X-RAY STRUCTURAL INVESTIGATION OF ALKALOIDS.

III. MOLECULAR STRUCTURE AND ABSOLUTE CONFIGURATION OF (+)-EXCELSINE

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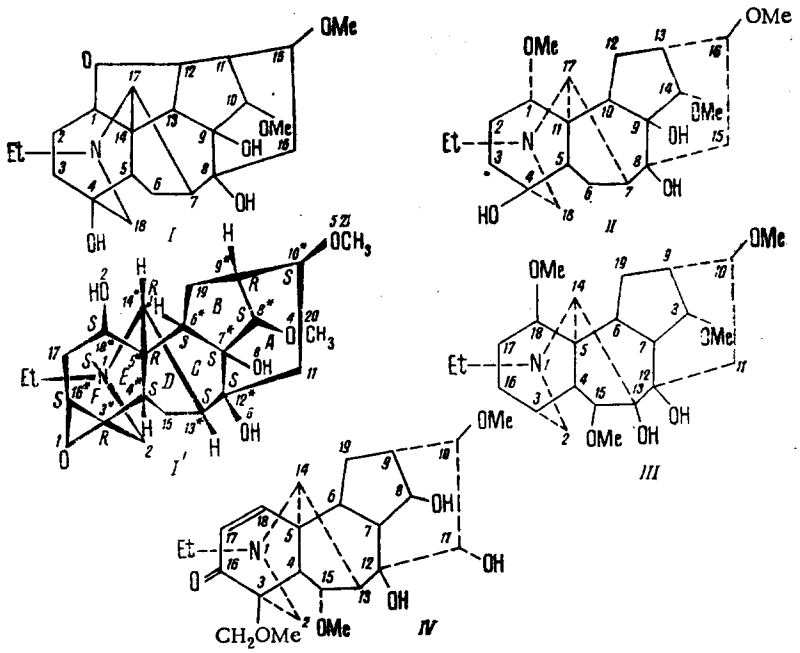
The alkaloid (+)-excelsine $C_{22}H_{33}NO_6$, isolated from the roots of *Aconitum excelsum (Leucostomum)* Worosch., family Ranunculaceae, was assigned the structure (I) on the basis of chemical and spectral characteristics [1]. Thus, this new alkaloid was assigned to the diterpene group with the lycoctonine skeleton and with an oxygen bridge forming a tetrahydrofuran ring.

In order to determine the structure and absolute configuration of (+)-excelsine independently and objectively, we have performed a complete x-ray structural investigation of the monohydrate of its hydriodide $C_{22}H_{33}NO_6 \cdot HI \cdot H_2O$ (we have shown the presence of a molecule of water of crystallization). Preliminary results of this investigation have been published previously [2].

In the formulas given below, the numbering of the atoms is given according to the corresponding publications in which, unfortunately, it varies (for (I) from [2], for (II) from [10], for (III) and (IV) from [14, 15]). In the discussion of the true structure of (+)-excelsine (I') in this paper use is made everywhere of the numbering of the lycoctonine skeleton introduced by Przybylska [14, 15].



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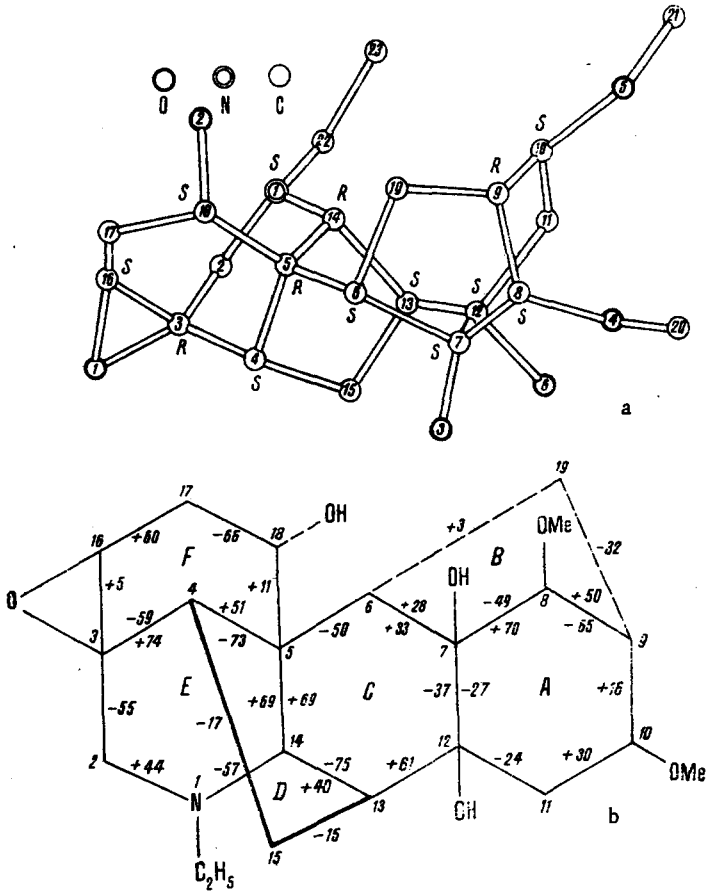

Fig. 1. The cation of (+)-excelsine in the structure studied: a) absolute stereochemistry; b) torsional angles (degrees).

EXPERIMENTAL METHOD AND INTERPRETATION OF STRUCTURE

The experimental investigation was performed on a Hilger–Watts automatic four-circle diffractometer with CuK_α radiation (graphite monochromator). The parameters of the rhombic elementary cell were refined by the method of least squares from 12 reflections with $\theta \geq 30°$. These and other crystallographic characteristics are as follows:

$C_{22}H_{33}NO_6 \cdot HI \cdot H_2O$	$a = 10.970(7)$ Å
M = 535.5	$b = 20.194(9)$ Å
$d_{meas} = 1.56$ g/cm³	$c = 10.747(7)$ Å
$d_{calc} = 1.55$ g/cm³	$V = 2381$ Å³
Space group $P2_12_12_1$	$Z = 4$

The intensities of the reflections (ω scanning by the method of ordinate analysis [3]) were measured in the two independent octants $hk\ell$ and $\bar{h}k\bar{\ell}$. After taking into account the Lorentz and polarization factors, the averaging of equivalents, and the rejection of weak reflections with $|F|^2 \leq 3\sigma$ we obtained a working group of 1817 reflections. A three-dimensional Patterson synthesis showed the position of the iodine atom, and the coordinates of the remaining atoms were determined by successive approximations of three-dimensional electron density series in which the molecule of the water of crystallization also appeared. The structure was refined in the block-diagonal anisotropic approximation to R = 0.068. The coordinates and thermal parameters obtained are given in Table 1.

In the calculations we made use of the atomic amplitudes given by Hanson et al. [4]. The calculation was performed by the Roentgen-70 program [5], and the anisotropic refinement and determination of the absolute configuration by the UMNKSA program [6].

The absolute configuration was determined by the method of Chekhlov et al. [7] in the process of refining the structure taking into account the effect of the anomalous scattering

TABLE 1. Position and Thermal Parameters*

Atom	x	y	z	$B_{11}\times10^4$	$B_{22}\times10^4$	$B_{33}\times10^4$	$B_{12}\times10^4$	$B_{13}\times10^4$	$B_{23}\times10^4$
J	0,1884 (1)	0,1407 (5)	0,1215 (1)	231 (1)	44 (1)	184 (1)	−42 (1)	−70 (2)	2 (1)
O (1)	0,6501 (9)	0,1515 (6)	0,2380 (13)	165 (2)	47 (4)	339 (20)	42 (11)	−50 (23)	−109 (15)
O (2)	0,3223 (8)	0,2167 (4)	0,4095 (8)	135 (9)	35 (3)	202 (12)	4 (9)	−65 (18)	17 (9)
O (3)	0,7143 (7)	0,3943 (4)	0,4932 (8)	127 (10)	27 (2)	186 (11)	9 (8)	17 (16)	−1 (8)
O (4)	0,5695 (9)	0,5124 (4)	0,5497 (9)	180 (12)	30 (3)	20 (13)	−5 (9)	22 (20)	−1 (9)
O (5)	0,2681 (11)	0,5114 (7)	0,4737 (15)	200 (15)	58 (5)	391 (25)	26 (13)	−78 (30)	−88 (18)
O (6)	0,6484 (8)	0,4686 (4)	0,2964 (9)	152 (11)	31 (3)	200 (13)	−40 (8)	58 (17)	48 (9)
O (H_2O)	0,3684 (8)	0,0054 (5)	0,4550 (10)	146 (10)	38 (3)	241 (15)	12 (9)	38 (19)	−26 (11)
N (1)	0,4057 (9)	0,2724 (5)	0,1895 (9)	117 (11)	33 (4)	166 (13)	24 (10)	−35 (19)	−11 (10)
C (2)	0,5108 (14)	0,2320 (7)	0,1354 (16)	186 (18)	44 (5)	186 (18)	16 (15)	−13 (32)	−37 (18)
C (3)	0,5836 (11)	0,2092 (7)	0,2445 (14)	97 (13)	33 (4)	226 (20)	−1 (12)	101 (26)	−40 (16)
C (4)	0,6274 (10)	0,2635 (6)	0,3310 (12)	111 (12)	21 (3)	180 (18)	13 (10)	40 (22)	−23 (12)
C (5)	0,5074 (10)	0,2830 (5)	0,4013 (12)	105 (12)	20 (3)	170 (16)	9 (9)	−5 (22)	20 (12)
C (6)	0,5274 (11)	0,3329 (5)	0,5090 (12)	109 (13)	31 (3)	133 (15)	−20 (11)	13 (22)	14 (11)
C (7)	0,5880 (11)	0,4016 (6)	0,4783 (13)	120 (14)	33 (4)	171 (7)	9 (12)	−1 (24)	7 (14)
C (8)	0,5335 (13)	0,4458 (7)	0,5805 (13)	186 (17)	32 (4)	159 (19)	−3 (14)	53 (27)	−20 (13)
C (9)	0,3950 (11)	0,4299 (7)	0.5718 (14)	113 (14)	49 (4)	194 (22)	−15 (14)	116 (26)	−24 (16)
C (10)	0,3369 (13)	0,4518 (6)	0,4462 (16)	170 (18)	22 (4)	275 (23)	56 (13)	66 (32)	−34 (14)
C (11)	0,4281 (11)	0,4673 (6)	0,3416 (14)	109 (12)	29 (4)	225 (22)	21 (11)	−71 (25)	38 (14)
C (12)	0,5526 (12)	0,4272 (6)	0,3455 (12)	111 (14)	33 (4)	−9 (24)	−6 (12)	−9 (24)	3 (13)
C (13)	0,5439 (12)	0,3687 (6)	0,2458 (13)	139 (15)	21 (3)	203 (18)	−38 (12)	90 (27)	−19 (14)
C (14)	0,4423 (11)	0,3204 (5)	0,2921 (12)	101 (13)	27 (3)	165 (16)	2 (11)	−56 (22)	−23 (11)
C (15)	0,6636 (11)	0,3233 (6)	0,2522 (14)	110 (14)	32 (4)	196 (17)	−15 (11)	−24 (24)	−12 (13)
C (16)	0,5272 (14)	0,1494 (8)	0,3121 (16)	156 (17)	38 (5)	266 (24)	23 (16)	−25 (32)	−19 (17)
C (17)	0,5187 (14)	0,1607 (7)	0,4531 (17)	140 (17)	50 (5)	241 (23)	2 (15)	22 (31)	36 (18)
C (18)	0,4395 (13)	0,2213 (6)	0,4593 (15)	136 (15)	27 (4)	259 (22)	−31 (13)	−70 (30)	51 (15)
C (19)	0,4018 (11)	0,3526 (6)	0,5747 (14)	146 (14)	25 (3)	221 (21)	−7 (12)	119 (26)	−28 (14)
C (20)	0,5602 (17)	0,5566 (8)	0,6572 (17)	240 (25)	51 (6)	253 (27)	15 (20)	57 (38)	−135 (2)
C (21)	0,1640 (19)	0,5212 (11)	0,4233 (26)	269 (30)	70 (9)	430 (54)	103 (27)	−403 (68)	−50 (34)
C (22)	0,3409 (13)	0,3072 (8)	0,0820 (15)	161 (19)	47 (5)	197 (22)	−6 (16)	−112 (29)	11 (16)
C (23)	0,2183 (15)	0,3381 (8)	0,1263 (21)	179 (20)	51 (6)	332 (31)	26 (16)	−221 (45)	−92 (23)

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

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

$A: 3{,}480x + 1{,}872y + 2{,}195z = 10{,}661$
$B: 4{,}848x + 0{,}433y + 9{,}638z = 7{,}623$
$C: 10{,}822x - 3{,}279y + 0{,}226z = 4{,}694$
$D: 3{,}210x + 9{,}737y + 8{,}872z = 7{,}521$
$E: 2{,}938x + 18{,}335y - 3{,}463z = 5{,}409$
$F: 8{,}889x - 2{,}783y + 6{,}121z = 6{,}141$

Ring A		Ring B		Ring C		Ring D		Ring E		Ring F	
atom	Δ	atom	Δ	atom	Δ	atom	Δ	atom	Δ	atom	Δ
C(7)	0,035	C(6)	0,016	C(8)	0,040	C(4)	0,000	N(1)	−0,122	C(3)	0,039
C(8)*	−0,830	C(7)	−0,011	C(6)	−0,037	C(5)*	0,387	C(2)	0,122	C(4)*	−0,728
C(9)	−0,035	C(8)*	−0,751	C(7)*	−0,460	C(14)*	−0,428	C(3)*	0,705	C(5)	−0,038
C(10)	0,032	C(9)	0,011	C(12)	0,036	C(13)	0,000	C(4)	−0,119	C(18)	0,039
C(11)*	−0,343	C(19)	−0,017	C(13)	−0,039	C(15)	0,000	C(5)	0,119	C(17)*	−0,796
C(12)	−0,032	—	—	C(14)*	0,891	—	—	C(14)*	−0,754	C(16)	−0,040

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

of the x rays, in this case the CuK_α radiation, by the iodine atoms. In addition to the other parameters, the absolute correction $\Delta f''$ was refined; its initial value was taken as zero while the final value proved to be 6.5 ± 0.3, i.e., agreeing well with the theoretical value of 6.835 [8]. The positive nature of the value of $\Delta f''$ found shows that the refined model corresponds to the true absolute configuration.

Structure of (+)-Excelsine and Molecular Geometry. The absolute stereochemistry of (+)-excelsine is shown in Fig. 1a, which corresponds to structural formula (I'). Although the lycoctine skeleton is actually confirmed, the new formula (I') does not coincide with the old one (I) in two important details. In the first place, the tetrahydrofuran ring is not closed: there is an OH group in the C(18) atom. In the second place, the presumed oxygen bridge is realized as an epoxy tie-piece C(3)—O(1)—C(16) "at a bridge head" like the epoxide of the sesquiterpene longifolene [9].

The molecule has a rigid three-dimensional skeleton consisting of seven rings (including the three-membered epoxide ring). The conformations of the rings can be judged from the figures in Tables 2 and 3.

The cyclohexane ring A is an unsymmetrical boat $^{8,11}B$ with different bendings of the angles (the C(8) departs from the plane of the bottom of the boat by 0.83 Å and the C(11) atom by 0.34 Å as compared with the ideal value of 0.73 Å [10]). The cyclopentane ring B has the ^{8}E envelope conformation: the deviation of the C(8) by 0.75 Å corresponds to its value for an ideal C_s envelope [11]. The cyclohexane ring C (atoms 5, 6, 7, 12, 13, 14) is a $^{7}C_{14}$ distorted chair; the C(7) and C(14) atoms deviate in opposite directions by 0.46 and 0.89 Å, respectively. In the ideal C_6 chair they deviate by ±0.73 Å [10]. The cyclopentane ring D (atoms 4, 5, 14, 13, 15) is an almost ideal $^{5}T_{14}$ half-chair; the deviations of the C(5) and C(14) atoms by 0.39 and 0.43 Å, respectively, in opposite directions are close to the ideal values (0.39 Å) [11]. The piperidine ring E (atoms 1, 2, 3, 4, 5, 14) is a $^{3}C_{14}$ distorted chair; deviations of the C(3) and C(14) atoms are 0.71 and 0.75 Å, respectively, i.e., almost ideal, but the remaining members of the ring depart from their mean plane by ±0.12 Å. The cyclohexane ring F (atoms 3, 4, 5, 18, 17, 16) is a $^{4,17}B$ boat close to the ideal form: the C(4) and C(17) atoms depart from the mean plane of the other four by 0.73 and 0.80 Å. Deviations of the rings from the ideal conformations are customary for alkaloids [10, 12] and are due to certain strains in them when they take part in a rigid condensed polycyclic system, and also to some steric hindrance between the substituents.

All the ring linkages A/C, B/C, C/E, and D/F are of the cis type, which corresponds to the 4α,6α,9α,14β configuration. The bonds from the rings to the substituents have the following orientation N—Et equatorial to ring F, the bonds with the epoxy bridge C(3)—O(1) and C(16)—O(1) are equatorial, and the C(18)—O(2)H bond is axial to ring F, the C(7)—O(3)H, C(12)—O(6)H, and C(10)—O(5)Me bonds are equatorial, and the C(8)—O(4)Me bond is axial to ring A.

The (+)-excelsine molecule has 14 asymmetric centers, including the N(1) nitrogen atom, inversion relative to which is impossible because of the rigid conformation of

TABLE 3. Comparison of the Torsional Angles, Degrees

Ring	Angle*	I'	II	Ideal	Ring	Angle*	I'	II	Ideal
A ($^{8,11}B$)	12—7—8—9	+70	+71	+60	D ($^{14}T_5$)	15—4—5—14	+41	+43	+50
	7—8—9—10	−65	−69	−60		4—5—14—13	−50	−51	−60
	8—9—10—11	+16	−19	0		5—14—13—15	+40	+41	+50
	9—10—11—12	+30	+31	+60		14—13—15—4	−15	−13	−19
	10—11—12—7	−24	−28	−60		13—15—4—5	−17	−19	−19
	11—12—7—8	−27	−25	0					
	Sum	0	−1	0		Sum	−1	+1	0
B (^{8}E)	19—6—7—8	+28	+26	+36,5	E ($^{3}C_{14}$)	14—1—2—3	+44	+44	+60
	6—7—8—9	−49	−49	−60		1—2—3—4	−55	−46	−60
	7—8—9—19	+50	+51	+60		2—3—4—5	+74	+64	+60
	8—9—19—6	−32	−34	+36,5		3—4—5—14	−73	−73	−60
	9—19—6—7	+3	+4	0		4—5—14—1	+69	+70	+60
						5—14—1—2	−57	−60	−60
	Sum	0	−2	0		Sum	+2	−1	0
C ($^{7}C_{14}$)	14—5—6—7	−50	−50	−60	F ($^{4,17}B$)	16—3—4—5	−59	−58	−60
	5—6—7—12	+33	+34	+60		3—4—5—18	+51	+49	+60
	6—7—12—13	−37	−36	−60		45—18—17	+11	−2	+60
	7—12—13—14	+61	+62	+60		5—18—17—16	−66	−47	−60
	12—13—14—5	−75	−78	−60		18—17—16—3	+60	+38	+60
	13—14—5—6	+69	+68	+60		17—16—3—4	+5	+16	0
	Sum	+1	0	0		Sum	+2	−4	0

*The numbers of the atoms are given: for example, 12-7-8-9 denotes the torsional angle around the C(7)—C(8) bond in the C(12)—C(7)—C(8)—C(9) tetrad.

ring E due to its linkage with the neighboring ring. In the Cahn—Ingold—Prelog nomenclature [13], the configuration found must be given the symbols 1(N)S,3R,4S,5R,6S,7S,8S,9R,10S, 12S,13S,14R,16S,18S.

The structure of (+)-excelsine is similar to that of lappoconine (II), another aconitum alkaloid from *Aconitum septentrionale* Koelle, which differs only by the absence of the epoxy bridge and by the presence of an MeO group (instead of OH) in position 18. An x-ray structural analysis (with the determination of the absolute configuration) [10] shows the complete identity of the absolute stereochemistry of the skeleton and the orientation of the substituents in the two alkaloids. They have the lycoctonine skeleton, the conformation of which has been determined previously by a complete x-ray structural analysis with determination of the absolute configuration of (+)-des(hydroxymethylene)lycoctonine (III) [14] and (+)-desmethanolaconinone (IV) [15]. The same carbon—nitrogen skeleton is contained in delcosine [16], delpheline [17], delphinine [18], and the most important alkaloid of plants of the genus *Aconitum* — aconitine [19].

The absolute configurations of the skeleton without substituents of (+)-excelsine (I') and of lycoctonine [judging from the structures of its derivatives (III) and (IV)] are identical: 1(N)S,3S,4R,5S,6R,7R,9R,12S,13R,14R. The conformations of all the rings are identical apart from ring F. In (+)-excelsine and lappaconine (II) it acquires the boat conformation stabilized by strong intramolecular N(1)•••H—O(2) hydrogen bonds with lengths of 2.77(1) and 2.73(1) Å, respectively. In the lycoctonine (III) derivative, where there is no such hydrogen bond, this ring has the chair conformation. Thus, with the exception of some details due to the difference in the substituents, (+)-excelsine has the same absolute stereochemistry of the molecule as other *Aconitum* alkaloids.

What has been said is illustrated by the closeness of the torsional angles [20] determining the conformations of the rings in (+)-excelsine (I') (Fig. 1b) and in lappaconine (II) [10]. These values are given in Table 3 together with the idealized values for the corresponding cyclohexane [20, 21] and cyclopentane [11] conformations. The difference between the ideal and experimental values is obviously due to a distortion of the real conformations of the rings in the alkaloids. However, for all the rings the sums of the torsional angles are practically equal to zero, which shows the accuracy of their determination.

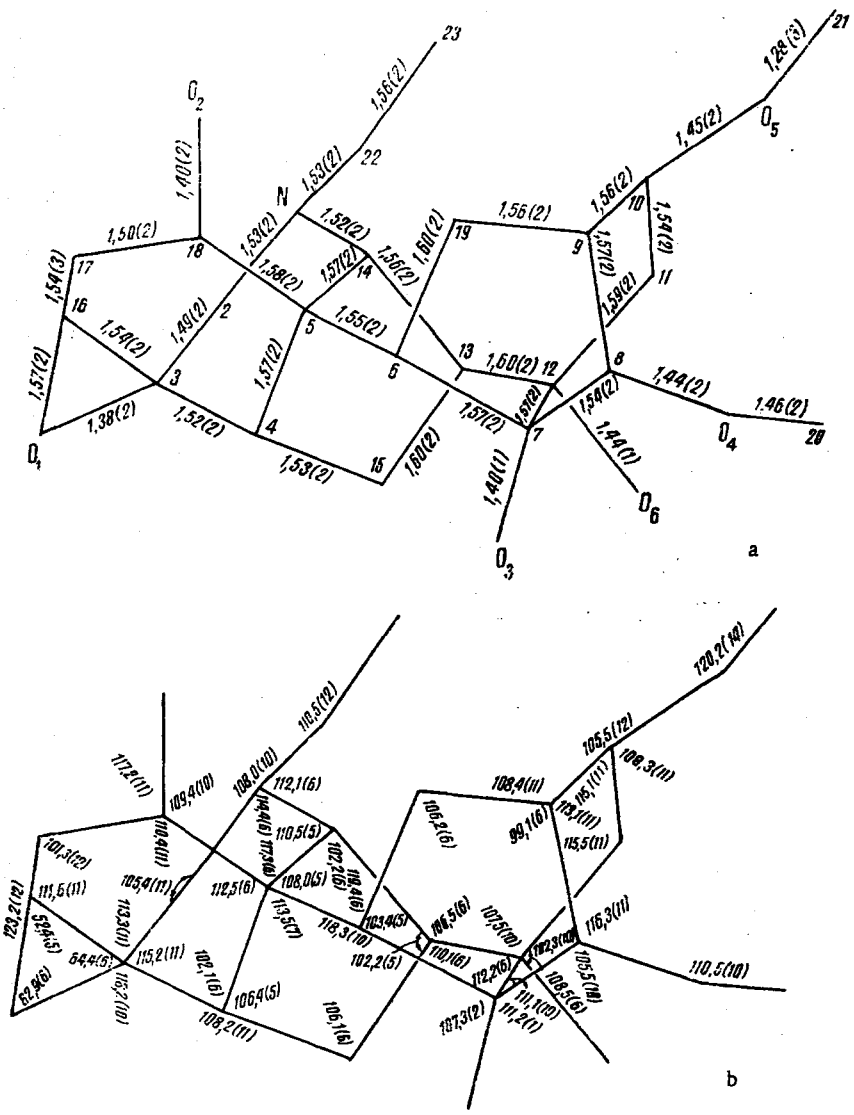

Fig. 2. Cation of (+)-excelsine in the structure studied: a) bond lengths (Å); b) valence angles (degrees).

The bond lengths (Fig. 2a) and the valence angles (Fig. 2b) in the cation and their standard deviations are given in Table 4. The lengths of the ordinary C–C bonds in the rings vary from 1.49 to 1.60 Å, but the mean value of 1.55(2) Å is close to the standard value of 1.541(3) Å [22]. These variations can be explained by some general strain of the condensed polycyclic system which is also shown in the substantial deviations of the real conformations of the rings from the ideal conformations mentioned above. The mean bond length at the nitrogen atom is 1.53(2) Å and is fairly close to the usual length of a N–C(sp^3) bond of a quaternary (ammonium) tetrahedral nitrogen atom, 1.549 Å [23]. The mean length of an O–C(sp^3) bond is 1.42(2) Å and is fairly close to the usual figure [22].

The nature of the variation in the valence angles is shown in Table 5. In spite of the considerable variations of the angles that are customary for alkaloids [10, 12], their mean values in the rings are close to the ideal values of 109.5° and 60° (in the epoxy ring).

Packing in the Crystal. Although the hydrogen atoms could not be localized, the interatomic distances show that all six active hydrogens (two from the water molecule, three from OH groups, and one from a quaternary nitrogen) participate in the hydrogen bonds shown by broken lines in Fig. 3 (the geometric parameters of the H bonds are also given in Table 6).

The N–H•••O(2) and O(3)–H•••O(6) bonds (lengths 2.77 and 2.69 Å, respectively) are intracationic bonds and stabilize the conformation of the cation. In the structure of the hydrobromide of lappaconine (II) [10], the corresponding distances are 2.73 and 2.55 Å.

TABLE 4. Bond Lengths d (Å) and Valence Angles (degrees)

Bond	d	Bond	d	Angle	ω	Angle	ω
C (2)—C (3)	1,49 (2)	C (3)—O (1)	1,38 (2)	O (1) C (3) C (2)	120,4 (3)	C (4) C (3) C (16)	113,9 (2)
C (3)—C (4)	1,52 (2)	C (16)—O (1)	1,57 (2)	O (1) C (3) C (4)	118,4 (3)	C (4) C (15) C (13)	106,1 (1)
C (3)—C (16)	1,54 (2)	C (18)—O (2)	1,40 (2)	O (1) C (3) C (16)	67,7 (1)	C (5) C (6) C (7)	118,5 (2)
C (4)—C (5)	1,57 (2)	C (17)—O (3)	1,40 (1)	O (1) C (16) C (3)	52,7 (1)	C (5) C (6) C (19)	111,7 (1)
C (4)—C (15)	1,53 (2)	C (8)—O (4)	1,44 (2)	O (1) C (16) C (17)	123,3 (3)	C (5) C (4) C (15)	106,7 (1)
C (5)—C (6)	1,55 (2)	C (20)—O (4)	1,46 (2)	O (2) C (18) C (5)	109,7 (2)	C (5) C (14) C (13)	102,3 (1)
C (5)—C (14)	1,57 (2)	C (10)—O (5)	1,45 (2)	O (2) C (18) C (17)	117,4 (2)	C (5) C (18) C (17)	110,7 (2)
C (5)—C (18)	1,58 (2)	C (21)—O (5)	1,28 (3)	O (3) C (7) C (6)	107,5 (1)	C (6) C (7) C (8)	101,5 (2)
C (6)—C (7)	1,57 (2)	C (12)—O (6)	1,44 (1)	O (3) C (7) C (8)	111,4 (2)	C (6) C (7) C (12)	112,2 (2)
C (6)—C (19)	1,60 (2)			O (3) C (7) C (12)	112,3 (2)	C (6) C (7) C (9)	106,4 (1)
C (7)—C (8)	1,54 (2)	Mean	1,42 (2)	O (4) C (8) C (7)	105,9 (2)	C (6) C (5) C (14)	108,0 (1)
C (7)—C (12)	1,57 (2)			O (4) C (8) C (9)	116,5 (2)	C (6) C (5) C (13)	106,5 (2)
C (8)—C (9)	1,57 (2)	C (2)—N	1,53 (2)	O (5) C (10) C (9)	105,9 (2)	C (7) C (8) C (9)	102,5 (2)
C (9)—C (10)	1,56 (2)	C (14)—N	1,52 (2)	O (5) C (10) C (11)	108,5 (2)	C (7) C (6) C (19)	103,7 (1)
C (9)—C (19)	1,56 (2)	C (22)—N	1,53 (2)	O (6) C (12) C (7)	110,2 (1)	C (7) C (12) C (11)	113,8 (2)
C (10)—C (11)	1,54 (2)			O (6) C (12) C (11)	108,8 (1)	C (7) C (12) C (13)	112,3 (1)
C (11)—C (12)	1,59 (2)	Mean	1,53 (2)	O (6) C (12) C (13)	103,0 (1)	C (8) C (7) C (12)	111,2 (2)
C (12)—C (13)	1,60 (2)			NC (2) C (3)	105,7 (2)	C (8) C (9) C (10)	113,2 (2)
C (13)—C (14)	1,56 (2)			NC (14) C (5)	110,9 (1)	C (8) C (9) C (19)	99,2 (1)
C (13)—C (15)	1,60 (2)			NC (14) C (13)	110,9 (1)	C (8) O (4) C (20)	110,9 (2)
C (16)—C (17)	1,54 (3)			NC (22) C (23)	110,8 (2)	C (9) C (10) C (11)	115,2 (2)
C (17)—C (18)	1,50 (2)			C (2) C (3) C (4)	115,3 (2)	C (10) C (11) C (12)	115,8 (2)
C (22)—C (23)	1,56 (2)			C (2) C (3) C (16)	113,5 (2)	C (10) O (5) C (21)	120,4 (2)
				C (2) NC (14)	114,9 (1)	C (10) C (9) C (19)	108,7 (2)
Mean	1,55 (2)			C (2) NC (22)	108,0 (2)	C (11) C (12) C (13)	107,8 (2)
				C (3) C (4) C (5)	102,2 (1)	C (12) C (13) C (14)	106,8 (1)
				C (3) C (4) C (15)	108,4 (2)	C (12) C (13) C (15)	110,2 (1)
				C (3) O (1) C (16)	62,2 (1)	C (14) C (13) C (15)	102,3 (1)
				C (3) C (16) C (17)	101,5 (2)	C (14) C (5) C (18)	117,5 (1)
				C (4) C (5) C (6)	113,8 (1)	C (14) NC (22)	112,2 (1)
				C (4) C (5) C (14)	98,2 (1)	C (16) C (17) C (18)	117,5 (1)
				C (4) C (5) C (18)	112,9 (1)		

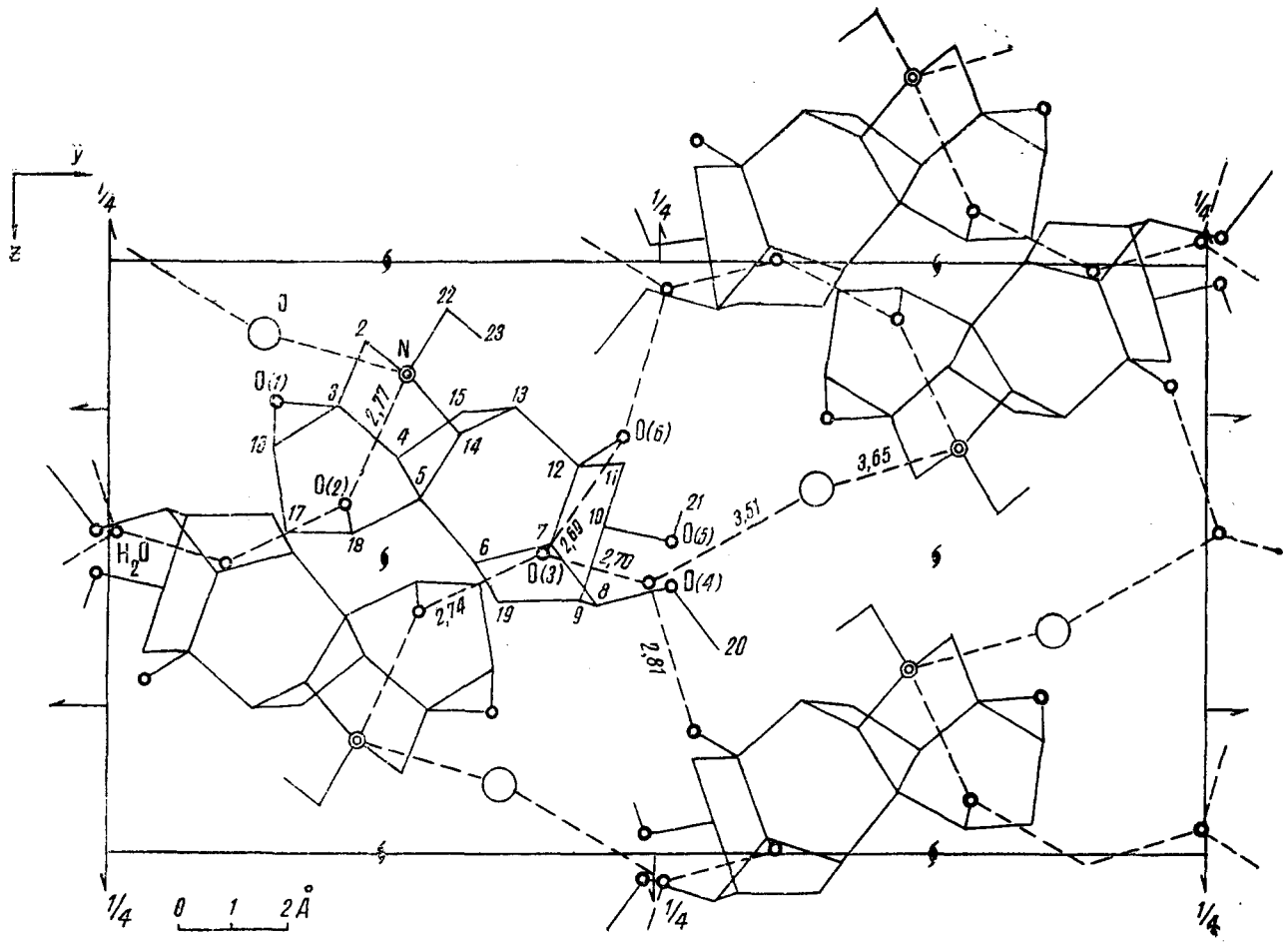

Fig. 3. Projection of the structure on the bc face.

TABLE 5. Variations of the Valence Angles (degrees) in the Rings

Ring	Limiting values of the angles	Mean angle
A (6-membered)	102,3—115,5	110,9
B (5-membered)	99,1—112,1	104,6
C (6-membered)	102,2—118,3	109,9
D (5-membered)	98,1—106,4	103,0
E (6-membered)	98,1—115,2	107,6
F (6-membered)	101,3—113,5	108,6
Epoxy (3-membered)	52,4—64,4	60,0

The O(2)—H•••O(3')H bond (2.74 Å) unites the cations into infinite helices about the 2_1 axes parallel to [100]. The HO(w)—H•••O(3') and O(6)—H•••O(w_1)H_2 bonds (2.70 and 2.81 Å, respectively) through the water molecules also unite the cations into helices about the 2_1 axes parallel to [001]. Finally, the HO(w')—H•••I^- and I'•••H—$\overset{+}{N}$H-bonds (3.51 and 3.65 Å, respectively) through the anions "crosslink" both types of helices in the direction of the 2_1 axes parallel to [010], forming a three-dimensional skeleton.

It must be mentioned that in the structure of (II), as well, the quaternary nitrogen participates by its one hydrogen in two H-bonds (a fairly rare case of a so-called "bifurcate" hydrogen bond [10, 24]). The water molecule participates in three H bonds, and each of the three OH groups in two bonds. Judging from their lengths, all seven H bonds are strong ones [25], and the angles between them and between them and the valence bonds are close to tetrahedral or trigonal (of course, only in those cases where it may be considered that the hydrogen atom is present on the donor—acceptor line; see Table 6).

TABLE 6. Hydrogen Bonds*

Donor–acceptor	Bond length, Å	Angle, deg	
N^+–H...O (2)†	2,77‡	O (2)–N–I	70 (75) **
N^+–H...I^-	3,65	O (2)–N–C (2)	111
		O (2)–N–C (14)	74
		O (2)–N–C (22)	133
		I –N–C (2)	93
		I –N–C (14)	141
		I –N–C (22)	83
O (2)–H...O (3′)	2,74	N –O (2)–O (3′)	143
		N –O (2)–C (18)	90
		O (3′)–O (2)–C (18)	108††
O (3)–H...O (6)	2,69‡	O (2′)–O (3)–O (6)	151
		O (2′)–O (3)–C (7)	124††
		O (6) –O (3)C (7)	67
		O (6)–O (3)–O (w′)	85
		O (2′)–O (3)–O (w′)	105‡‡
		O (w′)–O (3)–C (7)	124††
O (6)–H...(w′)	2,81	O (3)–O (6)–O (w′)	48
		O (3) –O (6)–C (12)	66
		O (w′)–O (6)–C (12)	117††
O (w)–H...O (3′)	2,70	O (3′)–O (w)–O (6′)	111††
O (w)–H...I^-	3,51	O (3)–O (w)– I′	115††
		O (6)–O (w)– I′	105††
		O (w)–I′–N′	146

*The primes denote atoms removed from their initial positions.
†Bifurcate bond.
‡Intracationic bonds.
**In structure (II) this angle is 75°.
††It is to be expected that these angles would be close to 109.5° or 120°.

The substances were made available by M. S. Yunusov and V. A. Tel'nov, and the single crystals investigated were obtained by G. N. Zakharova.

SUMMARY

On the basis of a complete x-ray structural investigation, the structural formula of (+)-excelsine has been refined and its absolute configuration has been determined.

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STRUCTURE AND FEATURES OF THE FRAGMENTATION OF THE PRODUCTS OF THE REDUCTION OF DUBINIDINONE

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Structures (I) and (II) have been put forward for dubinidine and the product of its periodic acid oxidation [1]. Structure (I) has been confirmed by the synthesis of dubinidine [2]. The present paper reports on the structure of products (III) and (IV) obtained previously in the Clemmensen reduction of (II) [3].

The UV spectra of (III) and (IV) are characteristic for 2-quinolone derivatives [4]. The phenolic nature of (IV) is confirmed by a hypsochromic shift of the UV spectrum in alkaline solution, which is typical for 4-hydroxy-2-quinolone bases [5], and also by the preparation of an O-methyl derivative (V) by the action of diazomethane on (IV).

The IR spectra of (III) and (IV) show intense adsorption with maxima at 1660 and 1655 cm^{-1}, respectively, which are due to the amide carbonyl of a 2-quinolone.

The molecular weights of products (III) and (IV), determined mass spectrometrically (245 and 231), differ by a methylene group. However, the methylation product (V) was not identical with (III). In the spectra of (IV) (Fig. 1a), and of (V), the ions $(M-43)^+$ (m/e 188 and 202, respectively) far exceed all the other peaks, which possibly shows the presence of an open chain. In the spectrum of (III) (Fig. 1c), a more uniform distribution of the intensities of the peaks of the ions M^+, $(M-15)^+$, and $(M-57)^+$ is observed, which indicates the cyclic structure of this molecule. The formation of the ion $(M-31)^+$, which is characteristic for an OCH_3 group at C_4 [6], shows the presence of a methoxy group of a different type. On deuteration with deuterodiethylamine $[ND(C_2H_5)_2]$, leading to the replacement of the hydrogens on the carbons adjacent to the carbonyl group [7], in compound (IV) the peak of the M^+ ion shifted by 7 m.u. (Fig. 1b). In view of the presence of the phenolic hydroxyl and the NH group in the 4-hydroxy-2-quinolone nucleus, the exchange of the additional five hydrogens means that substance (IV) has a $-CH_2-CO-CH_3$ grouping. The displacement of the maximum peak with m/e 188 by 4 m.u. confirms that the formation of this ion involved the elimination of a $COCD_3$ group. The peak of the ion with m/e 174 was displaced by two units,

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