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MOLECULAR AND CRYSTAL STRUCTURE OF LUTEIDINE

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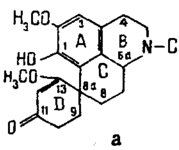
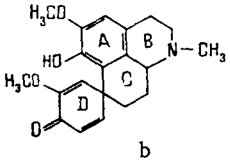
The crystal structure of luteidine has been deciphered by x-ray structural analysis; there are two molecules in the independent part of its elementary cell. These symmetrically independent molecules differ in structure. The position of the olefinic methoxy group of luteidine has been established. Its structure has been determined as 1-hydroxy-2,12-dimethoxy-9,10-dihydrohomoaporphine.

The present paper gives the results of an x-ray structural analysis of the alkaloid luteidine isolated previously [1] from the Central Asian species of the autumn crocus *Colchicum luteum* Baker. The structure of this alkaloid was determined as 1-hydroxy-2,13-dimethxy-9,10-dihydrohomoproaporphine (a) [2].



a



b

However, not all the questions relating to the structure of luteidine were resolved: The configurations of the C$_{6a}$ and C$_{8a}$ atoms were not elucidated and the positions of the olefinic methoxy group at C$_{13}$ did not agree with the biogenetic scheme of the proaporphine and homoproaporphine alkaloids [3, 4]. Furthermore, it was necessary to determine how comparable are the configurations of this alkaloid and of the alkaloid kreysiginone (b) for which the results of an x-ray structural analysis have been given [5].

We have established that in the independent part of the elementary cell of luteidine there are two molecules of the substance which we shall subsequently denote by (I) and (II), and therefore in the figures and tables we give individual details for the molecules (I) and (II) of this compound. Figure 1 shows the conformation of luteidine, the methoxy group in ring D being located at the C$_{12}$ atom, and not the C$_{13}$ atom as was assumed previously, and ring D being oriented in such a way that this methoxy group is in the syn position relative to the H atom at C$_{6a}$. It has also been established that the N-methyl group (C$_{18}$) of the base is present in different positions in molecules (I) and (II): In (I) it is in the equatorial position and in (II) in the axial position to ring B (Fig. 1).

The conformations of the rings can be judged from the figures of Table 1, which gives the equations of the planes of fragments of the rings and the deviations of the atoms from these planes. The aromatic ring A is practically planar, the deviations of the atoms in it

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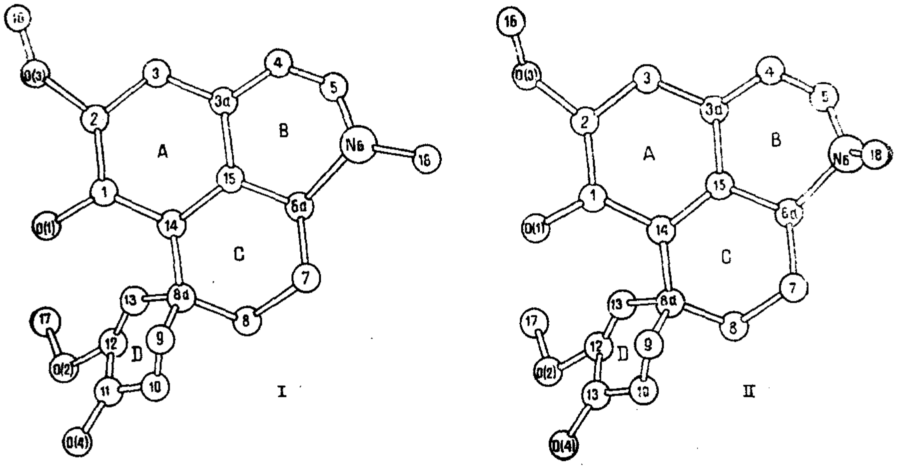

Fig. 1. Conformation of the luteidine molecule.

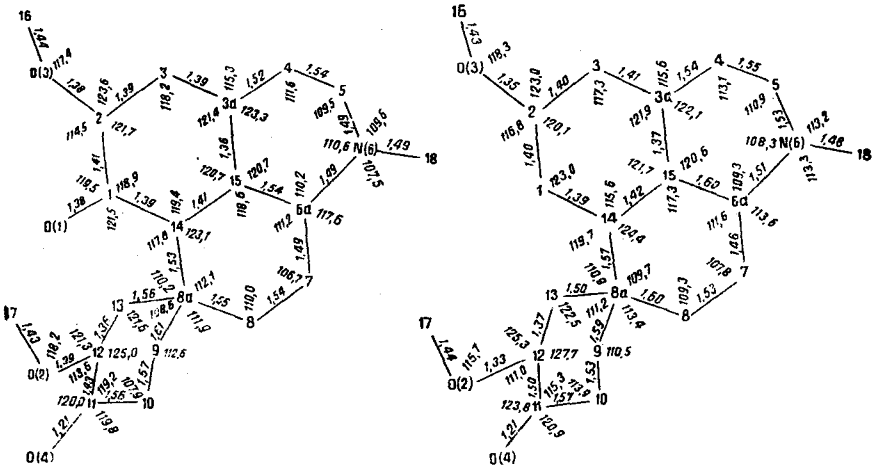

Fig. 2. Bond lengths and valence angles in molecules (I) and (II) of crystalline luteidine.

from the mean-square plane not exceeding 0.02 Å for molecule (I) and 0.03 Å for (II). The conformations of rings B and C are close to those of $^5H_6$ and $^7H_8$ half-chairs. Ring D of molecule (I) has the sofa conformation, while in molecule (II) the conformation of this ring is closer to the half-chair type (Table 1). Figure 2 gives the values of the bond lengths and valence angles. The standard deviations of these values do not exceed 0.02 Å and 0.9°, respectively. Some lengthening of the C_{8a}—C_9 bond in the molecule (II) and of the C_{6a}—C_{15} and C_8—C_{8a} bonds in the molecule (II) of the base and also deviations of the values of the bond lengths from the standard values [6] in ring D must be mentioned.

An analysis of the spatial structure of the molecules of luteidine shows that this compound has the relative 6aR,8aR configuration. In the conformations of rings A, B, and C, luteidine is similar to the alkaloid kreysiginone [5]. Some difference in the conformations of rings D of these compounds is due to the different numbers of double bonds in them. At the same time, the orientations of rings D in relation to the remainder of the molecule in luteidine and kreysiginone are similar. It is interesting to trace the interrelationship between the structures of luteidine and of dihydrokreysiginone, which has been isolated together with kreysiginone from the Australian plant *Kreysigia multiflora* [7]. The conformation of dihydrokreysiginone at the spiro center relative to kreysiginone remains undetermined, but the hypothesis may be expressed of the identity of dihydrokreysiginone and luteidine in spite of some difference in their physical constants and spectral characteristics.

Although the positions of the hydrogen atoms were not determined, the distance between the O_1 atoms in the molecules (I) and the N_6 atoms in the molecules (II), amounting to 2,64 Å, shows that a hydrogen bond of the OH...N type exists between them. Its formation becomes pos-

TABLE 1. Equations of the Planes of the Molecules (I) and (II) and the Deviations of the Atoms from These Planes (Δ, Å)

$A_{\mathrm{I}}: -4{,}948x+6{,}034y+15{,}114z=8{,}554$

$B_{\mathrm{I}}: -5{,}164x+6{,}003y+14{,}269z=8{,}348$

$C_{\mathrm{I}}: -4{,}795x+5{,}899y+15{,}874z=8{,}570$

$D_{\mathrm{I}}: -0{,}132x-0{,}991y-0{,}016z=13{,}718$

$A_{\mathrm{II}}: -5{,}214x+6{,}799y+12{,}662z=8{,}680$

$B_{\mathrm{II}}: -5{,}293x+6{,}690y+12{,}497z=8{,}516$

$C_{\mathrm{II}}: -5{,}153x+6{,}769y+13{,}010z=8{,}813$

$D_{\mathrm{II}}: -0{,}196x+0{,}888y-0{,}414z=3{,}525$

Ring A			Ring B			Ring C			Ring D		
atom	I	II	atom	I	II	atom	I	II	atom	I	II
C_1	0,010	−0,004	C_{3a}	−0,016	−0,038	C_{6a}	−0,008	−0,015	C_9^*	−0,637	−0,5[illegible]2
C_2	−0,011	0,013	C_4	0,007	0,017	C_{14}	−0,017	−0,035	C_{10}^*	−0,002	0,139
C_3	−0,002	−0,002	C_{15}	0,015	0,037	C_{8a}	0,008	0,017	C_{12}	0,012	0,018
C_{3a}	0,015	−0,016	C_{6a}	−0,007	0,016	C_8^*	−0,170	−0,271	C_{13}	−0,120	−0,017
C_{14}	0,002	−0,019	C_5^*	−0,286	−0,180	C_{15}	0,017	0,033	C_{8a}	0,054	0,007
C_{15}	−0,015	0,029	N_6^*	0,491	0,599	C_7^*	0,648	0,549	C_{11}	−0,055	−0,008
			C_{18}^*	0,316	2,055						

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

TABLE 2. Coordinates of Atoms of Molecules I and II in the Crystalline structure of Luteidine (standard deviation given in parentheses)

Atom	Molecule I			Molecule II		
	x/a	y/b	z/c	x/a	y/b	z/c
C_1	0,2951 (15)	1,1374 (10)	0,2078 (4)	0,3742 (14)	0 6939 (9)	0,4673 (4)
C_2	0,1181 (15)	1,0663 (9)	0.1796 (4)	0.2098 (15)	0.5796 (8)	0,4596 (4)
C_3	0,0493 (14)	1.1178 (8)	0,1359 (4)	0,0821 (15)	0 5662 (9)	0,4155 (4)
C_{3a}	0,1595 (16)	1,2436 (9)	0,1207 (4)	0,1279 (15)	0.6701 (10)	0,3799 (4)
C_4	0,0823 (18)	1,2908 (10)	0,0713 (4)	—0,0074 (20)	0,6478 (12)	0,3301(5)
C_5	0,1780 (19)	1,4383 (12)	0.0644 (5)	0,0311 (17)	0,7713 (11)	0,2961(5)
C_{6a}	0,4413 (17)	1,4566 (10)	0,1324 (4)	0,3386 (15)	0,8965 (9)	0,3463(4)
N_6	0,4044 (16)	1,4765 (8)	0,0758 (4)	0,2628 (13)	0 8450 (8)	0,2924 (3)
C_7	0,6658 (17)	1,4926 (11)	0,1456 (5)	0,5556 (14)	0,9764 (10)	0,3473 (4)
C_8	0,6801 (18)	1,4811 (10)	0,2057 (4)	0,6032 (17)	1,0290 (10)	0.4030 (4)
C_{8a}	0,5955 (14)	1,3370 (10)	0,2224 (4)	0,6107 (15)	0,9150 (9)	0,4419 (4)
C_9	0.7654 (16)	1,2637 (12)	0,2134 (4)	0,8104 (14)	0,8794 (10)	0,4350 (4)
C_{10}	0,9588 (19)	1,3159 (13)	0 2501 (5)	1,0059 (17)	0,9776 (11)	0,4511 (4)
C_{11}	0,8805 (15)	1.3057 (10)	0,3078 (4)	0,9921 (15)	1,0351 (9)	0.5058 (4)
C_{12}	0,6870 (14)	1,3257 (10)	0.3189 (4)	0,7784 (14)	1.0269 (9)	0 5245 (4)
C_{13}	0,5478 (15)	1,3364 (9)	0,2321 (4)	0,6033 (14)	0,9699 (8)	0,4957 (4)
C_{14}	0.4003 (14)	1,2638 (9)	0,1923 (4)	0,4215 (13)	0,7973 (8)	0.4322 (3)
C_{15}	0,3269 (16)	1,3163 (9)	0.1484 (3)	0,2949 (15)	0,7786 (9)	0,3865 (4)
C_{16}	—0,1558 (18)	0,8638 (11)	0,1706 (5)	0,0471 (18)	0.3597 (10)	0.4347 (5)
C_{17}	0,4580 (19)	1,3527 (15)	0,3879 (5)	0,5851 (16)	1,0529 (11)	0.5979 (4)
C_{18}	0,5012 (22)	1,6167 (11)	0,0641 (5)	0,3843 (24)	0 7679 (14)	0,2686 (5)
O_1	0,3604 (11)	1.0808 (7)	0,2502 (3)	0,4949 (10)	0,7053 (6)	0 5115 (2)
O_2	0.6456 (11)	1,3301 (7)	0.3723 (3)	0,7824 (9)	1,0808 ([illegible])	0.5717 (2)
O_3	0.0288 (13)	0.9410 (7)	0.1970 (3)	0.1832 (11)	0,4860 (6)	0,4863 (3)
O_4	0,9892 (12)	1.2888 (9)	0.3428 (3)	1,1472 (10)	1,0859 (7)	0,5321 (3)

sible because the N-methyl group of molecule (II) passes into the axial position in ring B thanks to the free inversion of the three-coordinate nitrogen atom. Thus, the requirements of optimum packing make the symmetrically independent molecules (I) and (II) nonidentical in spatial structure. The lengths of the other intermolecular contacts are within permissible limits from the point of view of crystal chemistry [8].

EXPERIMENTAL

The parameters of the elementary cell were determined and refined on a Syntex $P2_1$ diffractometer by the method of least squares from 15 reflections. The main crystallographic characteristics are as follows:

$C_{20}H_{25}O_4$

$a=6{,}798(1)$ Å

$b=10{,}878(3)$ Å

$c=25{,}511(5)$ Å

$\gamma=108{,}13(5)°$

$V=1792{,}8(6)$ Å^3

$z=4$

Sp.gr. $=P2_1$

$\rho=1{,}221$ g/cm^3

The intensities of 2593 reflections were measured on the above-mentioned diffractometer by the $\theta/2\theta$-scanning method (Cu K_α radiation, graphite monochromator). After taking into account the Lorentz and polarization factors, a working group of 2210 reflections with $I \geq 2\sigma$ was obtained. The structure was interpreted by the direct method and was refined first in the isotropic approximation and then in the anisotropic approximation to R = 0.093 with the aid of the Roentgen-75 group of programs [9]. The coordinates of the atoms of molecules (I) and (II) are given in Table 2.

SUMMARY

On the basis of the results of x-ray structural analysis, the position of the olefinic methoxy group in luteidine has been corrected, and its structure has been determined as 1-hydroxy-2,12-dimethoxy-9,10-dihydrohomoproaporphine.

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ACETYLSEVEDINE FROM *Korolkowia sewerzowii*

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The epigeal part of *Korolkowia sewerzowii* Regl. has yielded a new alkaloid — acetylsevedine with mp 189°C (with foaming), $[\alpha]_D$ −36.6°, $C_{29}H_{47}NO_4$. On the basis of the IR, PMR, and mass spectra of acetylsevedine, of the products of its transformation, and also a passage to the known alkaloid sevedine, the structure of 6β-acetoxy-3β, 14α-dihydroxycevanine has been established for acetylsevedine.

Continuing an investigation of the alkaloids of the epigeal part of *Korolkowia sewerzovii* Regl. collected in Fergana province [1], from the total ether-extracted bases we have isolated a new alkaloid with the composition $C_{29}H_{47}NO_4$ (I) with mp 189°C (foaming).

The spectral characteristics of the base (I) indicate the presence in it of hydroxy groups, two secondary and one tertiary methyl groups and an ester (acetoxy) group. The latter shows that this base belongs to the group of ester alkaloids.

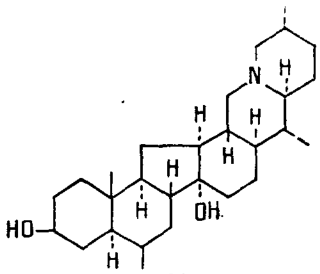
The results of a mass-spectrometric analysis showed the similarity of the structure of (I) to the alkaloid sevedine (their molecular weights differ by 42 units).

When (I) was saponified, an amino alcohol with the composition $C_{27}H_{45}NO_3$, mp 212-214°C, was obtained which proved to be identical with sevedine (mixed melting point, R_f, IR and mass spectra) [2]. Acetic acid was detected in the hydrolysate by paper chromatography.

The acetylation of (I) with acetic anhydride in pyridine led to the formation of a product identical with diacetylsevedine [2].

All the facts given above permit the statement that base (I) is a monoacetyl derivative of sevedine.

The acetic acid residue may be present at C_3 to C_6 in the acetylsevedine molecule.



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