X-RAY STRUCTURAL INVESTIGATION OF ALKALOIDS.

II. MOLECULAR STRUCTURE AND ABSOLUTE CONFIGURATION OF (−)-PSEUDOKOPSININE

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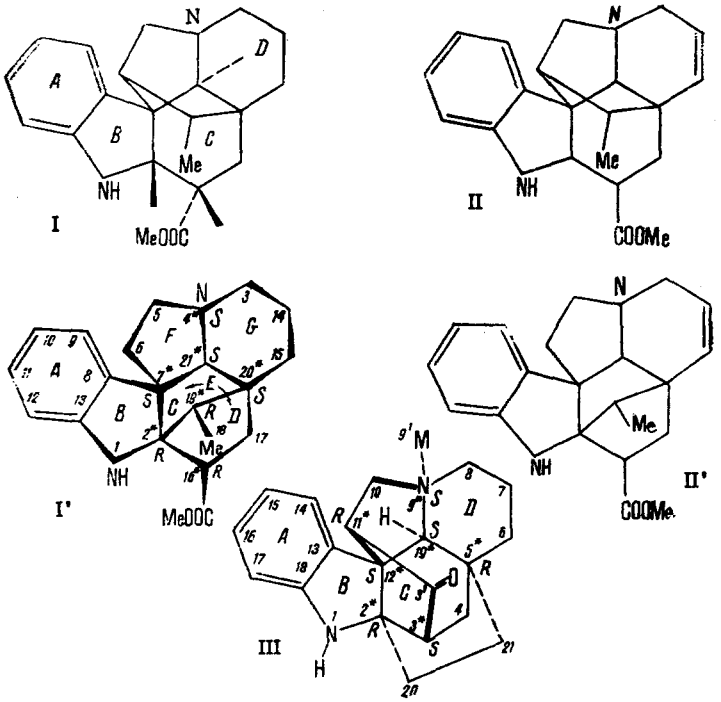
UDC 547.944/945+539.26

The alkaloid (−)-pseudokopsinine $C_{21}H_{26}N_2O_2$, $[\alpha]_D$ 30.4° (c 1.51; methanol) was isolated from the epigeal part of *Vinca erecta* Rgl. et Schmalh., family Apocynaceae [1]. On the basis of chemical characteristics and IR, UV, PMR, and mass spectra, structural formula (I) and the 2β,3β,19α configuration corresponding to the cis linkage of rings E and G have been proposed for it [2]. Thus, pseudokopsinine has been assigned to the group of dimeric indole alkaloids which also includes vindolinine, $C_{21}H_{24}N_2O_2$ — an alkaloid isolated from various species of plants of the family Catharanthus [3]. Although the mass spectrum [4] shows the same structure of pseudokopsinine and of 14,15-dihydrovindolinine (II), the different properties of these two compounds led to the conclusion [2] that they are stereoisomers.

In order to determine the structure and absolute configuration of (−)-pseudokopsinine independently and objectively, we have undertaken an x-ray structural investigation of the monohydrate of its hydrobromide $C_{21}H_{26}N_2O_2 \cdot HBr \cdot H_2O$ (the presence of a molecule of water of crystallization was established by us). The preliminary results of this investigation have been published previously [5, 6].



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Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 197-206, March-April, 1976. Original article submitted April 29, 1975.

TABLE 1. Position and Thermal Parameters*

Atom	x	y	z	$B_{11}\times10^4$	$B_{22}\times10^4$	$B_{33}\times10^4$	$B_{12}\times10^4$	$B_{13}\times10^4$	$B_{23}\times10^4$
Br	0,20600 (5)	0,25398 (3)	−0,13457 (4)	93 (1)	39 (1)	67 (1)	−1 (1)	−15 (1)	−8 (1)
N (1)	0,6301 (4)	0,4393 (2)	−0,4716 (3)	65 (4)	27 (2)	35 (2)	−9 (4)	7 (5)	11 (3)
C (2)	0,5871 (4)	0,4707 (3)	−0,3679 (3)	65 (4)	26 (2)	32 (3)	−1 (5)	6 (6)	10 (4)
C (3)	0,3970 (6)	0,4629 (4)	−0,0458 (4)	128 (6)	41 (2)	35 (3)	20 (7)	−18 (7)	14 (4)
N (4)	0,4323 (4)	0,3984 (3)	−0,1298 (3)	83 (4)	33 (2)	35 (2)	13 (5)	−13 (5)	1 (4)
C (5)	0,5774 (5)	0,3609 (3)	−0,1228 (4)	97 (6)	37 (2)	45 (3)	33 (6)	−25 (7)	3 (5)
C (6)	0,6026 (5)	0,3339 (3)	−0,2368 (4)	86 (5)	27 (2)	39 (3)	4 (5)	6 (6)	0 (4)
C (7)	0,5219 (4)	0,3931 (3)	−0,3113 (3)	68 (5)	21 (2)	30 (3)	−12 (5)	7 (5)	−10 (3)
C (8)	0,4689 (4)	0,3462 (3)	−0,4081 (3)	69 (4)	23 (2)	31 (3)	4 (5)	3 (5)	−1 (4)
C (9)	0,3738 (5)	0,2821 (3)	−0,4163 (4)	93 (6)	30 (2)	56 (3)	−22 (6)	−3 (7)	0 (5)
C (10)	0,3466 (6)	0,2483 (4)	−0,5157 (4)	123 (6)	35 (2)	71 (4)	−38 (8)	32 (8)	14 (6)
C (11)	0,4142 (6)	0,2788 (4)	−0,6036 (5)	125 (7)	41 (3)	59 (4)	−18 (7)	27 (9)	24 (5)
C (12)	0,5117 (5)	0,3408 (4)	−0,5964 (4)	83 (5)	45 (1)	47 (3)	8 (6)	18 (7)	15 (5)
C (13)	0,5354 (4)	0,3757 (3)	−0,4972 (3)	66 (5)	25 (2)	41 (3)	10 (5)	21 (6)	6 (4)
C (14)	0,2893 (6)	0,5244 (4)	−0,0860 (4)	121 (6)	37 (2)	60 (4)	13 (7)	−44 (8)	5 (5)
C (15)	0,3396 (5)	0,5770 (3)	−0,1846 (4)	102 (6)	32 (2)	52 (3)	32 (6)	−53 (7)	5 (5)
C (16)	0,6924 (5)	0,5190 (3)	−0,3019 (4)	70 (5)	29 (2)	39 (3)	−2 (5)	6 (6)	13 (4)
C (17)	0,5979 (5)	0,5517 (3)	−0,2121 (4)	83 (5)	28 (2)	39 (3)	−1 (5)	−13 (6)	11 (4)
C (18)	0,4809 (5)	0,6173 (3)	−0,4166 (4)	96 (5)	25 (2)	68 (4)	−1 (5)	10 (7)	−13 (4)
C (19)	0,4615 (4)	0,5311 (3)	−0,3674 (4)	66 (4)	31 (2)	37 (3)	0 (5)	−17 (6)	−8 (4)
C (20)	0,4503 (4)	0,5287 (3)	−0,2441 (3)	69 (5)	22 (2)	38 (3)	7 (5)	3 (6)	−2 (4)
C (21)	0,4168 (5)	0,4349 (3)	−0,2392 (3)	74 (5)	23 (2)	38 (3)	2 (5)	−8 (6)	−10 (4)
C (22)	0,8177 (5)	0,4759 (3)	−0,2643 (4)	79 (5)	28 (2)	37 (3)	−5 (5)	21 (6)	6 (4)
C (23)	1,0305 (6)	0,4157 (5)	−0,3181 (5)	79 (6)	54 (3)	86 (3)	21 (8)	33 (9)	−4 (6)
O (24)	0,8526 (4)	0,4666 (3)	−0,1739 (3)	106 (4)	62 (2)	51 (3)	29 (5)	21 (5)	18 (4)
O (25)	0,8984 (3)	0,4524 (3)	−0,3448 (3)	65 (3)	54 (2)	47 (2)	21 (4)	−3 (5)	−5 (3)
O (w)†	0,3624 (5)	0,2816 (4)	0,1105 (4)	152 (6)	88 (3)	99 (4)	35 (7)	−1 (8)	−8 (6)

*The anisotropic temperature factor has the form $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

†Oxygen atom of the water molecule.

EXPERIMENTAL METHOD AND INTERPRETATION OF STRUCTURE

A Hilger–Watts automatic four-circle diffractometer was used with CuK_α radiation (graphite monochromator). The parameters of the elementary cell were refined by the method of least squares from 14 reflections with $\theta \geq 30°$. These and other crystallographic characteristics are as follows:

$C_{21}H_{26}N_2O_2 \cdot HBr \cdot H_2O$	$a = 9.777(6)$ Å
$M = 437.4$	$b = 16.056(8)$ Å
$d_{meas} = 1.46$ g/cm³	$c = 12.714(6)$ Å
$d_{calc} = 1.46$ g/cm³	$V = 1996$ Å
Space group $P2_12_12_1$	$Z = 4$.

The intensities of the reflections (ω scanning by the method of ordinate analysis [7]) were measured in the two independent octants $hk\ell$ and $\bar{h}k\bar{\ell}$. After taking into account the Lorentz and polarization factors, averaging equivalents and rejecting weak reflections with $|F|^2 \leq 3\sigma$, we obtained a working group of 2765 reflections.

A three-dimensional Patterson synthesis showed the position of the Br atom, and the coordinates of the other atoms were determined by successive approximations of the three-dimensional series of electron density in which the molecule of water of crystallization also appeared. The structure was refined in the block-diagonal anisotropic approximation to R = 0.061. The position and thermal parameters obtained are given in Table 1.

In the calculations we used the atomic amplitudes given by Hanson et al. [8]. The calculations were performed by the Rentgen-70 program [9] and the anisotropic refinement and determination of the absolute configuration by the UMNKSA program [10].

The absolute configuration was determined by the method of Chekhlov et al. [11] in the process of refining the structure taking into account the effect of the anomalous scattering of x rays, in this case the CuK_α radiation by the Br atoms. In addition to other parameters, we refined the absolute correction $\Delta f''$, the initial value of which was taken as zero, and the final correction proved to be 1.27 ± 0.02, i.e., agreeing well with the theoretical value of 1.283 [12]. The positive nature of the value found shows that the refined model corresponds to the true absolute configuration.

Structure of (–)-Pseudokopsinine and Its Molecular Geometry. The absolute stereochemistry of the cation of (–)-pseudokopsinine found in a crystal of the monohydrate of its hydrobromide is shown in Fig. 1, which corresponds to structural formula (I'). It differs from structure (I) suggested previously by the fact that the methylene bridge C(19) connects the C(2) and C(20) and not the C(6) and C(20) atoms. This apparently insignificant change means in actual fact a radical rearrangement of the stereochemistry of the molecule, as can be seen well in models. Thus, in structure (I) there are four 6-membered and three 5-membered rings, and in structure (I') three 6-membered and four 5-membered rings.

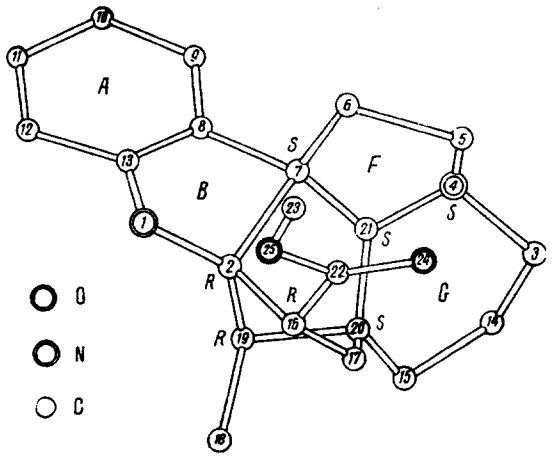

Fig. 1. Absolute stereochemistry of the cation of (–)-pseudokopsinine and number of the atoms.

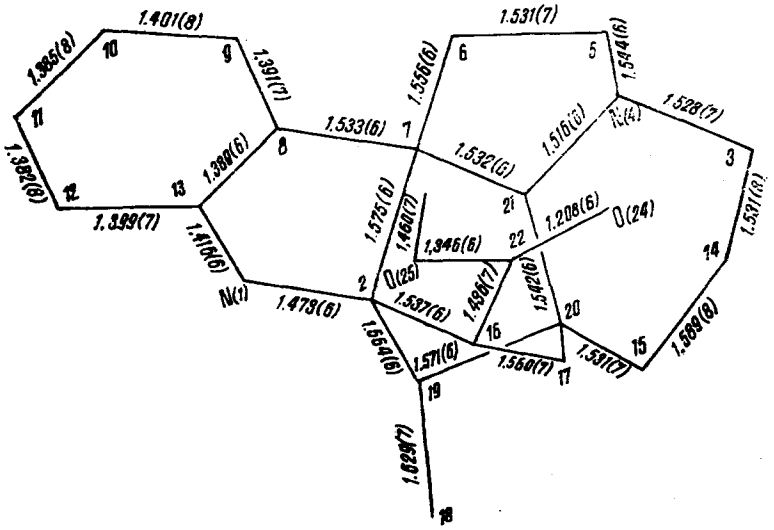

Fig. 2. Lengths of the bonds in the cation (Å).

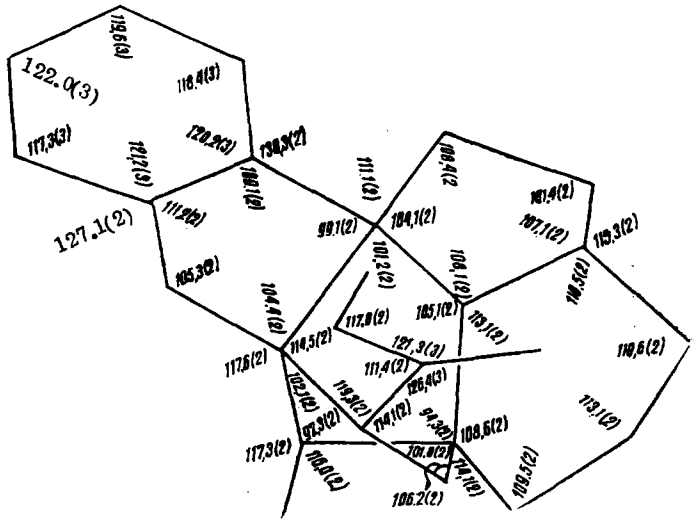

Fig. 3. Valence angles in the cation (deg).

The conformations of the rings can be judged from Table 2, which gives the equations of the planar fragments of the rings and the deviations of the individual atoms from these planes. The benzene ring A is plane. The pyrroline ring B is a flattened envelope ^{2}E: the tetrahedral C(2) atom departs from the plane of the other four atoms of the ring by 0.489 Å (in the ideal C_s envelope by 0.75 Å [13]). The cyclopentane ring C (atoms 2, 7, 21, 20, and 19) is a highly distorted ^{19}T half-chair; the C(19) and C(20) atoms deviate in different directions by 0.778 and −0.278 Å, respectively (in the ideal C_s half-chair by ±0.39 Å [13]). The cyclopentane ring D (atoms 2, 16, 17, 20, 19) is a ^{19}E envelope; the C(19) atom deviates by 0.906 Å, the ideal value being 0.75 Å [13]. The cyclohexane ring E (atoms 2, 16, 17, 20, 21, 7), being included in a norbornane system, has the $^{2,20}B$ boat configuration which is slightly distorted because of condensation with other rings. In actual fact, the deviations of the C(2) and C(20) atoms from the mean plane of the four other atoms of the ring (which, in any case, are not completely coplanar) amount to 0.778 and 0.716 Å, i.e., they are not the same (in the ideal C_6 boat, 0.73 Å [14]). The pyrrolidine ring F is a flattened ^{5}E envelope (deviation of the C(5) atom 0.486 Å instead of the ideal value of 0.75 Å [13]). The piperidine ring G, highly distorted by condensation with the norbornane fragment, is a twisted boat $^{20}S_{14}$: the deviation of the C(20) and C(14) atoms in opposite directions are −0.775 and 0.706 Å, respectively (in the ideal twisted C_6 boat, 0.64 Å [15]).

TABLE 2. Equations of the Planes of Some Fragments of the Molecule and Deviations of the Atoms from These Planes (Δ, Å)

$A: -7{,}073x + 10{,}840y - 1{,}819z = 1{,}177$
$B: -6{,}991x + 11{,}505y - 1{,}538z = 1{,}175$
$C: -4{,}562x + 8{,}001y - 9{,}287z = 3{,}727$
$D: 9{,}305x + 4{,}919y + 0{,}239z = 5{,}957$
$E: 6{,}313x + 11{,}738y + 2{,}801z = 7{,}052$
$F: 6{,}726x + 1{,}061y + 9{,}187z = 1{,}064$
$G: -1{,}068x + 13{,}335y - 6{,}941z = 8{,}234$

Ring A		Ring B		Ring C		Ring D		Ring E		Ring F		Ring G	
atom	Δ	atom	Δ	atom	Δ	atom	Δ	atom	Δ	atom	Δ	atom	Δ
C (8)	0,000	N (1)	0,000	**C** (2)*	−0,778	C (3)	−0,004	N (4)	0,010	C (2)	0,000	C (2)	0,030
C (9)	0,007	C (2)*	−0,489	C (16)	−0,071	N (4)	0,006	C (5)*	−0,485	C (7)	0,000	C (16)	−0,043
C (10)	0,000	C (7)	0,000	**C** (17)	0,071	C (21)	−0,004	**C** (6)	−0,010	C (21)	0,000	**C** (17)	0,044
C (11)	−0,012	C (8)	−0,001	**C** (20)*	−0,716	C (20)*	−0,775	**C** (7)	0,015	C (20)*	−0,278	**C** (20)	−0,030
C (12)	0,018	C (13)	0,001	**C** (21)	−0,072	**C** (15)	0,002	**C** (21)	−0,015	C (19)*	0,778	C (19)*	−0,906
C (13)	−0,012			**C** (7)	0,072	C (14)*	0,706						

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

TABLE 3. Lengths of the Bonds of d (Å) and the Valence Angles ω (deg.)

Bond	d	Bond	d	Angle	ω	Angle	ω
C (8)—C (9)	1,391 (7)	N (1)—C (2)	1,473 (6)	N (1) C (2) C (7)	104,4 (2)	C (7) **C** (8) **C** (9)	130,3 (2)
C (9)—C (10)	1,401 (8)	N (1)—C (13)	1,416 (6)	N (1) **C** (2) **C** (16)	117,6 (2)	C (7) C (8) C (13)	109,1 (2)
C (10)—C (11)	1,385 (8)	Mean		N (1) C (2) C (19)	116,1 (2)	**C** (7) C (21) C (20)	105,1 (2)
C (11)—C (12)	1,382 (8)	N (1)—**C**	1,445 (6)	N (1) C (13) C (8)	111,2 (2)	**C** (8) C (7) C (21)	117,6 (2)
C (12)—C (13)	1,399 (7)			N (1) C (13) C (12)	127,1 (2)	C (8) **C** (9) C (10)	118,4 (3)
C (13)—C (18)	1,389 (6)	N (4) – **C** (3)	1,528 (7)	C (2) N (1) **C** (13)	105,3 (2)	C (18) C (13) C (12)	121,2 (3)
		N (4)— **C** (5)	1,544 (6)	C (2) C (7) C (6)	123,5 (2)	**C** (9) **C** (8) C (13)	120,2 (3)
Mean	1,391 (7)	N (4)— **C** (21)	1,516 (6)	C (2) C (7) C (8)	99,1 (2)	**C** (9) C (10) C (11)	119,6 (3)
		Mean		C (2) **C** (7) C (21)	101,2 (2)	C (10) C (11) **C** (12)	122,0 (3)
C (2)– C(7)	1,575 (6)	N (4)– **C**	1,529 (6)	C (2) C (16) C (17)	99,5 (2)	C (11) **C** (12) C (13)	117,3 (3)
C (7)—C(8)	1,533 (6)			C (2) **C** (16) C (22)	119,3 (2)	C (14) **C** (15) C (20)	109,5 (2)
C (2)– C(16)	1,537 (6)	C (22)—O (24)	1,208 (6)	C (2) **C** (19) C (18)	117,3 (2)	C (15) **C** (20) C (17)	114,1 (2)
C (16) – C (17)	1,560 (7)	C (22)—O (25)	1,346 (6)	**C** (2) C (19) C (20)	92,3 (2)	C (15) C (20) C (19)	101,0 (2)
C (17)—C (20)	1,544 (7)	C (23)—O (25)	1,460 (7)	C (3) N (4) C (5)	115,3 (2)	C (15) C (20) **C** (21)	108,6 (2)
C (20)—C (21)	1,542 (6)			C (3) N (4) C (21)	110,5 (2)	C (16) C (2) C (19)	102,1 (2)
C (21)—C (7)	1,532 (6)			C (3) C (14) **C** (15)	113,1 (2)	O (16) C (17) C (20)	106,2 (2)
C (15)—C (20)	1,531 (7)			N (4) C (3) C (14)	110,6 (2)	C (16) **C** (22) O(24)	126,4 (3)
C (14)—C (15)	1,589 (8)			**N** (4) C (5) C (6)	101,4 (2)	C (16) **C** (22) **O** (25)	111,4 (2)
C (3)—C (14)	1,531 (8)			N (4) **C** (21) C (7)	108,1 (2)	C (17) C (16) C (22)	114,1 (2)
C (5)—C (6)	1,531 (7)			N (4) C (21) C (20)	113,1 (2)	C (17) C (20) C (21)	114,5 (2)
C (6)—C (7)	1,556 (6)			C (5) N (4) C (21)	107,1 (2)	C (17) C (20) **C** (19)	121,6 (2)
C (9)—C (20)	1,571 (6)			**C** (5) C (6) C (7)	108,4 (2)	C (18) C (19) C (20)	116,0 (2)
C (2)—C (19)	1,564 (6)			C (6) C (7) C (8)	111,1 (2)	C (19) C (20) **C** (21)	94,3 (2)
C (18)—C (19)	1,529 (7)			**C** (6) C (7) **C**(21)	104,1 (2)	C (22) O (25) C (23)	117,0 (2)
C (16) – C (22)	1,486 (7)			C (7) C (2) C (16)	114,5 (2)	O (24) C (22) O (25)	121,3 (3)
				C (7) C (2) C (19)	99,5 (2)		
Mean	1,544 (7)						

The linkages of the rings are as follows: B/C — cis; B/E — trans; C/F — cis/ C/G — trans; E/F — cis; E/G — cis; F/G — cis. The methoxycarbonyl group occupies the equatorial position in ring E at the C(16) atom.

Rings B, F, and G each have two and C and E each three common sides with neighboring rings. Thus, the molecule possesses a rigid three-dimensional structure, and only for the peripheral ring G are two conformations possible — chair or twisted boat — of which it "selects" the second. It is interesting that in another dimeric indole alkaloid, (—)-kopsanone [formula (III)], this ring has the chair conformation, as has also been established by x-ray structural investigations with a determination of the absolute configuration [16].

The (—)-pseudokopsinine molecule has seven asymmetric centers including the N(4) nitrogen atom, the configuration of which is rigidly fixed by its inclusion in the condensed rings G and F [formula (I'), Fig. 1]. In the Cahn—Ingold—Prelog nomenclature [17], the configuration found must be symbolized 2R,4(N)S,7S,16R,19R,20S,21S.

Recently, the structure (but not the relative and, still less, the absolute stereochemistry) of vindolinine and some of its derivatives, including 14,15-dihydrovindolinine, have been redetermined by the ^{13}C NMR method [18]. This structure (II') also differs from the structure (II) proposed previously on the basis of mass spectra [14], just as our structure of (—)-pseudokopsinine (I') differs from its old structure (I). Thus, in spite of the refutation of the old formulas, (—)-pseudokopsinine and 14,15-dihydrovindoline have the same skeleton, but their stereochemical interrelationship has not yet been elucidated, since the absolute configuration of 14,15-dihydrovindolinine is unknown. The solution of this question would be of interest, since the structure of a whole group of natural bases was assigned on the basis of the old erroneous structures (I) and (II) [19].

The bond lengths (Fig. 2) and valence angles (Fig. 3) in the cation and their standard deviations are given in Table 3. The mean length of the C-C bond in the benzene find is 1.391(7) Å, i.e., close to that found in crystalline benzene (1.398 Å) [20]. The lengths of the ordinary C-C bonds in the saturated rings vary from 1.531 to 1.589 Å, but the mean value of 1.544(7) Å is close to the standard value of 1.541(3) Å [21]. The variations mentioned can be explained by some general strain of the condensed polycyclic system also appearing in the substantial deviations of the conformations of the rings from the ideal conformations that have been mentioned above.

The lengths of the bonds in the methoxycarbonyl group — $C(sp^3)$—$C(sp^2)$ 1.486(7) Å, $C(sp^2)$ = O 1.208(6) Å, $C(sp^2)$—O 1.346(6) Å, and O—$C(sp^3)$ 1.460(7) Å — are close to the usual lengths (1.516(5), 1.23(1), 1.36(1), and 1.43(1), respectively [21]).

The lengths of the N(1)—C(2) and N(1)—C(13) bonds of 1.473(6) and 1.416(6) Å, respectively, are close to the standard values of ordinary N—$C(sp^3)$ and N—$C(sp^2)$ bonds of 1.472(5) and 1.426(12) Å for pyramidal tertiary nitrogen [21]. On the other hand, the lengths of the N-C bonds of the other nitrogen atom, N(4), are considerably greater and are close to one another [1.516(6), 1.528(7), and 1.544 (6) Å] and their mean value of 1.529(6) is close to the usual length of an $\overset{+}{N}$—$C(sp^3)$ bond of quaternary (ammonium) tetrahedral nitrogen of 1.549 Å [22]. Consequently, although the hydrogen atom has not been localized objectively, this difference in the lengths of the C—N bonds shows that in the formation of the hydrobromide, as was to be expected, the more basic N(4) atom is protonated, and not N(1), the basicity of which is lowered because of the bond with a benzene atom.

Below we give the nature of the variation of the valence angles:

Ring	Range of measurements of valence angles, deg	Mean valence angle
A(benzene)	117.3(3)—122.0(3)	119.8(3)
B(5-membered)	99.1(2)—111.2(2)	105.8(2)
C(6-membered)	99.5(2)—114.5(2)	106.8(2)
D(6-membered)	108.6(2)—113.1(2)	110.9(2)
E(5-membered)	101.4(2)—108.4(2)	105.8(2)
F(5-membered)	92.3(2)—105.1(2)	98.5(2)
G(6-membered)	92.3(2)—106.2(2)	100.2(2)

As the result of strains, the individual angles in the saturated rings differ substantially from the ideal tetrahedral value, but their average value in the whole ring is close to it. The deformations of some angles at the quaternary carbon atoms present in some rings are particularly great [at C(2), for example, 99.5°, at C(7), 99.1 and 123.5°; at C(20)

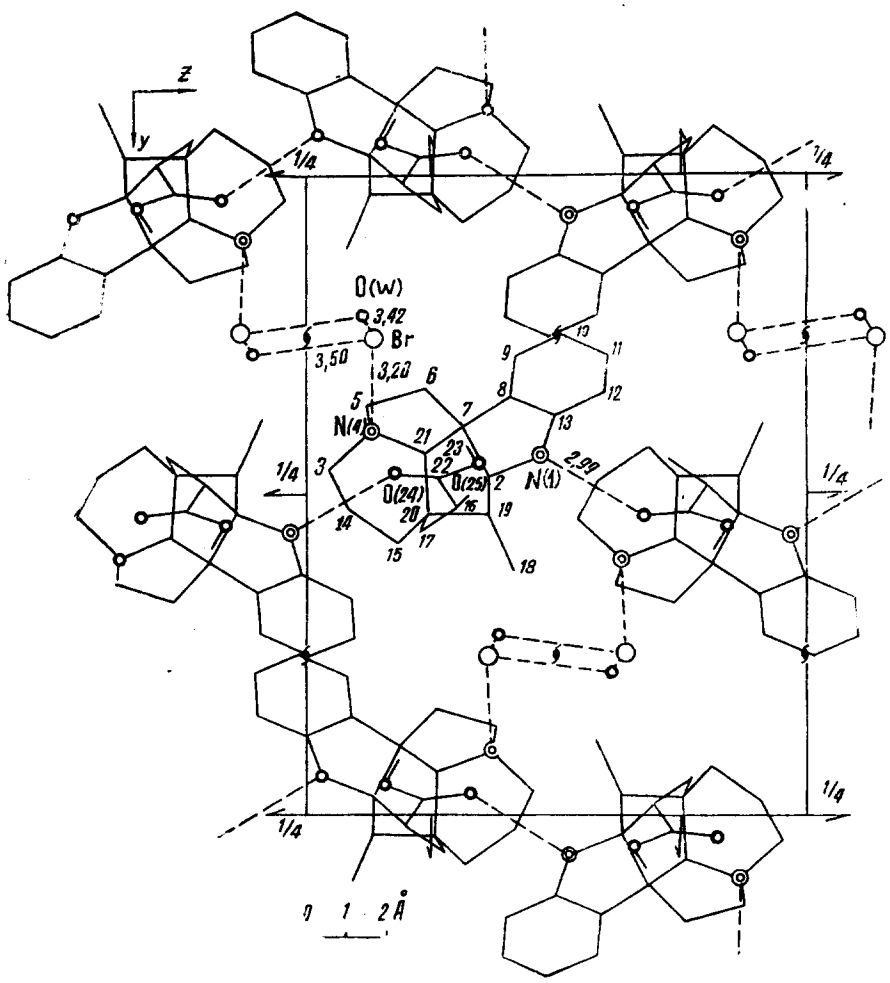

Fig. 4. Projection of the structure on the yz plane. The hydrogen bonds are shown by broken lines.

94.3°] and so are they at "bridge" tertiary atoms [at C(16) 99.5°; at C(19) 92.3°; at C(20) 94.3°]. The mean valence angle in the benzene ring A is practically ideal, and the sum of the angles at the trigonally hybridized (sp^2) atoms is close to 360°: C(8) 359.6°; C(13) 359.5°; C(22) 359.1°. The angle at the ester oxygen C(22)O(25)C(23) is 117.0(2)°, i.e., the usual.

Packing in the Crystal. The structure (Fig. 4) has four symmetrically independent hydrogen atoms capable of participating in hydrogen bonds. The hydrogen atoms in the molecule of water of crystallization form H bonds with two Br^- anions having lengths of 3.42 and 3.50 Å (the sum of the van der Waals radii of Br and O is 3.35 Å, and therefore these are weak bonds). As a result of rotation about the 2_1 axis, infinite $\cdots Br^- \cdots H\text{-}O\text{-}H \cdots$ helices are formed parallel to [100], the Br-O-Br' angle being 119.2°, i.e., fairly close to the tetrahedral value.

Below we give the angles at the H bonds:

Length of the hydrogen bonds, Å		Angles at the hydrogen bonds, deg	
HO(w)—H...Br	3,42(1)	Br...O...Br'	119,2(1)
HO(w)—H...Br'	3,50(1)	O...Br...O'	111,7(1)
$\overset{+}{N}$(4)—H...Br	3,20(1)	O(w)...Br...N(4)	142.8(1)
		O'(w)...Br...N(4)	65.8(1)
		Br...N—C(3)	110.4(1)
		Br...N—C(5)	117,0(1)
		Br...N—C(21)	101.2(1)
N(1)—H...O(24')	2,99(2)	C(22')=O(24')...N(1)	140.5(2)
		O(24')...N(1)—C(2)	127,8(2)
		O(24')...N(1)—C(13)	101,7(2)

The N(1)-H•••O(24) H-bonds with a length of 2.99 Å join the cations into infinite helices about the 2_1 axis parallel to [001] (the sum of the van der Waals radii of N and O is 2.90 Å, i.e., these bonds are also weak). Finally, H bonds of the quaternary type $\overset{+}{N}$(4)-H••• Br^- connect the two series of helices; the length of these bonds is 3.20 Å at a sum of the Br and N radii of 3.45 Å; i.e., they are very strong bonds.

The substances were made available by V. M. Malikov, the single crystals studied were obtained by G. N. Zakharova, and A. N. Chekhlov advised the use of the program of anisotropic refinement with the determination of the absolute configuration.

SUMMARY

By a complete x-ray structural investigation, the structural formula of (—)-pseudokopsinine has been refined and its absolute configuration has been determined.

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