristics (IR, PMR) and of some chemical properties of (I) (see below) showed that its molecule contains an aminated grouping and both nitrogen atoms are tertiary. With the aim of a reliable determination of the structure of schoberine, we have made an x-ray structural investigation of the base, the results of which have led to structure (I).

In agreement with the space group $P2_1/n$ in which schoberine crystallizes, the elementary cell contains molecules of both optical antipodes. The spatial structure of the molecule of (I) is shown in Fig. 2 in a projection on the bc plane. The molecule of (I) consists of four linked six-membered rings A, B, C, and D having chair conformations. The linkages of rings A/B and B/C are trans, and of B/D and C/D cis. The lengths of the valence bonds and the angles in the molecule of (I) are given in Fig. 2. The mean values of the $C_{sp^3}-C_{sp^3}$ and $N-C_{sp^3}$ bonds (1.520 and 1.471 Å, respectively) are close to the corresponding standard values [5] and correlate well with the values given for six-membered azacycles [6]. The errors in the determination of the lengths of the valence bonds and angles are not greater than 0.006 Å and 0.3°, respectively.

As has been mentioned above, schoberine exhibits the properties of tertiary bases and, in particular, it does not undergo methylation or acetylation under the usual conditions.

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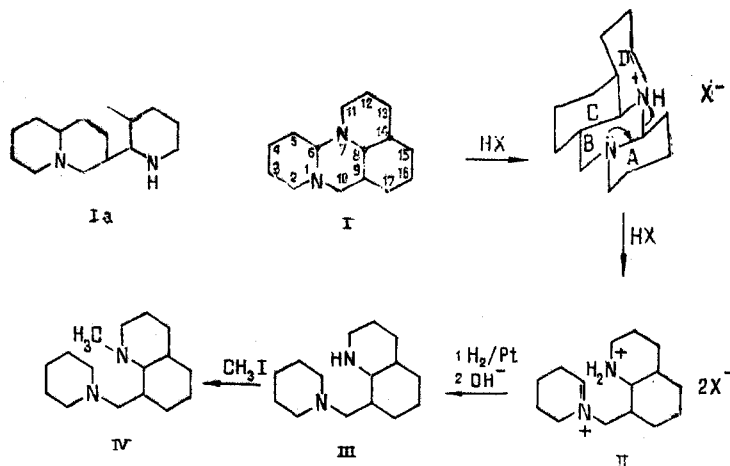


Fig. 1. Structure and chemical transformations of schoberine.

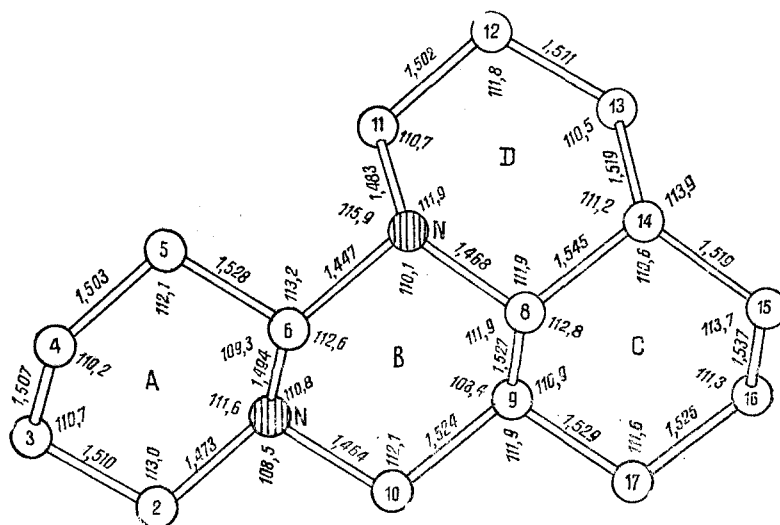


Fig. 2. Spatial structure of the schoberine molecule.

In the IR spectrum of (I) [1], no absorption bands of active hydrogen are observed. In the NMR spectrum of the base ($CDCl_3$) there is a doublet of doublets with $^3J = 10.5$ and 4.0 Hz in the 2.46 ppm region, obviously due to the $H_{ax}-2$ of N,N -disubstituted hexahydropyrimidines with the corresponding orientation of the unshared electron pairs of the nitrogen atoms [7].

The signals of the other protons in the spectrum of (I) are superposed and appear in the form of two humps at 2.60 - 2.80 ppm (section of hydrogen atoms attached to carbon atoms in the α positions with respect to nitrogen atoms) and 2.32 - 1.00 ppm. When the spectrum was taken in trifluoroacetic acid, the pattern changed sharply: a one-proton multiplet appeared at 8.29 ppm and another series of signals underwent downfield shifts - 3.75 (m, 2H), 3.46 (m, 2H), 3.20 (m, 3H), 2.70 (m, 3H), and 2.35 ppm (m, 1H) - and there was a rise in the 1.49 ppm region (4H). Apparently, in an acid medium there is the cleavage of one of the C-N bonds characteristic for aminals [8] with the formation of a compound (II) (see Fig. 1, $X = CF_3COO^-$). On the catalytic hydrogenation of (I) in acetic acid, after 4 h the schoberine had been converted completely into dihydroschoberine ((II) \rightarrow (III), $X = CH_3COO^-$). On reacting with methyl iodide, the latter formed monomethyldihydroschoberine (IV).

TABLE 1. Coordinates of the Nonhydrogen Atoms ($\times 10^4$) in the Structure of Schoberine

Atom	x	y	z
N1	1716 (1)	2334 (5)	4168 (3)
C2	2155 (1)	1844 (9)	4714 (5)
C3	2093 (2)	1040 (9)	6475 (5)
C4	1769 (2)	1250 (9)	6581 (5)
C5	1313 (2)	708 (9)	5820 (5)
C6	1393 (1)	55 (7)	4235 (4)
N7	961 (1)	455 (3)	3459 (3)
C8	1067 (1)	1067 (7)	1934 (4)
C9	1379 (1)	3445 (7)	1783 (4)
C10	1825 (1)	3027 (8)	2631 (4)
C11	622 (2)	2307 (9)	4120 (5)
C12	169 (2)	2354 (9)	3290 (5)
C13	254 (2)	3048 (9)	1714 (5)
C14	613 (1)	1232 (8)	1025 (5)
C15	736 (2)	1853 (8)	545 (5)
C16	1054 (2)	4233 (8)	714 (5)
C17	1500 (2)	3985 (9)	189 (5)

Thus, the structure of schoberine has been established; it consists of perhydro-1,10-propano-4a,8a-diazaphenanthrene. This structure is an original one, since all known saturated Nitraria alkaloids, in contrast to (I) contain a spiro carbon atom (see, for example, [9]). It has some analogy with ceruine - an alkaloid of the Lycopodium class [10] - in which two tertiary nitrogen atoms in positions different from schoberine in a similar tetracyclic system also form an amination grouping.

EXPERIMENTAL

PMR spectra were obtained on a JNM-4H-100 instrument (0-HMDS, δ -scale), and mass spectra on MKh-1303 and MH-1310 spectrometers.

The x-ray structural experiment on crystals of (I) was carried out on a Sintex P2₁ diffractometer using CuK α radiation: $a = 28.25(1)$, $b = 5.212(2)$, $c = 9.221(3)$ Å; $\beta = 89.08(3)^\circ$; $d_{\text{calc}} = 1.151$ g/cm³; space group P2₁/n; $z = 4$; $\theta \leq 57.5^\circ$. The calculations were carried out on 1310 reflections with $I > 2\sigma$. In the course of the experiment, some fall in the intensity of the control reflections (approximately 20%) was observed which was apparently due to the low melting point of the crystals ($\sim 60^\circ$).

The structural calculations were made by the direct method using the Rentgen-75 program [11]. Attempts to determine the structure in the centrosymmetric space group P2₁/n did not lead to success, and it was then decided to continue the calculations in the non-centrosymmetric space group P2₁, since, according to previous results, the substance exhibited slight optical activity ($[\alpha]_D = -7^\circ$) [1]. In this variant, in the automatic regime, the positions of all 34 nonhydrogen atoms were revealed, while it could be seen in the E-synthesis that 17 positions were interconnected by center of symmetry. Having shifted the origin of coordinates into this center of symmetry (i.e., passing to space group P2₁/n), we continued the refinement of the structure by the method of least squares (MLS) first in the isotropic and then in the full-matrix anisotropic approximation ($R = 0.131$). The placing of the nitrogen atoms was made on the basis of the lengths of the valence bonds. In the last stage of MLS we calculated an electron-density difference synthesis, which revealed the positions of 12 of the H atoms out of 26. Refinement by MLS in the light of the positions of the H atoms gave a final value of the divergence factor, R , of 0.111. The coordinates of the basis atoms of the schoberine molecule are given in Table 1.

Isolation of Schoberine. The extraction of 222 kg of the epigeal part of N. schoberi gave 1040 g of ether-extracted and 410 g of chloroform-extracted alkaloids. The combined ether-extracted alkaloids were separated in an apparatus for polybuffer separation into fractions with pH 9-2. The chloroform phases from the column with pH 7-2 were combined (55.0 g) and chromatographed on a column of alumina with elution by benzene. This gave 20.46 g of a fraction consisting, according to TLC, of three superposed spots of schoberine

isomers (M^+ 234). This mixture was subjected to chromatographic separation, first on a column of silica gel with elution by chloroform-methanol (99:1 and 98:2) and then of the individual fractions on a column of alumina using hexane-chloroform (1:1) as eluent. A fraction weighing 2.46 g was collected which consisted of a mixture of two substances, and was not simplified on further chromatography. On prolonged standing of the mixture, colorless prisms of schoberine sublimed onto the walls of the flask. In this way, 0.19 g of substance (I) was obtained with mp 62-63°C, $[\alpha]_D^{20} \pm 0^\circ$. MM, exp. 234.2109; calc. for $C_{15}H_{26}N_2$ 234.2096.

The extraction of 40 kg of the epigeal part of *N. sibirica* gave 66.9 g of ether-extracted and 33.3 g of chloroform-extracted alkaloids. The ethereal fraction was dissolved in chloroform and extracted with water. This gave 24.0 g of aqueous fraction and 42.4 g of nonaqueous fraction. The latter was separated according to basicity into fractions with pH 8-4. The chromatographic separation of the pH 6 fraction (20.6) as described above led to the isolation of 0.033 g of schoberine.

Mass spectrum (m/z , %): 234 (M^+ 67), 233 (36), 206 (22), 205 (48), 192 (100), 178 (33), 177 (17), 150 (11), 138 (3), 137 (4), 136 (7), 124 (7), 123 (4), 122 (4), 110 (7), 98 (8), 97 (10), 96 (20), 84 (7), 83 (8), 67 (6), 56 (4), 55 (8). In a round-bottomed flask 0.03 g of schoberine was treated with 1 ml of acetic anhydride and 0.5 ml of pyridine. When the mixture was kept at room temperature for 6 days the (I) did not undergo acetylation.

Dihydroschoberine (III). A conical flask, 0.122 g of (I) was treated with 0.027 g of platinum oxide and 10 ml of glacial acetic acid. With constant stirring (magnetic stirrer), the mixture was heated (80°C) in an atmosphere of hydrogen. After 4 h, the (I) had been converted almost wholly into (III) (TLC). The catalyst was filtered off, and the acid was driven off in vacuum. The oily residue was dissolved in chloroform and the solution was washed with 10% ammonia solution and then with water. The combined aqueous ammonia solutions were extracted with chloroform. The chloroform solutions were combined and were dried over anhydrous sodium sulfate, and the solvent was distilled off. This gave 0.0974 g of (III) in the form of a colorless mobile oil. Yield 80%. Mass spectrum (m/z , %): 236 (M^+ 5), 192 (3), 178 (2), 152 (14), 151 (60), 150 (14), 138 (6), 137 (6), 136 (15), 124 (5), 110 (3), 109 (11), 108 (6), 98 (100), 97 (20), 96 (11), 84 (14).

N-Methyldihydroschoberine (IV). A solution of 0.0306 g of (II) in 3 ml of acetone was treated with 0.3 ml of methyl iodide, the mixture was boiled under reflux and was stirred with a magnetic stirrer for 0.5 h. The solvent and the excess of reagent were driven off in vacuum. The residue was chromatographed on a column of silica gel in the chloroform-ethanol-25% ammonia (65:65:5) system. This gave 0.014 g of (IV). Mass spectrum (m/z , %): 250 (M^+ , 12), 235 (10), 190 (13), 178 (9), 166 (20), 165 (100), 164 (20), 152 (18), 151 (30), 150 (42), 149 (20), 138 (9), 137 (60), 136 (35), 124 (19), 123 (36), 122 (60), 111 (48), 110 (58), 98 (75), 84 (12).

SUMMARY

The structure of an alkaloid of a new type - schoberine - has been established by the x-ray structural method; it is perhydro-1,10-propano-4a,8a-diazaphenanthrene. Its chemical and spectral properties have been studied.

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ALKALOIDS OF *Korolkowia sewerzowii*.

STRUCTURE OF KORSELIDINE

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Two new alkaloids have been isolated from the combined alkaloids of the epigeal part of *Korolkowia sewerzowii* 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 3 β , 6 β , 20 β -tri-hydroxy-27 α -methylcevanine has been established for korselidine.

Continuing an investigation of the alkaloids of the epigeal part of *Korolkowia sewerzowii* [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 C₂₇H₄₅NO₃ (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 (trans-quinolizidine), 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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