LITERATURE CITED

1. I. M. Yusupova, I. A. Bessonova, B. Tashkhodzhaev, M. S. Yusupov, M. R. Yagudaev, and Z. M. Vaisov, Khim. Prir. Soedin., No. 3, 296 (1991).
2. I. A. Bessonova, M. S. Yusupov, V. T. Kondrat'ev, and I. A. Shreter, Khim. Prir. Soedin., 690 (1987).
3. G. C. Levy and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Chemists (1st edn.), Wiley, New York (1972).
4. K. Nakanishi, Infrared Absorption Spectroscopy. Practical (1st edn.), Holden-Day, San Francisco (1962).
5. S. W. Pelletier and T. N. Oeltmann, Tetrahedron, 24, 2019 (1968).
6. Y. C. Yu, T. S. Wu, M. Niwa, S. T. Lu, and Y. Hirata, Heterocycles, 26, 943 (1987).
7. N. V. Mody and S. W. Pelletier, Tetrahedron, 34, 2421 (1978); Fang Sun, Xiao-tian Liang, and De-quan Yu, Heterocycles, 24, 2105 (1986).
8. P. W. Jeffs, G. Ahmann, H. F. Campbell, D. S. Farrier, G. Ganguli, and R. L. Hawks, J. Org. Chem., 35, 3512, (1970); P. W. Jeffs, T. Capps, D. B. Johnson, J. M. Karle, N. H. Martin, and B. Rauckman, J. Org. Chem., 39, 2703 (1974).
9. P. W. Jeffs, in: The Alkaloids, Vol. XIX, R. H. F. Manske and A. G. A. Rodrigo (eds.), Academic Press, New York (1981), pp. 1-81.
10. I. A. Bessonova, L. N. Samusenko, M. S. Yunusov, M. R. Yagudaev, and V. G. Kondrat'ev, Khim. Prir. Soedin., 91 (1991).

ALKALOIDS OF Aconitum sajanense

I. STRUCTURE OF ACOSANINE

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From the epigeal part of the previously unstudied plant *Aconitum sajanense* we have isolated the new alkaloid acosanine, the structure of which has been established on the basis of spectral characteristics and has been confirmed by a direct comparison with a sample of demethyldelcorine.

Alkaloids of plants of the genus *Aconitum* L. (family Ranunculaceae) have been described in a large number of publications [1], but many representatives of this genus have not hitherto been investigated. These plants include *Aconitum sajanense* Kumin. There is no information in the literature available to us on the chemical composition and use of this plant in folk medicine [2].

A. sajanense is a tall plant (90-100 cm) found in Eastern Siberia [3]. It is the main component of the subalpine meadows of the Central Sayan mountains located at heights of 1500-2000 m above sea level [4].

We have studied the alkaloids of the epigeal part of the plant gathered by a VILR [All-Union Institute of Medicinal Plants] expedition on August 9, 1990, in Krasnoyarsk Territory (Ermakovskii region, Western Sayan mountains, Kedranskii range, environs of Lake Oiskoe on the route from Abakan to Kyzyl at a height of 1600 m above sea level). The total alkaloids were obtained by the usual method, and these amounted to 0.63% of the weight of the dry raw material. By column chromatography, a crystalline alkaloid with mp 78-80°C, composition $C_{25}H_{41}NO_7$ (HRMS) was isolated. The base was new, and we have called it acosanine.

The IR spectrum of acosanine (I) contained absorption bands at 3600-3300 cm^{-1} (OH) and 1100 cm^{-1} (C–O). There were no absorption bands of carbonyl groups.

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

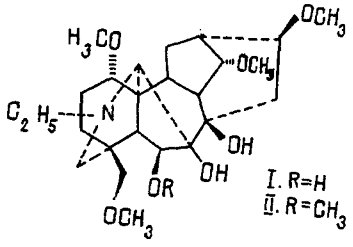
C atom	Multiplicity	I	II
1	d	84,33	83.9
2	t	25,73	26,2
3	t	32,01	32,4
4	s	38,54	38.1
5	d	44,07	43,3
6	d	80,75	90,1
7	s	87,47	88,4
8	s	78,71	77,5
9	d	54,37	49,8
10	d	37,27	38,1
11	s	48,29	48,9
12	t	29,02	28,7
13	d	45,75	46,1
14	d	84,33	84,3
15	t	36,30	33,5
16	d	82,43	82,6
17	d	65,81	64,8
18	t	79,21	78,1
19	t	53,57	52,8
$N-CH_2$	t	51,61	51.1
CH_3	q	14.56	14,2
1′	q	55,72	55,7
6′	q	—	57,3
14′	q	57,78	57,8
16′	q	56,25	56,3
18′	q	59,53	59,0

An analysis of the PMR spectrum of (I) showed the presence of an N-ethyl group (1.00 ppm, 3H, t, J = 7 Hz) and of four methoxy groups (3.15, 3.24, and 3.31 ppm, singlets, 3H, 6H, and 3H, respectively). Signals at 3.62 (1H, t, J = 4.5 Hz) and 4.22 (1H), assigned to H-14β and H-6α, respectively, showed the presence of an α-OCH_3 group at C-14 and β-OH group at C-6 [5].

The mass spectrum of acosanine contained the peak of ions with m/z (%) 467 (M^+, 4.6), 452 ($M - 15^+$, 4), and 436 ($M - 31^+$, 100). The fact that the M − 31 ion had the maximum intensity indicated the presence of a methoxy group at C-1 [6], and the low intensity of the peak of the M-15 ions showed the absence of an OCH_3 group at C-6 [7].

The structure of acosanine was elucidated with the aid of a comparative analysis of the ^{13}C NMR spectra of the base isolated and of delphatine (II). The CSs of the signals of the carbon atoms (Table 1) were assigned on the basis of the multiplicities of the signals in the spectrum of (I) taken under the conditions of a complete suppression of interaction with protons and of a comparison with the CSs of the carbon atoms of delphatine. A study of the spectra of (I) and (II) showed that the most substantial change related to the signal of the C-6 atom [80.75 ppm in (I) as compared with 90.1 ppm in (II)]. The δ-carbon atoms C-9 and C-15 had undergone slight descreening (Δδ = +4.57 and 2.8 ppm, respectively).

Thus, acosanine has the structure (I). A substance with such a structure has been obtained previously by treating delcorine with sulfuric acid [9]. A direct comparison of acosanine with a known sample of demethyldelcorine kindly given to us by A. S. Narzullaev showed their identity (TLC, mixed melting point, and IR spectra).



I. R=H
II. R=CH_3

EXPERIMENTAL

IR spectra were taken on a UR-20 instrument (KBr), mass spectra on MKh-1310 and MS-3301 instruments, and ^1H and ^{13}C NMR spectra on a BS-567 A instrument at 25.142 MHz (δ scale, $CDCl_3$, 0 – HMDS for the PMR spectrum; 0 – TMS for the ^{13}C NMR spectrum).

Chromatographic monitoring was done by TLC (alumina LSL 5/40, neutral; silica gel SL 5/40, and Silufol (Czechoslovakia) in the solvent systems: 1) chloroform–methanol (25:1); and 2) ethyl acetate–ethanol–ammonia (30:3:6 drops [sic]).

Isolation of Acosanine. The air-dry comminuted epigeal part (620 g) was 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 (3.9 g). The alkaloids so obtained were chromatographed on silica gel (Czechoslovakia, L, 100/160) in a ratio of 1:25. Elution was performed with hexane, ether, and ether–ethyl acetate (initially 10:1, with a successive increase in the concentration of the latter), 300-ml fractions of the eluates being collected. The ether–ethyl acetate eluates 8-13 deposited crystals of acosanine, mp 78-80°C (from petroleum ether). The substance dissolved well in chloroform, acetone, and ethanol, and less well in ether. Mass spectrum, m/z (%): 467 (M^+, 4.6), 452(4), 450(2), 449(2), 337(30), 436(100), 420(6), 418·(4.5), 71(1.5), 58(2).

LITERATURE CITED

1. S. Yu. Yunusov, The Alkaloids [in Russian], Tashkent (1981), pp. 89-117; S. Yu. Yunusov, The Alkaloids: Supplement [in Russian], Tashkent (1984), pp. 21-34; S. Yu. Yunusov, The Alkaloids. Supplement II [in Russian], Tashkent (1989), pp. 20-34.
2. Al. A. Fedorov, Plant Resources of the USSR. The Magnoliaceae-Limoniaceae Families [in Russian], Nauka, Leningrad (1985), p. 38.
3. S. K. Cherepanov, Summary of Additions and Changes to the "Flora of the USSR" [in Russian], Nauka, Leningrad (1973), p. 479.
4. E. M. Lavrenko and V. B. Sochav, The Plant Cover of the USSR [in Russian], Akad. Nauk SSSR, Moscow–Leningrad, Vol. 2 (1956), p. 486.
5. S. W. Pelletier, N. V. Mody, B. S. Joshi, and L. C. Schram, in: Alkaloids: Chemical and Biological Perspectives, S. W. Pelletier (ed.), Wiley, New York, Vol. 2 (1984), Ch. 5, pp. 205-462; Q. P. Jiang and W. L. Sung, Heterocycles, 24, 877 (1986).
6. M. S. Yunusov, Ya. V. Rashkes, V. A. Tel'nov, and S. Yu. Yunusov, Khim. Prir. Soedin., 515 (1969).
7. M. S. Yunusov, Ya. V. Rashkes, B. T. Salimov, É. F. Ametova, and G. V. Fridlyanskii, Khim. Prir. Soedin., 525 (1985).
8. S. W. Pelletier, N. V. Mody, R. S. Sawhney, and J. Bhattacharyya, Heterocycles, 7, 327 (1977).
9. A. S. Narzullaev, M. S. Yunusov, and S. Yu. Yunusov, Khim. Prir. Soedin., 497 (1973).

ALKALOIDS OF Haplophyllum perforatum

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The alkaloid composition of the seeds and roots of the plant Haplophyllum perforatum growing in Tadzhikistan (Karateg range) has been studied for the first time. In addition to the known furoquinoline alkaloids, the new alkaloid haplosine has been isolated and it has been shown to be identical with the product of the hydrogenolysis of haplopine. Among natural compounds, this is the first representative of derivatives of the 3-ethyl-4-methoxyquinolin-2-one series.

The chemical composition of Haplophyllum perforatum (M. B.) Kar et Kir. (family Rutaceae) [1] depends greatly on its conditions of growth. Of the 30 alkaloids isolated from this plant growing in various sites [2], only evoxine was present in all the samples studied. Skimmianine – the main alkaloid of H. perforatum from the foothills of the Babatag [3, 4] and the most widely distributed in representatives of the Rutaceae family [5] – was not found in the epigeal part of the plant gathered in the Dzhungarian Ala-Tau [6] and seeds collected in the Samarkand province [3]. Modified furoquinoline derivatives were found in

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