ALKALOIDS OF Aconitum coreanum.

VII. STRUCTURE OF CORYPHINE — A REPRESENTATIVE OF A NEW TYPE OF DITERPENE ALKALOIDS

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A new diterpene alkaloid, which has been called coryphine, has been isolated from the plant Aconitum coreanum (Levl.) Rapaics. This is the first diterpene alkaloid containing, like atisine, an oxazolidine ring with a C_{14}–C_{20} bridge and a 2,3,3a,6,7,7a-hexahydro-N-methylindolin-6-one fragment. The structure of coryphine was established by x-ray structural investigations of its perchlorate.

On continuing the separation of the total alkaloids of the epigeal part of Aconitum coreanum (Levl.) Rapaics [1], we isolated a new optically active base (I) with mp 199-200°C. According to its chromatographic mobility it was nonpolar, and according to its mass spectrum it had the composition $C_{31}H_{42}N_2O_2$ (M^+ 474.3227, HRMS); its IR and NMR presence showed that it did not contain hydroxy, ester, or exomethylene groups. We have called this previously unknown base coryphine.

The UV spectrum of (I) had an absorption maximum at 212 nm (log ε 4.04), which is characteristic for an α,β-unsaturated carbonyl chromophore. The presence of the latter was also confirmed by the IR spectrum, which exhibited intense absorption at 1690 cm^{-1}. In the mass spectrum of the base, the maximum peak of an ion with m/z 324 having the composition $C_{22}H_{31}NO$ (324.2327 HRMS) corresponded to the atisine type of diterpene alkaloids. A second nitrogen-containing fragment represented in the spectrum by an ion with m/z 149 had the composition $C_9H_{11}NO$. The PMR spectrum of coryphine showed signals from 18-methyl and N-methyl groups. In the weak-field region three one-proton signals were observed at (ppm) 5.38 (singlet), 5.87 (doublet, J = 10 Hz), and 6.60 (doublet of doublets, J = 10 and 1.8 Hz). The last two signals belonged to the olefinic protons of an α,β-unsaturated ketone, while a signal in the weak field at 6.60 ppm relating to the proton of a β-carbon atom had a long-range coupling constant (1.8 Hz). The pattern of the spectrum coincided completely with that of mesambrenone (II) isolated from plants of the genus Sceletium, family Aizoaceae [3], the heterocyclic part of which has the same composition, $C_9H_{11}NO$, as the corresponding fragment in coryphine.

The results of a comparison of the ^{13}C NMR spectra of coryphine (I), mesambrenone (II), and sceletenone (III) [4] showed that the spectrum of (I) contained, in addition to the signals of the 22 carbon atoms of the diterpene part, nine signals of carbon atoms of a second fragment of the molecule the values of the chemical shifts of which were close to those of the carbon atoms of the 2,3,3a,6,7,7a-hexahydro-N-metylindolin-6-one parts of alkaloids (II) and (III) (Table 1). This gave grounds for assuming that the substituent in coryphine had the structure of 2,3,3a,6,7,7a-hexahydro-N-methylindolin-6-one. The spectral characteristics were, however, insufficient for establishing the structure of coryphine, and we therefore made an x-ray structural investigation of its perchlorate, which showed that it had the structure (IV) (see scheme 1 on following page).

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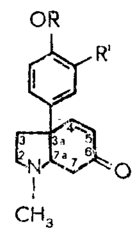
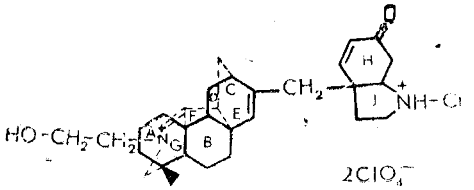
TABLE 1. Chemical Shifts of the Carbon Atoms of the $C_9H_{12}NO$ Fragment in (I), (II), and (III)

C atom	I	II	III
2[d]	54,60t	56,2	55,8
3	36,00t	38,3	35,9
3a	47,43s	50,9	50,6
4	156,11d	153,3	155,4
5	125,86d	126,2	125,9
6	197,57s	196,9	197,8
7	37,27t	38,6	38,4
7a	70,14d	73,8	73,4
$N-CH_3$	40,01q	40,1	40,0



II. $R=CH_3$, $R'=OCH_3$

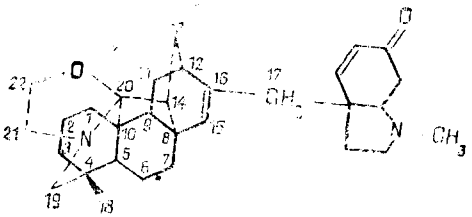
III. $R=R'=H$



IV

Scheme 1

Hence, coryphine has the structure (I).



I

The spatial structure of the dication in the structure of (IV) is shown in Fig. 1, from which can be seen that the dication consists of two main parts: an atisine part having a rigid structure consisting of seven rings, and a hexahydro-N-methylindolin-6-one fragment.

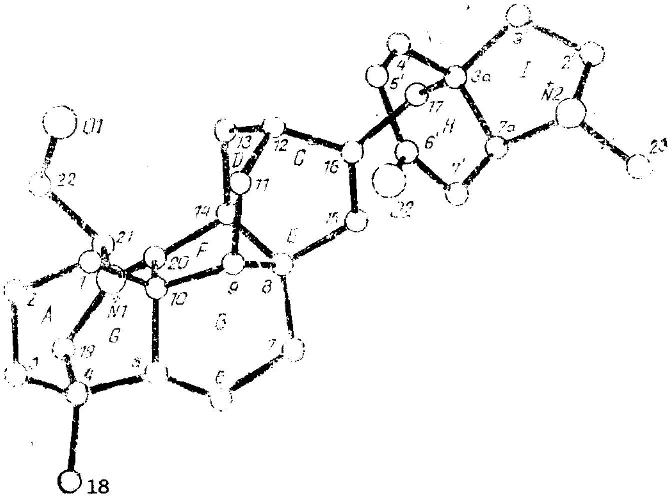


Fig. 1. Spatial structure of the cation of the perchlorate (IV).

TABLE 2. Exocyclic Torsional Angles in the Rings of Structure (IV)

Angle	φ	Angle	φ	Angle	φ
Ring *A*		Ring *D*		Ring *G*	
C1C2C3C4	54	C12C13C14C8	2	C10C20N1C19	12
C2C3C4C5	−64	C13C14C8C9	−66	C20N1C19C4	4
C3C4C5C10	63	C14C8C9C11	72	N1C19C4C5	19
C4C5C10C1	−55	C8C9C11C12	−13	C19C4C5C10	−57
C5C10C1C2	47	C9C11C12C13	−54	C4C5C10C20	68
C10C1C2C3	−45	C11C12C13C14	59	C5C10C20N1	−49
Ring *B*		Ring *E*		Ring *H*	
C9C10C5C6	56	C12C13C14C8	2	C3aC4′C5′C6′	2
C10C5C6C7	−30	C13C14C8C15	51	C4′C5′C6′C7′	5
C5C6C7C8	29	C14C8C15C16	−55	C5′C6′C7′C7a	−23
C6C7C8C9	−51	C8C15C16C12	−2	C6′C7′C7aC3a	31
C7C8C9C10	71	C15C16C12C13	61	C7′C7aC3aC4′	−26
C8C9C10C5	−77	C16C12C13C14	−57	C7aC3aC4′C5′	8
Ring *C*		Ring *F*		Ring *I*	
C12C11C9C8	−13	C14C20C10C9	2	C3aC7aN2C2′	39
C11C9C8C15	−39	C20C10C9C8	30	C7aN2C2′C3′	−43
C9C8C15C16	51	C10C9C8C14	−51	N2C2′C3′C3a	30
C8C15C16C12	−2	C9C8C14C20	51	C2′C3′C3aC7a	−5
C15C16C12C11	−54	C8C14C20C10	−33	C3′C3aC7aN2	−20
C16C12C11C9	61				

The conformations of the rings are characterized by the torsional angles given in Table 2. The six-membered rings A and B have the chair conformations. Rings C, D, and E, forming a bicyclo[2.2.2]octane system, have the boat conformation. The heterocycle G is present in the half-chair form: the C4, C19, C20, and N1 atoms are coplanar to within ±0.02 Å, while the C5 and C10 atoms deviate from their plane by −0.55 and 0.35 Å, respectively. The six-membered ring H has the half-chair conformation that is characteristic for cyclohexene rings (the C4′=C5′ bond is double). The conformation of each of the five-membered rings F and I is the envelope conformation: in the first of them the C8 atom deviates in the α-direction by −0.82 Å from the plane of the C9, C10, C14, and C20 atoms, (± 0.01 Å), while in the second the N2 atom deviates in the β-direction by 0.61 Å from the plane of the C3a, C7a, C2′, and C3′ atoms (± 0.03 Å). The conformations of the rings agree completely with those observed in heterophylloidine [5].

The linkage of rings A/B is trans (the C20C10C5H5 torsional angle is −169.9°) and those of B/C and H/I are cis (C15C8C9H9 73.6° and C17C3aC7aH7a −25.1°). In dication of coryphine the methyl groups at C4 and N2 and the carbonyl group at C6′ are β-oriented, while the β-hydroxymethyl group at the N1 atom has the α orientation. Bond lengths and valence angles are given in Table 3. The lengths of the ordinary C_{sp^3}–C_{sp^3} bonds range between 1.48 and 1.58 Å, but within the 3σ limits they agree with the generally adopted value of 1.54 Å. The scatter in the length of the bonds with the heteroatoms is insignificant and their values are close to the standard values [6]; the values of the valence angles were determined with an error of not more than 0.6°. Coryphine is the first alkaloid with a diterpene structure including an oxazolidine ring with a C_{14}–C_{20} bridge. Among the diterpene alkaloids, coryphine is also the first representative containing a 2,3,3a,6,7,7a-hexahydro-N-methylindolin-6-one fragment.

The determination of the structure of coryphine made it possible to carry out an assignment of the chemical shifts of the signals of the 22 carbon atoms of its diterpene moiety in its ^{13}C NMR spectrum taken in the regime of complete and incomplete decoupling from protons (Table 4). Here we made use of information on the ^{13}C NMR chemical shifts of the alkaloids closest in structure – atisine [7] and spirasine [8]. Weak-field signals at (ppm) 146.48 (s), 136.26 (d), and 105.70 (s) were assigned to the C-16, C-15, and C-20 atoms, respectively.

The alkaloid zeraconine has been isolated previously from the plant Aconitum zeravschanicum Steinb., and structure (V) has been established for it [9]. The isolation from the same plant of a base with mp 206.5°C has also been reported [10]. At the present time, its composition has been established as $C_{31}H_{42}N_2O_3$ (490.3205, HRMS). The pattern of weak-field signals in the PMR spectrum of this base is practically identical with that of coryphine.

TABLE 3. Interatomic Distances (r, Å) and Valence Angles (ω, degrees)

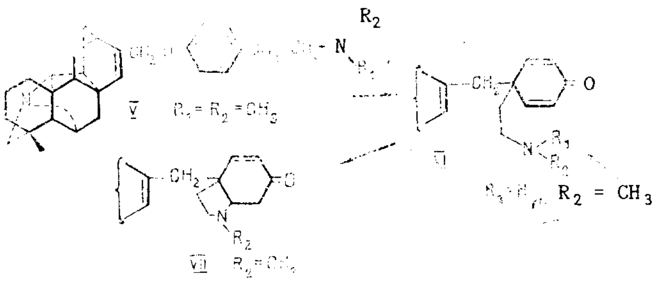
Distance	r	Distance	r	Angle	ω	Angle	ω	Angle	ω
C1—C2	1,521 (10)	C14—C20	1,503 (8)	C2C1C10	113,9	C1C10C9	112,5	C20N1C19	121,9
C1—C10	1,549 (8)	C15—C16	1,308 (9)	C1C2C3	112,3	C9C10C20	104,0	C20N1C21	123,9
C2—C3	1,498 (12)	C16—C17	1,513 (9)	C2C3C4	111,3	C1C10C20	115,1	C19N1C21	113,9
C3—C4	1,513 (10)	C19—N1	1,497 (8)	C3C4C5	109,2	C9C10C5	109,7	C4′C3aC3′	108,9
C4—C5	1,563 (10)	C20—N1	1,263 (8)	C3C4C19	109,7	C5C10C20	101,5	C7aC3aC3′	103,8
C4—C18	1,569 (11)	C21—N1	1,486 (8)	C5C4C18	111,3	C9C11C12	109,3	C17C3aC3′	108,4
C4—C19	1,599 (10)	C21—C22	1,515 (9)	C3C4C18	108,7	C11C12C13	107,0	C4′C3aC7a	113,2
C5—C6	1,548 (9)	C22—O1	1,425 (9)	C5C4C19	110,5	C11C12C16	109,8	C4′C3aC17	110,5
C5—C10	1,534 (9)	C17—C3a	1,577 (10)	C18C4C19	107,5	C13C12C16	106,5	C7aC3aC17	111,5
C6—C7	1,559 (10)	C3a—C4′	1,499 (9)	C4C5C10	106,7	C12C13C14	109,5	C3aC4′C5′	126,9
C7—C8	1,525 (8)	C4′—C5′	1,305 (10)	C4C5C6	111,6	C13C14C8	109,3	C4′C5′C6′	121,4
C8—C9	1,552 (8)	C5′—C6′	1,491 (10)	C10C5C6	111,3	C20C14C13	113,1	C7′C6′O2	120,3
C8—C14	1,582 (8)	C6′—O2	1,224 (9)	C5C6C7	115,3	C20C14C8	98,1	C5′C6′C7′	117,9
C8—C15	1,504 (9)	C6′—C7′	1,495 (9)	C6C7C8	116,7	C8C15C16	117,3	C5′C6′O2	122,1
C9—C10	1,558 (8)	C7′—C7a	1,516 (9)	C7C8C9	107,3	C15C16C12	113,0	C3aC7aN2	103,5
C9—C11	1,546 (9)	C7a—N2	1,505 (8)	C7C8C15	112,5	C12C16C17	121,8	C3aC7aC7′	116,2
C10—C20	1,502 (8)	C23—N2	1,511 (10)	C9C8C15	113,3	C15C16C17	124,1	C7′C7aN2	112,3
C11—C12	1,546 (9)	C2′—N2	1,477 (11)	C9C8C14	98,3	C16C17C25	116,6	C7aN2C23	114,7
C12—C13	1,548 (9)	C2′—C3′	1,483 (10)	C14C8C15	106,9	C10C20C14	109,4	C7aN2C2′	104,0
C12—C16	1,496 (8)	C3′—C3a	1,559 (10)	C8C9C10	100,1	C14C20N1	125,1	C2′N2C23	113,2
C13—C14	1,556 (8)			C8C9C11	109,4	C10C20N1	123,9	N2C2′C3′	103,1
				C10C9C11	117,2	C22C21N1	109,1	C2′C3′C3a	107,0
				C1C10C5	113,1	C21C22O1	110,6		

TABLE 4. Chemical Shifts of the Carbon Atoms of Coryphine* ($CDCl_3$, 0—TMS)

C atom	Multiplicity	δ, ppm	C atom	Multiplicity	δ, ppm
1	t	44,44	12	d	35,68
2	t	23,08	13	t	31,37
3	t	41,46	14	d	54,38***
4	s	34,95	15	d	136,26
5	d	53,26***	16	s	146,48
6	t	19,94	17	t	34,66**
7	t	34,36 *	18	q	28,45
8	s	43,82	19	t	57,82
9	d	48,25	20	s	105,70
10	s	47,13	21	t	51,69
11	t	27,93	22	t	61,40

*The signals of the C_{22}-diterpene moiety are given.
,*The assignments may be interchanged.

The base contains aminomethyl and tertiary methyl groups (2.17 and 0.82 ppm, respectively, singlets of 3 H each). The mass spectrum showed, in addition to the peak of the molecular ion, intense peaks of ions with m/z 462, 447, 341, 149, and 121. The IR spectrum exhibited intense absorption bands at 1670 and 1710 cm^{-1}. The empirical formula differs from that of coryphine by one oxygen atom. The facts presented show that this base belongs to the coryphine type and contains, like the latter, a fragment with the composition $C_9H_{11}NO$ having the 2,3,3a,6,7,7a-hexahydro-N-methylindolin-6-one structure. The elucidation of the structure of this alkaloid is continuing, but it is interesting to note the obvious biogenetic link between the alkaloid zeraconine, the base with mp 206.5°C, and coryphine, all the more since the first two were isolated from the same plant. The biosynthesis of the hexahydro-N-methylindoline moiety (VII) in alkaloids of the coryphine type probably takes place from compounds containing, like zeraconine (V), a p-hydroxy-β-aminophenethyl residue in accordance with the scheme given below.



A compound of type (V) first undergoes a Claisen rearrangement in the para position, and the resulting dienone (VI) cyclizes into (VII). An analogous cyclization has been observed in the synthesis of mesembrenone (II) [3].

EXPERIMENTAL

IR spectra were obtained on a UR-20 spectrometer with the use of KBr tablets, UV spectra on a Specord UV-VIS spectrophotometer, PMR spectra on a Varian XL 400 MHz spectrometer ($CDCl_3$, 0—TMS), and ^{13}C NMR spectra on a Tesla BS 567 A instrument (frequency 25.142 MHz, $CDCl_3$, 0—TMS under conditions of complete and incomplete decoupling from protons). Chromatographic monitoring was effected by TLC (alumina LSL 5/40, neutral) in the chloroform—methanol (50:1 and 25:1) solvent systems.

For the Isolation and Separation of the Alkaloids, see [1, 11]. The first hexane—ether (4:1) eluates obtained by chromatographing the total akaloids of the epigeal part of *A. coreanum* gathered in the withering [11] and flowering [1] phases yielded a crystalline mixture of nonpolar bases (0.95 and 0.26 g, respectively). Rechromatography of the total crystalline mixture gave coryphine (0.29 g).

TABLE 5. Coordinates of the Nonhydrogen Atoms (× 10^4) in the Structure of (IV)

Atom	x	y	z	Atom	x	y	z
C1	−2319 (4)	−1811 (4)	1794 (4)	O1	606 (4)	419 (4)	477 (4)
C2	−3461 (4)	−944 (4)	1757 (4)	N1	−145 (4)	50 (4)	2483 (4)
C3	−3882 (4)	−639 (4)	2748 (4)	C2′	6632 (4)	−6027 (4)	2392 (4)
C4	−2460 (4)	−411 (4)	3415 (4)	C3′	6017 (4)	−5407 (4)	1557 (4)
C5	−1481 (4)	−1389 (4)	3576 (4)	C3a	4448 (4)	−4965 (4)	1832 (4)
C6	−84 (4)	−1226 (4)	4325 (4)	C4′	3233 (4)	−5213 (4)	1046 (4)
C7	1365 (4)	−1878 (4)	4167 (4)	C5′	1954 (4)	−5704 (4)	1138 (4)
C8	1601 (4)	−2180 (4)	3123 (4)	C6′	1520 (4)	−6055 (4)	2105 (4)
C9	66 (4)	−2649 (4)	2687 (4)	C7′	2541 (4)	−5744 (4)	2975 (4)
C10	−960 (4)	−1692 (4)	2580 (4)	C7a	4194 (4)	−5478 (4)	2805 (4)
C11	358 (4)	−3226 (4)	1747 (4)	O2	357 (4)	−6552 (4)	2200 (4)
C12	1965 (4)	−2942 (4)	1424 (4)	N2	5229 (4)	−6387 (4)	2810 (4)
C13	2009 (4)	−1783 (4)	1347 (4)	Cl1	4616 (4)	1639 (4)	898 (4)
C14	1745 (4)	−1313 (4)	2352 (4)	Cl2	2660 (4)	1062 (4)	4994 (4)
C15	2973 (4)	−2856 (4)	3054 (4)	O1 (Cl1)	4046 (4)	709 (4)	657 (4)
C16	3187 (4)	−3229 (4)	2198 (4)	O2 (Cl1)	4059 (4)	1943 (4)	1803 (4)
C17	4616 (4)	−3793 (4)	1952 (4)	O3 (Cl1)	6230 (4)	1625 (4)	982 (4)
C18	−2983 (4)	4 (4)	4401 (4)	O4 (Cl1)	4104 (3)	2385 (4)	199 (4)
C19	−1527 (4)	399 (4)	2972 (4)	O1 (Cl2)	3042 (4)	425 (4)	4291 (4)
C20	161 (4)	−869 (4)	2393 (4)	O2 (Cl2)	3819 (4)	1746 (4)	5359 (4)
C21	859 (4)	877 (4)	2181 (4)	O3 (Cl2)	−1365 (3)	−3431 (4)	5323 (4)
C22	345 (4)	1197 (4)	1153 (4)	O4 (Cl2)	−2309 (3)	−4398 (4)	4213 (4)
C23	5533 (3)	−6863 (4)	3799 (4)				

Coryphine (I): mp 199-200°C, $[\alpha]_D^{20}$ + 150° (c 0.4; methanol), readily soluble in chloroform, and crystallizing from ethanol and from acetone.

PMR spectrum, ppm: 1.00 (3H, s, 18-CH_3), 2.26 (3H, s, N—CH_3), 2.42 and 2.61 (d, 1H each, J = 11.4 Hz, H_β-19 and H_α-19), 2.60 (2H, m, 2H-2'), 2.84 (1H, ddd, J = 2.0, 7.0, 12.3 Hz, H-7a) 3.02 and 3.10 (dt, 1H each, J = 3.9, 2H-21), 3.55, 3.78 (1H each, complex signals, 2H-22), 5.38 (1H, s, H-15), 5.87 (1H, d, J = 10 Hz, H-5'), 6.60 (1H, dd, J = 1.8, 10 Hz, H-4').

Mass spectrum, m/z (%): 474 (M^+, 3.4), 459(1.1), 446(1.6), 445(1), 431(1.3), 324(100), 150(3.4), 149(6.9), 148(3.1).

Coryphine Percholate (IV). When perchloric acid was added to an ethanolic solution of the base to give a neutral reaction, the perchlorate precipitated in form of crystals with mp 225-226°C. They were recrystallized from ethanol—water or methanol. Colorless crystals of rectangular form grew from solution in methanol.

X-Ray Structural Investigation of (IV). The space group and parameters of the cell were determined by the photo method and were refined on a SYNTEX $P2_1$ four-circle automatic diffractometer (CuK_α, graphite monochromator, θ/2θ scanning, 2θ ≤ 123°). The crystals were monoclinic, a = 8.693(3), b = 13.330(3), c = 13.801(3), β = 94.5(2)°; d_{calc} = 1.42 g/cm^3. Space group $P2_1$, Z = 2. In the calculations we used 2244 independent reflections with $I \geq 2\sigma$. The structure was interpreted by the direct method using the SHELXS-86 program [12]. It was refined by the method of least squares using the SHELXS-76 program [13] in the isotropic-anisotropic approximation for all the nonhydrogen atoms. On refinement, the hydrogen atoms linked to carbon atoms and the hydrogen atoms of OH and NH groups found from a different synthesis were included in the calculation. The final values of the indices were R = 0.66 and R_w = 0.071. All the calculations were made on an IBM PC/AT computer. The coordinates of the nonhydrogen atoms are given in Table 5.

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ALKALOIDS OF Aconitum rubricundum

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The known alkaloids isolappaconitine (I), 9-deoxylappaconotine (II), lycaconitine (III), puberaconitine (IV), lycoctonine (V), ranaconitine (VI), ajacine (VII), and septentriodine (VII), and an unidentified alkaloid with mp 203-205°C have been isolated from the epigeal part of the Far-Eastern plant *Aconitum rubricundum.*

We have investigated the alkaloids from the roots of the previously unstudied plant *Aconitum rubricundum* Firsh gathered in the fruit-bearing period in the environs of the village of Grudinino, Irkutsk region, Irkutsk province. The air-dry roots were extracted with aqueous ethanol to give 2.9% of total alkaloids on the weight of the dry raw material. From the total extract were isolated nine alkaloids, designated as bases (I)-(IX).

Base (V) was identified as lycoctonine [1] from its spectral characteristics and a mixed melting point. Base (VI) was identified as ranaconitine [2, 3] by a comparison of physical constants and spectral characteristics. Bases (VII) and (VIII) were identified as ajacine [4] and septentriodine [3], respectively from spectral characteristics and the production of lycoctonine on alkaline hydrolysis.

Base (I) had the composition $C_{32}H_{44}N_2O_8$, mp 186-188°C (ether). Its IR spectrum showed absorption bands of hydroxy and ester groups. In its PMR spectrum there were the signals of N-ethyl, acetoxy, and three methyl groups, and those of four aromatic protons the nature of the splitting of which agreed with that of the alkaloid lappaconitine containing an acetylanthranilic acid residue. The presence in the IR spectrum of an absorption band at 1693 cm^{-1} and also the peak of a $M^+ - 179$ ion in the mass spectrum confirmed the presence of the acetylanthranilic fragment in the alkaloid, and the fact that this ion had the maximum intensity showed its presence at C-4, as in lappaconitine [5] and ranaconitine [2, 3].

The mass spectrum of the alkaloid contained the peak of an ion $M^{+\cdot} - 31$ (20%), which was connected with the presence of a methoxy group at C-1 [6]. In the PMR spectrum there was the signal of a β-C-14 proton at 3.63 ppm in the form of a triplet (J = 4.5 Hz). From the magnitude of the chemical shift it was possible to conclude that the substituent at C-14 was a methoxy group, while the multiplicity of the signal indicated that positions 9 and 13 were unsubstituted [7].

The above facts permitted the assumption that the alkaloid that had been isolated was isolappaconitine [8], having the structure (I).

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