

VII. STRUCTURE AND ABSOLUTE CONFIGURATION OF SEVERIDINE

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A physicochemical and complete x-ray structural investigation of the new alkaloid severidine isolated from the epigeal part of *Korolkowia sewerzowii* Regel has been performed. The crystals were investigated in the form of severidine hydrochloride, $C_{27}H_{43}NO_5 \cdot HCl$, rhombic, $a = 12.642$, $b = 12.882$, $c = 16.621$ Å, $z = 4$, space group $P2_12_12_1$, at $-120^\circ C$. The structure was interpreted by the direct method and was refined to $R = 0.039$. The hydrogen atoms were revealed. The absolute configuration was established by means of the Hamilton test. The skeleton of the cation is constructed of bicyclic and tricyclic fragments linked by an ordinary C-C bond. All the rings have the chair conformation. The bond lengths and valence angles are normal.

From the epigeal part of *Korolkowia sewerzowii* Regel have previously been isolated seveline, a base with mp $145-147^\circ C$, a base with mp $200-202^\circ C$, $[\alpha]_D -97.7^\circ$, $C_{27}H_{43}NO_5$ (I) [2], which has proved to be a new alkaloid and has been named severidine. The IR spectrum of (I) shows absorption bands at (cm^{-1}) 3400 (OH), 2990-2817, 1482-1400 ($-CH_3$, $-CH_2-$), 2780, 2760 (trans-quinolizidine) [3], 1710, and 1700 (C=O). The mass spectrum of (I) shows the peak of ions with 97, 98, 111, 112, 124, 125, 139, 162, 164, 178, 180, 196, 233, 234, 250 (100%), 251, 413, 430, $(M - 17)^+$, $(M - 15)^+$, 461 M.

The NMR spectrum of (I) contained the signals from four C-methyl groups. The acetylation of (I) with acetic anhydride in pyridine gave triacetylseveridine (II). The IR spectrum of (II) contains absorption bands at (cm^{-1}), 1740, 1225 (C=O ester), and 1715 (C=O), but not that of a hydroxy group. The PMR spectrum of (II) shows the signals from three acetoxy groups and two protons geminal to the acetoxy groups. Consequently, in severidine acetylation takes place at two secondary and one tertiary hydroxyl groups.

The methanolysis of triacetylseveridine led to diacetylseveridine (III). The IR spectrum of (III) contained absorption bands of ester (1735 , 1260 cm^{-1}), carbonyl (1710 cm^{-1}), and hydroxy (3450 cm^{-1}) groups. In its NMR spectrum, the signal from one acetoxy group had disappeared and no shift in the signals of the protons geminal to acetoxy groups was observed. This shows that methanolysis of the group acetylating the tertiary hydroxyl had taken place. A confirmation of this is the fact that diacetylseveridine did not undergo oxidation by chromium trioxide in acetic acid. The reduction of (I) with sodium tetrahydroborate formed tetrahydroseveridine (IV), the IR spectrum of which contained no absorption bands of a carbonyl group. When (IV) was acetylated with acetic anhydride in pyridine, pentaacetyltetrahydroseveridine (V) was obtained. Its IR spectrum lacked the band of a hydroxy group. The NMR spectrum of (IV) contains signals from five acetoxy groups and four protons geminal to acetoxy groups.

The features of the NMR spectra of compounds (I-V) are given in Table 1. In the NMR spectra of (I) and (IV), the signals from the protons of the secondary C-methyl groups were not resolved and were observed in the form of singlets.

Thus, in severidine, out of the five oxygen atoms two are present in carbonyl groups, two in secondary hydroxy groups, and one in a tertiary hydroxy group.

In order to establish the structure and to determine the absolute configuration, a complete x-ray structural investigation of the alkaloid severidine in the form of its hydrochloride was performed.

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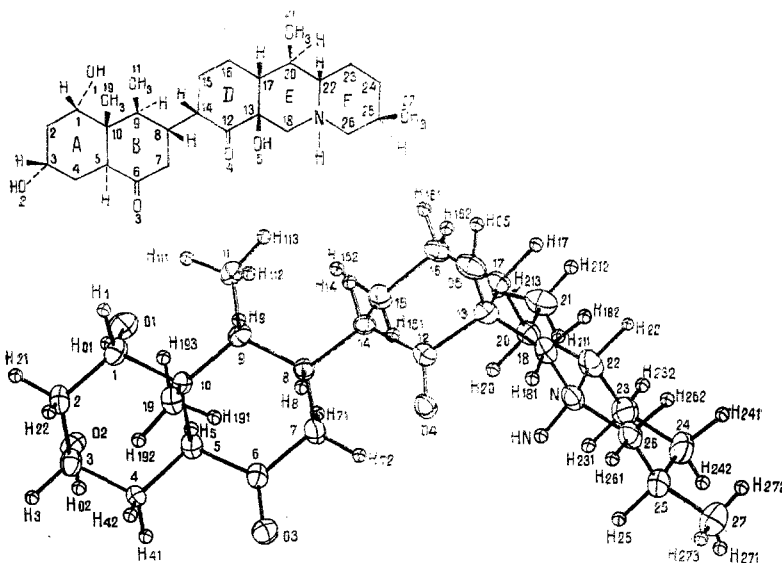


Fig. 1

TABLE 1

Sub- stance	Chemical shifts (δ , ppm)					
	19-CH_3 , s	CH-CH_3 , d	CH-CH_3 , d	CH-CH_3 , d	OCOCH_3 , s	HCOCOCH_3 , m
I	0.59	0.81	0.81	0.81		
II	0.68	0.65	0.75	0.81	1.96; 2.01; 2.05	5.05; 4.85
III	0.70	0.67	0.74	0.80	1.96; 2.06	5.04; 4.83
IV	0.82	0.82	0.82	0.82		
V	0.77	0.74	0.86	0.86	1.95; 1.97 (6H) 2.02 (6H)	4.99; 4.88 4.78 (2H)

Note: s -- singlet; d -- doublet; m -- multiplet.

TABLE 2. Equations of the Planes of the Fragments of the Cation (I) and the Deviations of the Atoms from the Planes (\AA)

$$A: 0.5753x + 0.7764y - 0.2775 = -8.3184$$

$$B: 0.5420x + 0.7659y - 0.3459 = -6.5200$$

$$D: -0.6878x + 0.6623y - 0.2972 = -4.7576$$

$$E: 0.5486x + 0.5836y - 0.5987 = 15.2992$$

$$F: 0.3650x - 0.8804y - 0.3028 = 16.3244$$

Ring A		Ring B		Ring D		Ring E		Ring F	
atom	dev.	atom	dev.	atom	dev.	atom	dev.	atom	dev.
C (1)*	0.6641	C (5)	-0.0066	C (12)*	-0.5639	C (13)	-0.0420	N	0.0000
C (2)	0.0241	C (6)*	-0.6566	C (13)	0.0179	C (18)*	-0.6263	C (22)*	0.6360
C (3)	-0.0245	C (7)	0.0067	C (17)	-0.0177	N	0.0426	C (23)	0.0000
C (4)*	-0.6627	C (8)	-0.0067	C (16)*	0.6858	C (22)	-0.0425	C (24)	0.0000
C (5)	0.0238	C (9)*	0.6892	C (15)	-0.0179	C (20)*	0.7166	C (25)*	-0.6906
C (10)	-0.0235	C (10)	0.0066	C (14)	0.0177	C (17)	0.0419	C (26)	0.0000

*Atoms not included in the calculation of the equations of the planes.

The absolute stereochemistry of the severidine cation, which is shown in Fig. 1, corresponds to the structural formula (I) given in the same figure. The skeleton of the cation is constructed of bicyclic and tricyclic fragments linked by an ordinary C(8)-C(14) bond. The five-membered ring C formed by the closure of a bond between C(11) and C(15) atoms that was suggested previously is absent, and in place of the expected hydroxy group the ring contains a keto group. Thus, severidine has an 11,12-secocevanine heterocyclic skeleton,

TABLE 3. Torsional Angles τ (deg)

Ring	Angle	τ	Ring	Angle	τ	Ring	Angle	τ	Ring	Angle	τ	Ring	Angle	τ
A $1C_4$	1-2-3-4*	52	B $9C_6$	5-6-7-8	59	D $18C_{12}$	14-12-13-17	-47	E $20C_{18}$	13-18-11-22	58	F $23C_{26}$	22-23-24-25	56
	2-3-4-5	-52		6-7-8-9	-57		12-13-17-16	49		18-11-22-20	-62		23-24-25-26	-57
	3-4-5-10	58		7-8-9-10	57		13-17-16-15	-57		11-22-20-17	62		24-25-26-11	58
	4-5-10-1	-58		8-9-10-5	-56		17-16-15-14	61		22-20-17-13	-57		25-26-11-22	-57
	5-10-1-2	55		9-10-5-6	54		16-15-14-12	-54		20-13-13-18	50		26-11-22-23	52
	10-1-2-3	-55		10-5-6-7	-58		15-14-12-13	49		17-13-18-11	-51		11-22-23-24	-52
	Sum	0		Sum	-1		Sum	1		Sum	0		Sum	0

*1-2-3-4 denotes torsional angle C(1)-C(2)-C(3)-C(4).

The conformations of the rings can be judged from the figures of Table 2 which give the equations of the planes of the fragments of the cation, and also from Table 3, which gives the values of the torsional angles in the rings.

Rings A and B have the trans type of linkage and the chair configurations (in Schwarz's symbols [4], 1C_4 and 9C_6 , respectively). The C(1) and C(4) atoms of ring A deviate from the plane of the other four atoms by 0.66 and -0.66 Å, and in ring B the C(9) and C(6) deviate from the plane of the C(5), C(7), C(8), and C(10) atoms by 0.69 and -0.66 Å, respectively,

In the nitrogen-containing moiety of the molecule, rings D and E have the cis type of linkage and E and F the trans type; all the rings have the chair configuration (${}^{16}C_{12}$, ${}^{20}C_{18}$, and ${}^{23}C_{26}$, respectively). The C(16) and C(12) atoms of ring D deviate from the plane of the other four atoms by 0.69 and -0.56 Å. In ring E, the C(20) and C(18) atoms deviate by 0.72 and -0.63 Å. The C(22) and C(25) atoms of ring F deviate by 0.64 and -0.69 Å. These values are somewhat smaller than the ideal deviation for the chair conformation, which is 0.73 Å [5], and this shows some flattening of the ideal chair conformation, and also some decrease (in comparison with the ideal value of 60°) in the mean values of the torsional angles: 55, 57, 53, 57, and 55° in rings A, B, D, E, and F, respectively.

The bonds from the ring to the substituents have the following orientations: C(1)-O(1)H and C(3)-O(2)H, α -axial to ring A; C(13)-O(5)H, β -axial to rings D and E; C(9)-C(11)H₃, β -equatorial to ring B; C(10)-C(19)H₃, β -axial to rings A and B. The C(20)-C(21)H₃ and C(25)-C(27)H₃ bonds are oriented β -equatorially relative to rings E and F, respectively.

The severidine molecule has thirteen asymmetric centers including the nitrogen atom, the inversion of the pyramidal configuration of which is impossible because of the rigidity of the conformation of rings E and F. In the Cahn-Ingold-Prelog nomenclature [6] the configuration found is denoted as follows: NS, 1S, 3S, 5S, 8R, 9S, 10R, 13S, 14S, 17R, 20R, 22S, 25R.

The bond lengths (Fig. 2a) and valence angles (Fig. 2b) in the cation of (I) are quite normal and close to the corresponding standard values [7]. The bond lengths at the nitrogen atom [mean value 1.509(4) Å] are close to the usual bond lengths for N-(sp³) of quaternary (ammonium) tetrahedral nitrogen of 1.500 Å [8] and coincide with those found in other alkalooids [9].

In the structure investigated there are four "active" hydrogen atoms participating in the formation of hydrogen bonds.

The O(5)H hydroxy group forms a hydrogen bond with the Cl⁻ anion. The distances of O(5)-Cl, 2.994(2) Å, O(5)H...Cl 0.86 Å, and H(05)•••Cl, 2.20 Å, and the angle at the hydrogen atom H(05) of 153° show that this bond is fairly strong [10]. The hydrogen atom attached to the N atom also participates in the formation of a H bond with the Cl⁻ anion obtained on the basis of the transformation $-x, 1/2 + y, 1/2 - z$ (2₁ axis [0, y, 1/4]). The parameters of this bond are as follows: N•••Cl 3.097(2), N-H 1.02, H•••Cl 2.15 Å, angle at the H(N) atom 154°. In the crystal, through such interactions, the anions and cations are combined into infinite chains along the b axis.

In the cation there is an intramolecular O-H•••O H bond in which the donor is the O(1)-H hydroxy group and the acceptor the O(2)-H group. The distances O(1)•••O(2) 2.784(3) Å, O(1)-H(01) 0.93 Å, and H(01)•••O(2) 2.15 Å and the angle at the H(01) atom of 124° correspond to a medium-length hydrogen bond.

At the same time, the O(2)H hydroxy group plays the part of a donor in an intermolecular H bond with the O atom of the O(5)H hydroxy group of the molecule obtained from the base transformation $x - 1/2, 1/2 - y, -z$ (2₁ axis [x, 3/4, 0]). The distances are O(2)•••O(5) 2.804(3) Å, O(2)-H(02) 0.98 Å, and H(02)•••O(5) 1.84 Å, and the angle at the H(02) atom is 169°. Because of this H bond, the chains of alternating cations and anions described above fuse into layers perpendicular to the c axis.

On the basis of the facts presented and also of a study of biogenesis [12], it may be concluded that severidine has the structure and absolute configuration of 1S,3S,13R-trihydroxy-(20R,25R)-11,12-secocevanine-6,12-dione.

EXPERIMENTAL

Thin-layer chromatography (TLC) was performed on a fixed layer of KSK silica gel (100 μ m) using the chloroform-methanol (20:1) solvent system. IR spectra (KBr) were taken on a UR-20

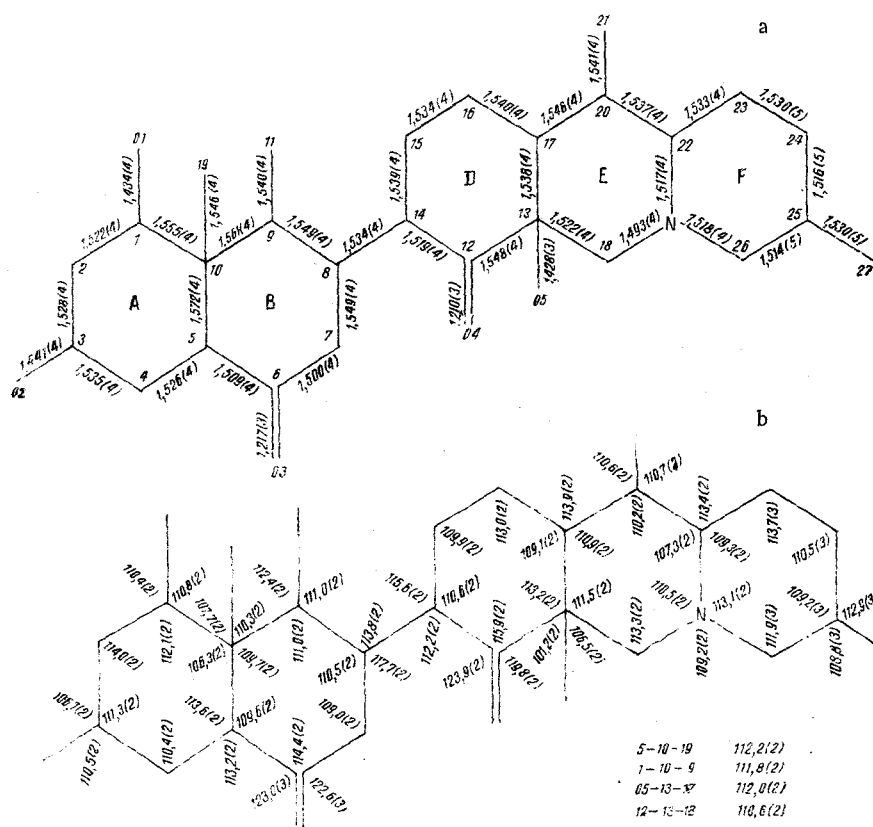


Fig. 2

spectrometer, NMR spectra on a JNM-4H-100/100 MHz instrument in deuteriochloroform with HMDS as internal standard (for the results, see Table 1), and mass spectra on a MKh 1303 instrument.

Severidine. Crystallizes from acetone, mp 200–202°C, $[\alpha]_D^{25}$ 97.7° (c 1.504; ethanol), R_f 0.18. Found, %: C 70.19; H 9.85; N 3.56. $C_{27}H_{43}NO_5$. Calculated, %: C 70.28; H 9.33; N 3.04; M^+ 461 (mass spectrometrically).

Severidine Hydrochloride. Severidine hydrochloride with mp 235–237°C [methanol–acetone (1:1)] was obtained from 0.13 g of the base by the addition of an ethanolic solution of hydrogen chloride.

Triacetylseveridine. A mixture of 0.3 g of severidine, 1.5 ml of pyridine, and 1.5 ml of acetic anhydride was kept at room temperature for 3 days. After elimination of the pyridine, the residue was dissolved in 5% sulfuric acid, and the solution was made alkaline with ammonia and extracted with chloroform. This gave amorphous triacetylseveridine with R_f 0.82.

Mass spectrum: m/z 98, 112, 124, 149, 162, 164, 178, 180, 192, 204, 233 (100%), 234, 250, 424, 468, 486, 527, 528, 529, 544, 545, 559, $(M - 15)^+$, 587 M^+ .

Diacetylseveridine. A solution of 0.08 g of triacetylseveridine in 5 ml of methanol and two drops of water was boiled for 36 h. The methanol was evaporated off, the residue was dissolved in 5% sulfuric acid, and the solution was made alkaline with ammonia and extracted with chloroform. This gave diacetylseveridine with R_f 0.42, M^+ 545 (mass spectrometrically).

Tetrahydroseveridine. In portions, 0.5 g of sodium tetrahydroborate was added over 60 min to a solution of 0.3 g of severidine in 8 ml of methanol. The reaction mixture was kept at room temperature for 1 h. The solvent was evaporated off, and the residue was diluted with water and extracted with chloroform. The residue from the evaporation of the chloroform was treated with acetone, which gave tetrahydroseveridine having mp 243–245°C (acetone), R_f 0.1.

IR spectrum, ν_{max} , cm^{-1} : 3360 (OH), 2773 (trans-quinolidine). Mass spectrum: m/z 98 (100%), 112, 124, 125, 140, 152, 162, 178, 180, 182, 198, 210, 234, 236, 238, 252, 253, 306, 434, $(M - 15)^+$, 465 M^+ .

TABLE 4. Coordinates of the Nonhydrogen Atoms ($\times 10^4$) and the Parameters B_{ij} of the Anisotropic Temperature Factor

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	-1854 (1)	12068 (0)	2431 (0)	2.00 (3)	1.53 (2)	2.58 (3)	0.18 (2)	0.46 (2)	0.23 (2)
O (1)	509 (2)	843 (2)	-2244 (1)	1.92 (8)	2.01 (9)	2.02 (8)	-0.32 (7)	0.39 (6)	0.58 (7)
O (2)	1693 (2)	6387 (2)	-2622 (1)	1.80 (8)	3.16 (9)	2.24 (8)	0.40 (7)	0.42 (7)	0.35 (8)
O (3)	810 (2)	5421 (2)	182 (1)	4.3 (1)	1.76 (8)	1.90 (8)	0.04 (8)	-0.10 (8)	0.49 (7)
O (4)	-583 (2)	7625 (1)	1918 (1)	2.61 (9)	1.97 (7)	1.91 (7)	-0.32 (7)	0.30 (7)	-0.21 (6)
O (5)	-1560 (2)	9795 (2)	2132 (1)	1.57 (8)	1.61 (7)	3.25 (9)	-0.05 (6)	0.12 (7)	-0.42 (7)
N	523 (2)	8715 (2)	3473 (1)	2.4 (1)	1.54 (9)	1.68 (9)	-0.29 (8)	0.13 (8)	-0.38 (7)
C (1)	-315 (2)	7407 (2)	-2078 (2)	1.3 (1)	2.6 (1)	1.35 (9)	-0.17 (9)	0.04 (8)	-0.37 (9)
C (2)	-191 (2)	6451 (2)	-2607 (2)	1.8 (1)	3.3 (1)	1.4 (1)	-0.2 (1)	-0.02 (9)	-0.4 (1)
C (3)	774 (2)	5788 (2)	-2403 (2)	2.0 (1)	2.7 (1)	1.8 (1)	0.10 (9)	0.3 (1)	-0.22 (9)
C (4)	802 (2)	6514 (2)	-1505 (2)	2.4 (1)	1.8 (1)	1.7 (1)	0.22 (9)	0.06 (9)	-0.29 (9)
C (5)	697 (2)	6194 (2)	-995 (2)	1.6 (1)	1.57 (9)	1.51 (9)	-0.13 (9)	0.03 (9)	0.01 (8)
C (6)	791 (2)	6290 (2)	-104 (2)	1.4 (2)	2.0 (1)	1.7 (1)	0.01 (9)	0.07 (9)	0.00 (9)
C (7)	805 (2)	7250 (2)	407 (2)	1.9 (1)	2.1 (1)	1.7 (1)	0.20 (9)	-0.17 (9)	-0.29 (9)
C (8)	-228 (2)	7809 (2)	261 (2)	1.7 (1)	1.28 (9)	1.57 (9)	-0.18 (9)	0.04 (8)	0.05 (9)
C (9)	-352 (2)	8133 (2)	-644 (2)	1.21 (9)	1.6 (1)	1.71 (9)	-0.08 (9)	0.15 (8)	0.21 (8)
C (10)	-341 (2)	728 (2)	-1168 (1)	1.42 (9)	1.74 (9)	1.40 (9)	-0.12 (9)	0.13 (8)	-0.02 (8)
C (11)	-1346 (2)	8798 (2)	-790 (2)	2.1 (1)	2.1 (1)	1.8 (1)	0.20 (9)	-0.29 (9)	0.22 (9)
C (12)	-438 (2)	8507 (2)	1694 (2)	1.18 (9)	1.47 (9)	1.8 (1)	-0.11 (8)	0.12 (8)	-0.17 (8)
C (13)	-522 (2)	9414 (2)	2302 (2)	1.50 (9)	1.52 (9)	1.8 (1)	-0.18 (8)	0.28 (9)	-0.32 (8)
C (14)	-307 (2)	8816 (2)	817 (2)	1.7 (1)	1.35 (9)	1.62 (9)	-0.13 (9)	0.03 (9)	0.13 (8)
C (15)	580 (2)	9625 (2)	726 (2)	2.2 (1)	1.7 (1)	1.9 (1)	-0.45 (9)	0.13 (9)	-0.03 (9)
C (16)	366 (2)	10553 (2)	1282 (2)	2.1 (1)	1.24 (9)	2.2 (1)	-0.23 (9)	0.05 (9)	0.14 (8)
C (17)	329 (2)	10252 (2)	2178 (2)	1.8 (1)	1.16 (9)	1.9 (1)	-0.21 (9)	0.03 (9)	-0.23 (8)
C (18)	-511 (2)	9028 (2)	3167 (2)	1.9 (1)	1.9 (1)	1.9 (1)	-0.33 (9)	0.3 (9)	-0.44 (9)
C (19)	-1350 (2)	6480 (2)	-1013 (2)	1.8 (1)	2.1 (1)	1.7 (1)	-0.54 (9)	0.21 (9)	-0.15 (9)
C (20)	1405 (2)	9893 (2)	2521 (2)	1.48 (9)	1.44 (9)	2.1 (1)	-0.19 (8)	0.10 (9)	-0.29 (9)
C (21)	2252 (2)	10741 (2)	2402 (2)	1.7 (1)	1.8 (1)	3.4 (1)	-0.33 (9)	-0.01 (1)	-0.2 (1)
C (22)	1293 (2)	9615 (2)	3416 (2)	2.3 (1)	1.6 (1)	2.1 (1)	-0.68 (9)	-0.06 (9)	-0.55 (9)
C (23)	2342 (3)	9305 (2)	3811 (2)	2.7 (1)	2.4 (1)	2.7 (1)	-0.5 (1)	-0.7 (1)	-0.2 (1)
C (24)	2216 (3)	8875 (3)	4664 (2)	4.2 (2)	3.2 (1)	2.4 (1)	-0.5 (1)	-1.1 (1)	-0.3 (1)
C (25)	1463 (3)	7959 (3)	4668 (2)	4.5 (2)	2.6 (1)	1.8 (1)	-0.3 (1)	-0.3 (1)	-0.0 (1)
C (26)	410 (3)	8293 (2)	4321 (2)	3.8 (2)	1.9 (1)	1.6 (1)	-0.2 (1)	0.5 (1)	-0.09 (9)
C (27)	1282 (4)	7514 (3)	5510 (2)	6.2 (2)	4.3 (2)	2.5 (1)	0.6 (2)	0.3 (2)	0.4 (1)

TABLE 5. Coordinates of the Hydrogen Atoms ($\times 10^4$) and Distances d (Å) to the Atoms to Which They Are Attached

Atom	x	y	z	q	To the atom	Atom	x	y	z	d	To the atom
H (01)	1136	7955	-2500	0.93	O (1)	H (162)	992	11132	1188	1.10	C (16)
H (02)	2273	5909	-2500	0.98	O (2)	H (17)	109	10949	2516	1.06	C (17)
H (05)	-1591	10455	2045	0.86	O (5)	H (181)	-2100	8360	3223	1.12	C (18)
H (N)	747	8048	3191	1.02	N	H (182)	-872	9629	3572	1.11	C (18)
H (1)	-1082	7775	-2241	1.11	C (1)	H (191)	-1364	6354	-455	1.03	C (19)
H (21)	-132	6688	-3233	1.09	C (2)	H (192)	-1237	5757	-1302	1.06	C (19)
H (22)	-901	5973	-2547	1.09	C (2)	H (193)	-1363	6964	-1168	0.94	C (19)
H (3)	738	5048	-2733	1.10	C (3)	H (20)	1684	9232	2167	1.09	C (20)
H (41)	1544	5114	-1317	1.09	C (4)	H (211)	2931	10445	2606	1.00	C (21)
H (42)	161	4970	-1368	1.10	C (4)	H (212)	2058	11349	2666	0.93	C (21)
H (5)	1350	6979	-1199	1.09	C (5)	H (213)	2351	10760	1812	0.99	C (21)
H (71)	1484	7744	251	1.10	C (7)	H (22)	901	5973	-2547	1.10	C (22)
H (72)	881	7053	1040	1.09	C (7)	H (231)	2847	9983	3823	1.10	C (23)
H (8)	-889	7356	412	1.10	C (8)	H (232)	2724	8722	3435	1.09	C (23)
H (9)	304	8607	-832	1.08	C (9)	H (241)	1911	9475	5076	1.10	C (24)
H (111)	-1364	8864	-1364	1.06	C (11)	H (242)	2981	8626	4926	1.11	C (24)
H (112)	-2045	8636	-455	1.07	C (11)	H (25)	1754	7322	4287	1.10	C (25)
H (113)	-1198	9554	-573	0.96	C (11)	H (261)	-162	7641	4326	1.11	C (26)
H (14)	-1023	9221	599	1.11	C (14)	H (262)	69	8893	4710	1.09	C (26)
H (151)	1324	9292	890	1.07	C (15)	H (271)	1884	7289	5578	0.86	C (27)
H (152)	621	9904	110	1.09	C (15)	H (272)	829	8012	5821	1.00	C (27)
H (161)	-377	10918	1103	1.09	C (16)	H (273)	744	6987	5533	0.96	C (27)

Pentaacetyltetrahydroseveridine. The acetylation of 0.06 g of tetrahydroseveridine was carried out with 1 ml of pyridine and 1 ml of acetic anhydride in a similar manner to that of severidine. This gave pentaacetyltetrahydroseveridine with R_f 0.86.

IR spectrum, ν_{\max} , cm^{-1} : 760 (trans-quinolizidine), 1735, 1255 (C=O, ester). Mass spectrum: m/z 98, 111, 112, 124, 125, 159, 164, 167, 178, 180, 206, 213, 234 (100%), 303, 329, 378, 396, 400, 414, 486, 514, 530, 556 ($M-18$) $^+$, ($M-17$) $^+$, ($M-15$) $^+$, 675 M^+ .

Severidine hydrochloride formed colorless crystals, $\text{C}_{27}\text{H}_{43}\text{NO}_5 \cdot \text{HCl}$, rhombic: at -121°C ; $a = 12.642(4)$, $b = 12.882(3)$, $c = 16.621(4)$ Å, $V = 2706.9(1.2)$ Å 3 , $z = 4$, space group $P2_12_12_1$. The parameters of the cell and the intensities of 3419 reflections were measured at -120°C on a Syntex P2 $_1$ automatic diffractometer (Mo K_α radiation, graphite monochromator, $\theta/2\theta$ scanning to $\theta_{\max} = 30^\circ$). In the interpretation and refinement of the structure we used 3089 reflections with $F^2 > 2\sigma$.

The structure was interpreted by the direct method using the EXTL programs on an Eclipse S/200 computer. From the best space variant we calculated a E-synthesis revealing all the nonhydrogen atoms. To refine the positional parameters of the atoms, F-syntheses were constructed with respect to the phases calculated from the atomic coordinates found in the E-syntheses. The structure was refined by the method of least squares first in the full-matrix isotropic approximation ($R = 10.39\%$), and then in the anisotropic approximation ($R = 7.09\%$). The difference synthesis calculated at this stage revealed the hydrogen atoms of the methyl and hydroxy groups, and the positions of the other H atoms were calculated geometrically,

Further refinement was carried out in the anisotropic approximation of fixed values of the position and temperature parameters ($B_{\text{iso}} = 3.5$ Å, H atoms). At this stage corrections were introduced for the anomalous scattering of the x rays by chlorine atoms and a final anisotropic refinement to $R = 0.0390$ ($R_2 = 0.0523$) was performed; for the inverted structure, $R = 0.0403$ ($R_2 = 0.0538$). The absolute configuration was determined with a probability of 99.99% according to the Hamilton test.

The coordinates of the atoms and their anisotropic temperature parameters are given in Tables 4 and 5.

SUMMARY

On the basis of physicochemical data and a complete x-ray structural investigation the structure of the new alkaloid severidine has been established and its absolute configuration has been determined.

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