^1H and ^{13}C NMR spectra were taken in deuteropyridine on Bruker AM-400 and Bruker WM-250 instruments (δ, ppm; O – TMS). ^{13}C NMR spectra were also obtained under the conditions of J-modulation.

For the isolation of cycloaraloside B, see [1].

Cycloaraloside B (I) – substance (5) [1], $C_{44}H_{72}O_{15}$, mp 181-183°C (from system 1); $[\alpha]_D^{24}$ 0 ± 3° (c 0.7; methanol); ν_{max}^{KBr} cm^{-1}; 3550-3310 (OH), 1740, 1260 (ester group). GLC [4] showed that cycloaraloside B contained D-glucose and L-rhamnose residues in a ratio of 1.00:0.86.

Cyclosieversigenin (II) from (I). Cycloaraloside B (45 mg) was hydrolyzed with 10 ml of a 0.5% methanolic solution of sulfuric acid at 60°C for 4 h. Then the reaction mixture was diluted with water and extracted with chloroform. The chloroform extract was washed with water and was evaporated. The residue was chromatographed on a column, with elution by system 2. This led to the isolation of 20 mg of cyclosieversigenin (II), mp 239-241°C (from methanol), $[\alpha]_D^{24}$ = 52 ± 2° (c 0.8; methanol), which was also identified by direct TLC comparison with an authentic specimen [3].

Cycloaraloside D (III) from (I). Cycloaraloside B (37 mg) was hydrolyzed with 5 ml of a 0.1% solution of sodium hydroxide at room temperature for 1 h. The reaction mixture was diluted with water and was treated with n-butanol. The butanolic extract was washed with water and evaporated. The reaction product was chromatographed on a column, with elution by system 3. This gave 30 mg of glycoside (III), mp 226-228°C (from methanol), $[\alpha]_D^{24}$ –12 ± 2° (c 0.7; methanol), which was identified as cycloaraloside D by the usual methods [5].

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ALKALOIDS OF Aconitum sajanense

II. STRUCTURE OF DEHYDROACOSANINE

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UDC 944/945

The new alkaloid dehydroacosanine has been isolated from the roots of Aconitum sajanense Kumin, and its structure has been established by spectral and chemical methods.

The isolation from the epigeal part of Aconitum sajanense Kumin of the new alkaloid acosanine, having the structure of 6-O-demethyldelphatine, has been reported previously [1]. In the present paper we give the results of a study of alkaloids from the roots of this plant gathered in Krasnoyarsk Territory (Ermakovskii region, Western Sajan mountains, Kedranskii range, environs of Lake Oiskoe, on the Abakan–Kyzyl trail, at a height of 1600 m above sea level).

Extraction of the roots with chloroform yielded the total alkaloids (1.78% of the weight of the dry roots), which were separated into nonpolar (hexane, ether, and chloroform) and polar (aqueous) fractions. By chromatography the hexane fraction yielded a base with mp 140-141°C (I), while the aqueous fraction yielded acosanine (II).

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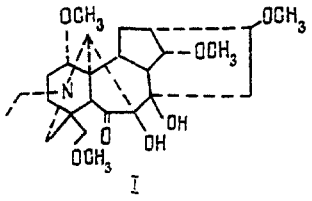
Base (I) dissolved well in organic solvents, and crystallized from a mixture of methanol and hexane. It had the composition $C_{25}H_{39}NO_7$, differing from that of acosanine by two hydrogen atoms. Its IR spectrum showed absorption bands at (cm^{-1}) 3548 and 3480 (hydroxy groups) at 1743 (carbonyl group in a five-membered ring). The PMR spectrum contained the signals of an N-ethyl group (1.00 ppm, 3H, t, J = 7.5 Hz), of four methoxy groups (3.23 and 3.27 ppm, 3 H and 9 H each, respectively) and of a β-proton at C-14 (3.57 ppm, 1 H, t, J = 4.5 Hz) [2]. The mass spectrum included the peak of the molecular ion with m/z 465 and the peaks of ions with m/z 450 $(M - 15)^+$ and 434 $(M - 31)^+$. The fact that peak of the $(M - 31)^+$ ion had the maximum intensity showed the presence of one methoxy group at C-1 [3], while the triplet at 3.57 ppm showed the presence of a second methoxy group at C-14 [2]. These results made it possible to assume that the alkaloid that had been isolated differed from acosanine by the presence of carbonyl group instead of a hydroxyl in position 6. We have called the new base dehydroacosanine.



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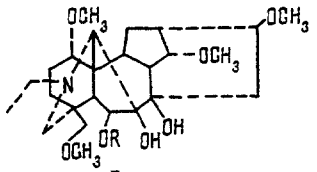

II R = H
III R = CH_3

Structure (I) proposed for dehydroacosanine was completely confirmed by its ^{13}C NMR spectrum. The assignment of the chemical shifts of the signals of the carbon atoms (Table 1) was based on the multiplicities of the signals in the spectrum of (I) obtained under the conditions of incomplete suppression of interaction with protons, and by comparison with the ^{13}C NMR spectra of acosanine (II) [1], delphatine (III) [4], and other alkaloids of the lycoctonine series [2]. The comparative analysis of the ^{13}C NMR spectra of (I-III) showed that the chemical shifts of the signals of the carbon atoms in the psectra of these compounds were close. The main difference consisted in the fact that in the spectrum of (I) the signal of the C-6 atom was observed in the form of a singlet at 219.60 pm in place of the doublets at 80.75 ppm in the spectrum of (II) and at 90.1 ppm in the spectrum of (III). The presence of the carbonyl substituent at C-6 caused a considerable downfield shift of the doublet signal of the α-carbon atom C-5 (~12 ppm). Considerable screening shifts were observed for the doublet signal of the γ-carbon atom, C-9, and the singlet signal of the β-carbon atom, C-11. It must be mentioned that a diamagnetic shift of the signal of tetrasubstituted C-11 atom takes place in the spectra of known lycoctonine alkaloids with a keto group in position 6 and a methylenedioxy group at C-7–C-8 (Table 2), the average value of Δδ (−4.2 ppm) agreeing with that observed for the C-11 carbon atom of dehydroacosanine (Δδ = −4.6 ppm).

Thus, structure (I) has been established for dehydroacosanine. This structure has been confirmed chemically: dehydroacosanine was obtained by the oxidation of acosanine with chromium trioxide in acetone solution or with silver oxide.

TABLE 1. Chemical Shifts of the Carbon Atoms of Dehydroacosanine (I) Acosanine (II) [1], and Delphatine (III) [4] in Deuterochloroform (δ, ppm)

C atom	I	II	III	C atom	I	II	III
1	83,38	84,33	83,9	14	83,96	84,33	84,3
2	28,22	25,73	26,2	15	34,28	33,30	33,5
3	32,64	32,61	32,4	16	81,94	82,43	82,6
4	38,99	38,54	38,1	17	63,04	65,80	64,8
5	56,65	44,07	43,3	18	76,79	79,21	78,1
6	219,60	80,75	90,1	19	52,73	53,57	52,8
7	84,78	87,47	88,4	NCH_2	50,72	51,61	51,1
8	75,47	78,71	77,5	CH_3	15,31	14,56	14,2
9	45,79	54,37	48,8	1′	56,32	55,72	55,7
10	37,72	37,27	38,1	6′			57,3
11	43,47	48,29	48,9	14′	57,74	57,78	57,8
12	28,33	20,02	28,7	16′	57,56	56,25	56,3
13	45,79	45,75	46,1	18′	59,23	59,53	59,0

TABLE 2. Chemical Shifts of the C-11 Carbon Atoms of the Alkaloids (IV-XIII)

Compound	ppm	Compound	ppm	Δδ, ppm
Delcorine (IV) [5]	50.2	6-Dehydrodelcorine (V)	46.1	4.1
Delpheline (VI) [5, 6]	50.4	6-Dehydrodelpheline (pacinine) (VII) [6]	46.1	4.3
Deltamine (VIII) [5]	56.2	6-Dehydrodeltamine (IX) [5]	51.7	4.5
Dictyocarpinine (X) [5]	55.4	6-Dehydrodictyocarpinine (XI) [5]	51.5	3.9
14-Acetyldictyocarpinine (XII) [5]	55.8	Barbinidine (XIII) [8]	51.2	4.6

EXPERIMENTAL

IR, mass, and ^1H and ^{13}C NMR spectra were obtained on UR-20 (KBr), MKh-1310, and BS 567A 100 and 25.412 MHz instruments, respectively (δ scale, $CDCL_3$, 0 – HMDS for the PMR spectrum and 0 – TMS for the ^{13}C NMR spectrum).

Chromatographic monitoring was conducted by TLC (alumina, Silufol) in the following solvent systems: 1) chloroform–methanol (25:1), (50:1), and (100:1); 2) ethyl acetate–ethanol–ammonia (30:3:6 drops).

Isolation of the Alkaloids. The air-dry comminuted roots (1.3 kg) were wetted with a 5% solution of sodium carbonate, and the alkaloids were extracted with chloroform. The chloroform extract was shaken with a 5% solution of sulfuric acid. With cooling, the acid solution was made alkaline with sodium carbonate, and the alkaloids were exhaustively extracted with chloroform. The total alkaloids so obtained (23.26 g) were separated into fractions soluble in ether (7.2 g), in chloroform (10 g), and in water (6.0 g). The ether-soluble bases were treated with hexane. The hexane-soluble fraction (2.7 g) was chromatographed on silica gel. Hexane–ether eluates yielded crystalline dehydroacosanine (268 mg). When the water-soluble fraction (6 g) was chromatographed on alumina, crystalline acosanine (0.6 g) was obtained from chloroform eluates.

Dehydroacosanine, mp 140-141°C (from methanol–hexane). Mass spectrum, m/z (%): 465 (M^+, 7.4), 450(3), 448(1), 447(1), 435(29), 434(100), 422(2), 416(22), 407(3), 406(8.5), 71(8.5), 58(8.5).

Oxidation of Acosanine. a) A mixture of acetone solutions of acosanine (0.12 g in 20 ml) and of chromium trioxide (0.2 g in 9 ml) was left at room temperature for three days. After filtration, the acetone was distilled off, the residue was dissolved in 5% sulfuric acid, and the solution was made alkaline with NaOH and was extracted with chloroform. After the solvent had been distilled off, the residue (0.08 g) was chromatographed on alumina (1:100), with elution by benzene–chloroform (1:2). A substance obtained in the form of a noncrystallizing mass (5 mg) was identical with dehydroacosanine according to TLC in systems 1 and 2 (alumina, Silufol).

b) A Mixture of acosanine (50 mg), silver oxide (220 mg), ethanol (3 ml), and water (0.5 ml) was boiled under reflux for 3 h. The mixture was filtered, the solution was evaporated, and the residue was chromatographed on alumina (1:70), with elution of the products by ether. This gave a substance (10 mg) identical with dehydroacosanine in terms of TLC, melting point, and IR spectrum

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ALKALOIDS OF Aconitum kirinense.

STRUCTURE OF AKIRINE

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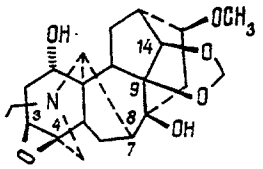
The known alkaloid lepenine and the new diterpene alkaloid akirine have been isolated from the epigeal part of Aconitum kirinense Nakai. To establish the structure of akirine, its spectral characteristics have been studied and an x-ray structural analysis has been made. It is 1α,8β-dihydroxy-16β-methoxy-9β,14β-methylenedioxy-3β,4β-epoxy-N-ethylaconitane – the first diterpene alkaloid with a lycoctonine skeleton containing a 9,14-methylenedioxy group and a β-oriented substituent at C14.

Continuing the separation of the total alkaloids of the epigeal part of Aconitum kirinense Nakai [1], we have isolated lepenine [2] and a new alkaloid with the composition $C_{22}H_{31}NO_6$, which has been called akirine (I). Its IR spectrum contained absorption bands of hydroxy groups at 3515 and 3200 cm^{-1} and of ether bonds at 1110 cm^{-1}. The PMR spectrum showed the signals of N-ethyl, methoxy, and methylenedioxy groups. The mass spectrum of (I) was characteristic for alkaloids with a lycoctonine skeleton containing a hydroxy group at C1 and a 3,4-epoxy function, and was similar to that of excelsine [3, 4].

In all previously known alkaloids with a methylenedioxy group it is located in the 7, 8 position. The mass spectra of these alkaloids have a number od diagnostic features due to the presence of the methylenedioxy group – in particular, the peak of the $(M - 30)^+$ ion [5]. In the mass spectrum of akirine the peak of the $(M - 30)^+$ ion was observed at a level far below that of the $(M - 31)^+$ ion and, consequently, is not evidence in favor of the 7, 8 position.



I

An x-ray structural investigation of akirine showed that this alkaloid had the structure (I) and is the first alkaloid with a lycoctonine skeleton containing a 9,14-methylenedioxy group and a β-oriented substitutent at C14. Thus, alkaloid (I) was 1α,8β-dihydroxy-16β-methoxy-9β,14β-methylenedioxy-3β,4β-epoxy-N-ethylaconitane. The biosynthesis of such alkaloids apparently takes place through the 14-dehydro derivative, the enzymatic reduction of which can give not only the usual α- but also the β- epimer, with the subsequent formation of a methylenedioxy group.

The spatial structure of the (I) molecule as a projection on the plane of the three atoms C1C4C9 is shown in Fig. 1. The molecule has a rigid bridge structure with the following orientations of the substituents: α-hydroxy group at C1, β-3,4-epoxy group, β-3,4-methylenedioxy group, β-hydroxy group at C16. Conformations of the main rings: six-membered

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