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STRUCTURE OF ALLINE

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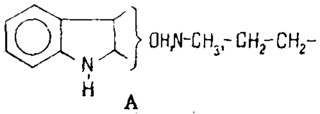
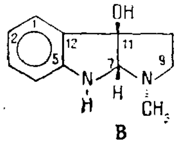
The spatial structure of the alkaloid alline has been determined by x-ray structural analysis. It has been established that alline has a physostigmine skeleton containing one tryptamine unit.

A base $C_{11}H_{14}N_2O$ has been isolated previously from the epigeal part of *Allium odorum* L. (family *Liliaceae*); it has proved to be new and we have called it alline (I).

UV spectrum of (I): λ_{max} 245, 303 nm (log ε 3.68, 3.14). The IR spectrum showed absorption bands at (cm^{-1}) 3350 (OH, NH); 1615, and 1495 (aromatic ring); and 710 and 760 (1,2-disubstituted benzene ring). The PMR spectrum of (I) had signals in the 7.12-6.45 ppm region (m, 4 H, Ar—H), singlets at 4.18 (1 H), 4.03 (2 H) (OH, NH, CH), and 2.21 ppm (s, 3 H, $N—CH_3$), and multiplets at 2.7 and 2.0 ppm (2 H each, $N—CH_2—CH_2—$). On the basis of its UV, IR, and PMR spectra and its composition, the partial structure (A) can be suggested for alline.



A



B

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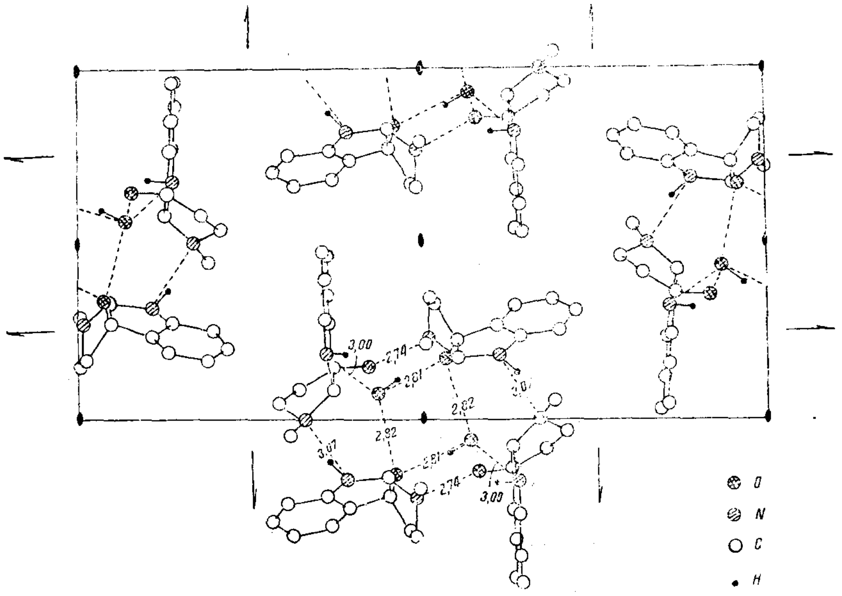

Fig. 1. Packing of the alline molecule.

TABLE 1. Coefficients of the Equations Ax + By + Cz = D of the Main Planes of the Fragments of the (Ia) and (Ib) Molecules and the Deviations of the Atoms from the Planes (δ, Å)

Plane	Atom	δ_{Ia}	δ_{Ib}	*A*	*B*	*C*	*D*
Indoline fragment, rings A and B	C(1)	0,02	0,04	(Ia) 24,57	−0,81	−0,41	2[illegible],99
	C(2)	0,00	0,01	(Iб) 4,34	10,55	−3,2[illegible]	10,59
	C(3)	−0,04	−0,04				
	C(4)	−0,04	−0,03				
	C(5)	0,0[illegible]	0,02				
	C(6)	0,09	0,09				
	C(7)	−0,08	−0,07				
	C(11)	−0,02	−0,02				
	C(12)	0,04	0,00				
Ring C	C(7)	0,06	0,06	(Ia) 15,81	7,75	3,10	16,83
	C(8)	−0,04	−0,04	(Iб) 17,66	− 7,03	2,83	12,67
	C(10)	0,04	0,04				
	C(11)	−0,06	−0,05				
	C(9)*	0,63	0,62				

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*Atom not included in the calculation of the equation of the plane.

In order to establish the structure and stereochemistry unambiguously, an x-ray structural investigation of alline was performed. The results of the x-ray structural analysis showed that base (I) has a physostigmine skeleton [2] and contained a tryptamine unit [3] with the relative orientation of the substituents shown in formula B. (The numbering of the atoms corresponds to that of chimonanthine [4]). The spatial structure — the geometry and linkage of the rings and the orientation of the substituents — coincides with that of chimonanthine which was established by x-ray structural analysis [5].

In the independent part of the elementary cell of the crystal that was investigated there were two alline molecules (Ia and Ib) and a molecule of water (Fig. 1). The two crystallographically independent alline molecules had similar structures. The indoline fragment of each of the molecules (Ia) and (Ib) had a plane structure to within an accuracy of 0.09 Å (see Table 1) and cis-linkage with the five-membered heterocycle C. The five-membered heterocycle C (the C(7)N(8)C(9)C(10)C(11) atoms) had the envelope configuration (to within an accuracy of 0.06 Å); the departure of the C(9) atom from the plane of the other four atoms amounted to 0.62 Å (see Table 1).

TABLE 2. Interatomic Distances, (r, Å) and Valence Angles (ω, degrees)

Distance	r_{Ia}	r_{Ib}	Angle	ω_{Ia}	ω_{Ib}
C(1)—C(12)	1,391(6)	1.385(5)	C(12)C(1)C(2)	118.6(5)	119.3(4)
C(1)—C(2)	1.399(6)	1,384(5)	C(1)C(2)C(3)	119.4(5)	120.0(5)
C(2)—C(3)	1,386(9)	1.388(7)	C(2)C(3)C(4)	122,3(5)	122.2(4)
C(3)—C(4)	1,388(7)	1,416(6)	C(3)C(4)C(5)	118,0(5)	115.8(4)
C(4)—C(5)	1.382(6)	1,413(4)	C(4)C(5)C(12)	120.7(4)	121,7(4)
C(5)—N(6)	1.395(5)	1,381(4)	C(4)C(5)N(6)	129,0(4)	126 4(4)
N(6)—C(7)	1,464(5)	1.457(4)	C(12)C(5)N(6)	110.3(4)	111,9(3)
N(8)—C(9)	1,466(5)	1,461(5)	C(5)N(6)C(7)	110.0(3)	109,4(3)
N(8)—C(7)	1,447(4)	1,459(4)	C(11)C(7)N(6)	105,7(3)	105.6(3)
N(8)—C(13)	1,478(6)	1.486(5)	C(11)C(7)N(8)	103,7(3)	104 4(3)
C(9)—C(10)	1.502(6)	1,497(6)	C(6)C(7)N(8)	116.3(3)	115,3(3)
C(10)—C(11)	1,523(5)	1,537(5)	C(7)N(8)C(9)	105.5(3)	105.3(3)
C(11)—C(12)	1,504(5)	1.499(4)	C(7)N(8)C(13)	115.5(4)	114.5(3)
C(11)—C(7)	1 556(5)	1,559(5)	C(9)N(8)C(13)	115,8(4)	114.4(4)
C(11)—O	1,427(4)	1.432(4)	N(8)C(9)C(10)	101,6(3)	102,5(3)
C(12)—C(5)	1,394(6)	1.380(5)	C(9)C(10)C(11)	103,6(3)	104,0(3)
			C(10)C(11)C(12)	113,7(3)	114,3(3)
			C(10)C(11)C(7)	104,7(3)	103.9(3)
			C(10)C(11)O	109,7(3)	111,4(3)
			C(12)C(11)O	112,6(3)	110.0(3)
			C(7)C(11)O	113,0(3)	114 1(3)
			C(12)C(11)C(7)	102,8(3)	102.7(3)
			C(11)C(12)C(1)	128.6(4)	129 5(4)
			C(11)C(12)C(5)	110.4(4)	109,6(3)
			C(1)C(12)C(5)	121,0(4)	120,9(3)

Analysis of the interatomic distances showed that the mean values of the various types of valence bonds – $C_{sp^2} \ldots C_{sp^2}$ (1.392 Å), $C_{sp^2} - N$ 1.388Å), $C_{sp^3} - N$(1.465Å), $C_{sp^3} - O$(1.429Å), $C_{sp^3} - C_{sp^2}$(1.502Å), $C_{sp^3} - C_{sp^3}$ (1.531Å), – agreed well with the standard values [6] and those observed in related indole alkaloids [5, 7]. No anomalies were observed in the sizes of the valence angles. The discrepancies between identical valence bonds and angles, which form a criterion of the accuracy of the experiment, in the (Ia) and (Ib) molecules were of the order of 0.01 Å and 1°, respectively, with the exception of the C(4)—C(5) bond and the C(3)C(4)C(5), C(4)C(5)C(6), and C(12)C(11)O angles (Table 2).

The packing of the (Ia) and (Ib) molecules is shown in Fig. 1 in projection on the plane of the a and b axes. An analysis of the intermolecular contacts showed that all the active hydrogens in OH and NH groups and the molecule of the water of crystallization participated in hydrogen bonds. The shortest intermolecular distances with possible hydrogen bonds are shown in Fig. 1. Thus, four molecules of the alkaloid alline and two water molecules interlinked by H-bonds and twofold crystallographic axes form a framework at the points (1/20 0) and (0 1/2 0).

EXPERIMENTAL

Thin-layer chromatography was performed in a fixed layer of KSK silica gel (90 mμ) with the chloroform–methanol (10:2) solvent system. The IR spectrum (KBr) was taken on a UR-20 spectrometer, the PMR spectrum on a JNM-4H-100/100 MHz instrument in deuterochloroform with HMDS as internal standard (δ scale), and the mass spectrum on a MKh1310 instrument.

Isolation and Separation of the Total Alkaloids. The total alkaloids were extracted with ethanol from the epigeal (4130 g) and hypogeal (480 g) parts of *Allium odorum* gathered in July, 1982, in the flowering phase in the environs of the village of Sibir', Buryat ASSR. The ethanol was distilled off in vacuum. The concentrated ethanolic extract was diluted with 5% sulfuric acid and washed with ether. The acid solution was made alkaline with sodium bicarbonate and was then extracted exhaustively with chloroform. In this way, 5.28 g (0.13%) of total alkaloids was obtained from the epigeal part and 0.48 g (0.10%) from the hypogeal part.

Alline. The total alkaloids (5.28 g) were dissolved in chloroform and chromatographed on a column of silica gel with elution by benzene–methanol (9:3). The eluate was collected as a total of 170 10-ml fractions. Fractions 12-45 yielded 0.21 g of alline with mp 91-92°C

TABLE 3. Coordinates ($\times 10^4$) of the Basic Atoms of (Ia) and (Ib) Molecules

	Atom	*x/a*	*y/b*	*z/c*	*BJ*, Å $^{-2}$
Molecule (Ia)	C(1)	8614(2)	1460(3)	1870(7)	6,62
	C(2)	8577(2)	359(4)	1207(9)	8,03
	C(3)	8557(2)	206(4)	—541(9)	8,01
	C(4)	8568(2)	1112(4)	—1672(7)	7,05
	C(5)	8591(1)	2198(3)	—1009(6)	6,14
	N(6)	8585(1)	3238(3)	—1863(4)	5,91
	C(7)	8703(1)	4162(3)	—672(5)	5,42
	N(8)	8304(1)	5061(3)	—571(5)	6,16
	C(9)	7875(1)	4624(3)	543(7)	7,84
	C(10)	8199(1)	4149(3)	1997(5)	6,49
	C(11)	8690(1)	3615(3)	1130(5)	5,09
	C(12)	8621(1)	2372(3)	743(6)	5,08
	C(13)	8122(2)	5527(4)	—2222(7)	9,58
	O	9166(1)	3844(2)	2102(3)	6,00
Molecule (Ib)	C(1)	8667(2)	8173(4)	5480(6)	7,56
	C(2)	8114(2)	8366(4)	5455(7)	8,18
	C(3)	7807(2)	8023(4)	4065(7)	7,35
	C(4)	8044(1)	7501(3)	2621(6)	6.17
	C(5)	8610(1)	7331(3)	2695(5)	4,86
	N(6)	8933(1)	6882(3)	1425(4)	5,18
	C(7)	9479(1)	6707(3)	2079(5)	4.20
	N(8)	9909(1)	7270(3)	1123(4)	5,89
	C(9)	9910(1)	8444(3)	1728(5)	6,64
	C(10)	9878(1)	8301(3)	3618(6)	6,51
	C(11)	9489(1)	7293(3)	3859(5)	4,77
	C(12)	8908(1)	7625(3)	4115(5)	5,16
	C(13)	9865(2)	7149(5)	- 754(5)	7,32
	O	9663(1)	6566(3)	5215(3)	7,21
H_2O		10719(1)	5688(3)	5434(4)	7,35

(acetone), $[\alpha]_D+136.3°$ (*c* 1.218 ; chloroform), R_f 0.33. Alline hydrochloride had mp 196-197°C (acetone).

Mass spectrum *m/z* (%): 77(46), 78(12), 91(33), 92(28), 93(55), 103(14), 104(34), 105(16), 106(19), 117(28), 118(48), 119(32), 120(32), 128(19), 130(77), 131(88), 132(55), 133(55), 134(20), 146(100), 147(98), 148(19), 161(23), 162(32), 171(14), 172(27), 173(42), 189(11), 190(100) M^+.

When the total alkaloids obtained from the hypogeal part were separated similarly, alline was again obtained (0.04 g).

The x-ray structural investigation was performed on a Syntex $P2_1$ diffractometer using CuK_α radiation: a = 24.664(II), b = 11.768(4), c = 7.856(3) Å, d_{calc} = 1.166 g/cm^3, space group $P2_12_12$, z = 8. The complete set of experimental results (1957 reflections) was obtained on the diffractometer mentioned. The calculation was performed with 1608 independent reflections with intensities exceeding 2 σ.

The structure was interpreted by the direct method using the Rentgen-75 program [8] in the automatic regime. An E-series was constructed from the best variant (R = 0.36) in which 20 out of the 28 nonhydrogen atoms of molecules (Ia) and (Ib) were determined. For a more accurate localization of the atoms and to find the missing atoms several ρ(xyz) syntheses were calculated. In this procedure the presence of a molecule of water of crystallization was detected. A model of the alline molecule was not known a priori, and therefore we arranged the atoms with respect to the heights of the peaks in the ρ(xyz) synthesis and to the values of the valence distances. The structure was refined in the full-matrix manner, first in the isotropic (R = 0.100) and then in the anisotropic approximation.

To localize the H atoms a calculation was made of an electron-density difference synthesis. The positions of 22 out of the 30 H atoms were found. The hydrogens in the methyl and hydroxy groups and 1 H atom each in the benzene ring and in the water molecule were not found. The final value of the convergence factor taking the H atoms into account was 0.054. Table 3 gives the coordinates of the C, N, and O atoms and their isotropic temperature corrections.

SUMMARY

The spatial structure of the alkaloid alline has been determined by x-ray structural analysis. It has been established that alline has the physostigmine skeleton containing one tryptamine unit.

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THE STRUCTURE OF THE ALKALOID NITRARAMINE FROM *Nitraria schoberi*

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The spatial structure of the alkaloid nitraramine has been determined by x-ray structural analysis. This has shown that it has the structure of 2,1'-epoxy-1,3-propanoperhydrobenzo[3',2'-d]-1,8-naphthyridine.* Its reactivity has been studied.

The alkaloid nitraramine (I) has previously been isolated from the epigeal part of *Nitraria schoberi* L. [1, 2]. On the basis of spectral characteristics and chemical properties [2], a modified sparteine structure [3] of the type of *Ormosia* alkaloids was proposed for it. Having isolated this base again, having repeated some reactions, and having analyzed the available information, we have come to the conclusion that the formula proposed previously is doubtful. Thus, the dehydrogenation of (I) and of the *Ormosia* alkaloids under comparable conditions [2, 4] led to different products. The IR and PMR spectra of the N-acetyl derivative (II) showed the absence of active hydrogen from it. An x-ray structural study performed with the aim of establishing the structure of nitraramine unambiguously showed that its molecule was based on a 2-azaspiroundecane system. Compound (I) contained the nitramine (isonitramine) skeleton [5], to which, in positions 1 and 11, a piperidine ring has been attached to its positions 1 and 3. Furthermore, the C(2) atom of the piperidine moiety and the C(7) atom of the isonitramine (nitramine) moiety are linked by an oxygen bridge.

Structure (I) established by x-ray structural analysis makes it possible to suggest the following scheme of chemical transformations and of treating the spectral results.

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*The original nomenclature and numbering (based on that of nitramine) have been retained. [Translator].

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