1750, 3468. ^{1}H spectrum (δ, ppm): 0.84 (s, 3H), 0.89 (s, 3H), 0.92 (s, 3H), 0.96 (s, 3H), 1.16 (s, 3H), 1.31 (s, 3H), 1.61 (s, 3H), 1.67 (s, 3H), 2.00-2.09 (s, 24H, 8 × OAc), 3.34 (t, 1H, 2 × J = 1.8 Hz, H_e-3), 3.68 (m, 3H, 2 × H-5', H_a-12), 4.12-4.24 (m, 4H, 2 × H-6'), 4.51 (d, 1H, $J_{1',2'}$ = 7.5 Hz, H-1' at C-3), 4.79 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1' at C-20), 4.91-5.23 (m, 2H-2', 2H-3', 2H-4', H-24).

SUMMARY

1. The condensation of dammar-24-ene-3α,12β,17α,20(S)-tetraol (betulalafolienetetraol), isolated from birch leaves, with α-acetobromoglucose in the presence of silver oxide and silicate has been studied.

2. Betulafolienetetraol 3- and 12- mono- and 3,12- and 3,20-di-O-β-D-glucopyranoside — analogs of ginseng glycosides — have been obtained for the first time.

LITERATURE CITED

1. N. D. Pokhilo, V. A. Denisenko, V. V. Makhan'kov, and N. I. Uvarova, Khim. Prir. Soedin., 179 (1986).
2. F. G. Fischer and N. Seiler, Ann. Che., 626, p. 185 (1959).
3. Y. Takemoto, T. Ueyama, H. Saito, S. Horio, S. Sanada, J. Shoji, S. Yahara, O. Tanaka, and S. Shibata, Chem. Pharm. Bull., 32, No. 8, p. 3128.
4. L. N. Atopkina, V. A. Denisenko, V. L. Novikov, and N. I. Uvarova, Khim. Prir. Soedin., 301 (1986).
5. H. Paulsen, and O. Lockhoff, Chem. Ber., 114, p. 3102 (1981).

TRITERPENE SAPONINS OF Caltha polypetala.

GLYCOSIDES G and I

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From the epigeal organs of the great march marigold (family Ranunculaceae) two triterpene glycosides, a tetra- and a pentaoside of hederagenin, have been isolated. Their chemical structures have been established by chemical methods of investigation and by ^{1}H and ^{13}C NMR spectroscopy. Glycoside G is hederagenin 3-O-α-L-arabinoside 28-O-[O-α-L-rhamnopyranosyl-(1 → 4)-O-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside]. Glycoside I is hederagenin 3-O-[O-β-D-glucopyranosyl-(1 → 2)-α-L-arabinoside 28-O-[O-α-L-rhamnopyranosyl-(1 → 4)-O-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside].

A series of compounds of triterpene nature had previously been isolated from the epigeal organs of Caltha polypetala Hochst. (great marsh marigold), family Ranunculaceae, and the results of investigations of the weakly polar glycosides have been given [1].

In the present paper are considered the results of establishing the structures of the most polar triterpene glycosides — G and I. As shown previously [1], the triterpene glycosides of the great march marigold are hederagenin derivatives and contain in the carbohydrate moiety arabinose and glucose in various ratios. After the acid hydrolysis of glycosides G and I, followed by reduction of the hydrolysates and acetylation, rhamnitol, arabitol, and sorbitol acetates were identified by the GLC method in ratios of 1:1:2 and 1:1:3, respectively. Consequently, glycosides G and I are a hederagenin tetraoside and pentaoside.

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TABLE 1. ^{13}C NMR Chemical Shifts of the Carbohydrate Residues in Glycosides G and I (δ, ppm, pyridine, 40°C)

Carbon atom	Monosaccharide residue				
	Ara_p	Rha_p	Glc_p (1)	Glc_p (2)	Glc_p (3)
1 (G)	106,52	102,86	95,78	104,86	
1 (I)	103,99	102,88	95,82	104,83	105,72
2 (G)	73,20	72,82	75,38	74,02	
2 (I)	80,98	72,78	75,36	74,01	73,61
3 (G)	74,76	72,59	78,77	78,10	
3 (I)	76,24	72,57	78,86	78,12	78,37
4 (G)	69,59	74,02	71,11	78,77	
4 (I)	68,38	74,01	71,07	78,72	71,65
5 (G)	68,85	70,48	76,68	77,19	
5 (I)	65,04	70,54	76,67	77,19	78,25
6 (G)		18,57	69,45	61,56	
6 (I)		18,61	69,48	61,58	62,76

TABLE 2. Parameters of the PMR Spectra of Carbohydrate Moieties of Glycosides G and I [chemical shifts (δ, ppm) and SSCCs (J, Hz), pyridine, 30°C]

H	Monosaccharide residue				
	Ara_p	Rha_p	Glc_p (1)	Glc_p (2)	Glc_p (3)
1	4,95d (5,11) $J_{1,2}=7,2$	5,82 d $J_{1,2}=1,6$	6,20d $J_{1,2}=8,1$	4,94d $J_{1,2}=7,8$	5,12d $J_{1,2}=7,8$
2	4,41dd (4,32) $J_{2,3}=8,9$	4,65dd $J_{2,3}=3,4$	4,08dd $J_{2,3}=9,1$	3,91 dd $J_{2,3}=9,0$	4,00 dd $J_{2,3}=9,4$
3	4,04 dd (4,23) $J_{3,4}=3,2$	4,53 dd $J_{3,4}=9,0$	4,31t $J_{3,4}=9,1$	4,11t $J_{3,4}=9,0$	4,16 d $J_{3,4}=9,4$
4	4,21q (4,19) $J_{4,5e}=2,9$	4,31t $J_{4,5}=9,0$	4,21t $J_{4,5}=9,1$	4,38t $J_{4,5}=9,0$	
5e	4,23 dd (4,23) $J_{5a,5e}=13,0$	4,94dq $J_{5,6}=6,2$		4,20m	
5a	3,70 dd (3,69) $J_{5a,4}=3,0$				
6		1.66d			

The figures for the arabinopyranose residue in glycoside I are given in parentheses.

The IR spectrum of each of the compounds investigated has an absorption band in the 1740 cm^{-1} region indicating the presence of an ester bond at the C-28 atom of the genin. In order to establish the localization of the carbohydrate chains, glycosides G and I were subjected to alkaline hydrolysis, and identical oligosaccharides that had been attached to the genin in the initial compounds by ester bonds were obtained in the two cases. As a result of the acid hydrolysis of the progenin from glycoside G, arabinose and the genin were identified, and, in the case of glycoside I, arabinose, glucose, and the genin. Thus, the glycosides under investigation are bisglycosides of hederagenin.

A preliminary analysis of the ^{13}C NMR spectra of glycosides G and I revealed, in a comparison with the spectrum of hederagenin [2], all the lines of the aglycon residue. So far as concerns the carbohydrate moieties of the molecules, the presence in them of four and five carbohydrate residues, respectively, follows unambiguously from the number of signals in the ^{13}C NMR spectra in the regions of resonance of anomeric carbon atoms (Table 1). In the ^{13}C NMR of glycoside I there are six additional, as compared with the spectrum of glycoside G, signals at 60-105 ppm; all the signals of the aglycon remain unchanged.

TABLE 3. Parameters of the PMR Spectra of the Carbohydrate Moieties of the Acetates of Glycosides G and I [chemical shifts (δ, ppm) and SSCCs (J, Hz), $CDCl_3$]

H	Monosaccharide residue				
	Ara_p	Rha_p	Glc_p (1)	Glc_p (2)	Glc_p (3)
1	4,36 d (4,35) $J_{1,2}$=7,0	4,75 d $J_{1,2}$=2,2	5,49 d $J_{1,2}$=7,9	4,45 d $J_{1,2}$=7,9	4,66 d $J_{1,2}$=8,0
2	5,10 dd (3,84) $J_{2,3}$=9,6	4,98 dd $J_{2,3}$=3,1	5,04 dd $J_{2,3}$=9,5	4,74 dd $J_{2,3}$=9,4	5,07 dd $J_{2,3}$=9,4
3	4,95 dd (4,92) $J_{3,4}$=3,5	5,11 dd $J_{3,4}$=10,1	5,15 t $J_{3,4}$=9,5	5,09 t $J_{3,4}$=9,4	5,18 t $J_{3,4}$=9,4
4	5,17 ddd (5,17) $J_{4,5e}$=3,0	4,95 t $J_{4,5}$=10,1	4,91 dd $J_{4,5}$=9,1	3,75 t $J_{4,5}$=9,4	4,94 t $J_{4,5}$=9,4
5		3,76 dq $J_{5,6}$=6,0	3,68 ddd $J_{5,6_A}$=3,0	3,49 ddd $J_{5,6_A}$=2,0	3,51 ddd $J_{5,6_A}$=2,0
5e	3,93 dd (3,93) $J_{5a,5e}$=13,0				
5a	3,54 dd (3,54) $J_{5a,4}$=2,0				
6		1,07 d			
6_A			3,78 dd $J_{6_A,6_B}$=12,5	4,38 dd $J_{6_A,6_B}$=12,5	4,40 dd $J_{6_A,6_B}$=12,4
6_B			3,48 dd $J_{6_B,5}$=2,0	4,22 dd $J_{6_B,5}$=3,6	4,21 dd $J_{6_B,5}$=3,5

The figures for the arabinopyranose residue in glycoside I are given in parentheses.

In the PMR spectra of glycosides G and I, again, in the region of resonance of anomeric protons four and five signals, respectively, are observed. The use of the method of homonuclear selective double resonance in the difference variant (a modified experiment that we have described previously [3]) and an analysis of the magnitudes of the SSCCs enabled the monosaccharide compositions of the carbohydrate moieties of the glycoside molecules to be established: an α-L-arabinopyranose, an α-L-rhamnopyranose, and two β-D-glucopyranose residues in glycoside G, and an additional β-D-glucopyranose residue in glycoside I (Table 2).

The change in the chemical shifts of the protons of the arabinopyranose residue in glycoside I permits the assumption that this residue is substituted by the additional glucopyranose residue. The changes in the chemical shifts of the other monosaccharide residues are negligible. The substitution of the aglycon at the C-28 atom by glucopyranose residue (1) follows from the H-1 and C-1 chemical shifts of this residue, which are characteristic for 1-O-acyl derivatives of pyranoses. The types of substitution in the other monosaccharide residues and the sequence of their linkage could not be determined at this stage of the investigation because of the unfavorable correlation time of the protons in glycosides for the given working frequency of the instrument (zero Overhauser effects).

To determine the types of substitution of the carbohydrate residues, the full acetates of the glycosides under investigation were prepared and PMR spectra were recorded of their solutions in $CDCl_3$ (Table 3). The downfield shifts of all the signals of protons at carbon atoms bearing O-acyl substituents in the spectra of the acylated glycosides, as compared with the spectra of the initial glycosides, enabled the signals of the protons at the substituted carbon atoms to be isolated (C-6 in the glucopyranose residue (1), C-4 in the glucopyranose residue (2), and C-2 in the arabinopyranose residue for glycoside I). Because

TABLE 4. Parameters of the PMR Spectra of the Carbohydrate Moieties of the Acetates of Glycoside G and I [chemical shifts (δ, ppm) and SSCCs (J, Hz) C_6D_6]

H	Monosaccharide residue				
	Ara_p	Rha_p	Glc_p (1)*	Glc_p (2)	Glc_p (3)
1	4,54d (4,41) $J_{1,2} = 7,1$	4,93d $J_{1,2} = 2,2$	5,77	4,48d $J_{1,2} = 7,9$	4,83d $J_{1,2} = 8,0$
2	5,55dd (4,16) $J_{2,3} = 9,5$	5,39 dd $J_{2,3} = 3,1$	5,38	5,11dd $J_{2,3} = 9,4$	5,32dd $J_{2,3} = 9,4$
3	5,17dd (5,19) $J_{3,4} = 3,6$	5,57 dd $J_{3,4} = 10,4$	5,38	5,34t $J_{3,4} = 9,4$	5,39t $J_{3,4} = 9,4$
4	5,29ddd (5,27) $J_{4,5e} = 3,0$	5,48t $J_{4,5} = 10,4$	5,12	3,77t $J_{4,5} = 9,4$	5,46t $J_{4,5} = 9,4$
5		4,11 dq $J_{5,6} = 6,1$	3,59	3,20 ddd $J_{5,6_A} = 3,0$	3,35 ddd $J_{5,6_A} = 5,0$
5e	3,83 dd (3,82) $J_{5a,5e} = 13,0$				
5a	3,20dd (3,16) $J_{5a,4} = 2,0$				
6		1,32			
6_A			3,86	4,50dd $J_{6_A,6_B} = 12,3$	4,46dd $J_{6_A,6_B} = 12,0$
6_B			3,59	4,39dd $J_{6_B,5} = 3,8$	4,12dd $J_{6_B,5} = 2,6$

*Spectrum doubly degenerate because of the coincidence of the H-2 and H-3 signals and also of the H-5 and H-6_B signals. The figures for the arabinopyranose residue in glycoside I are given in parentheses.

TABLE 5. ^{13}C NMR Chemical Shifts of the Carbohydrate Residues in the Progenins of Glycosides G and I (δ, ppm, pyridine, 40°C)

Carbon atom	Monosaccharide residue		
	Ara_p^*	Ara_p^{**}	Glc_p^{**} (3)
1	106,59	103,96	105,78
2	73,23	81,06	73 65
3	74,81	76,24	78,37
4	69,66	68,38	71 68
5	66,90	65,04	78,37
6			62,79

*Monosaccharide residue in glycoside G.
**Monosaccharide residue in glycoside I.

TABLE 6. Parameters of the PMR Spectra of the Carbohydrate Moieties of the Progenins from Glycosides G and I [chemical shifts (δ, ppm) and SSCCs (J, Hz), pyridine, 50°C]

H	Monosaccharide residue		
	Ara_p (G)*	Glc_p (I)**	Ara_p (G)**
1	4,92d $J_{1,2}$=7,0	5,11d $J_{1,2}$=7,9	5,12d $J_{1,2}$=7,2
2	4,34dd $J_{2,3}$=8,9	3,99dd $J_{2,3}$=9,5	4,49dd $J_{2,3}$=8,9
3	4,04dd $J_{3,4}$=3,2	4,15t $J_{3,4}$=9,5	4,23dd $J_{3,4}$=3,2
4	4,21t $J_{4,5e}$=2,9	4,08t $J_{4,5}$=9,5	4,20t $J_{4,5}$=3,0
5		3,76ddd $J_{5,6_A}$=3,0	
5e	4,23dd $J_{5e,5a}$=13,0		4,23dd $J_{5e,5a}$=13,0
5a	3,70dd $J_{5a,4}$=3,0		3,68dd $J_{5a,4}$=3,0
6_A		4,39dd $J_{6_A,6_B}$=11,5	
6_B		4,26dd $J_{6_B,5}$=5,0	

*Monosaccharide residue in glycoside G.
**Monosaccharide residue in glycoside I.

of the coincidence of the rhamnopyranose H-1 signals and of the glucopyranose H-2 signals in the spectra, the glycoside acetates were transferred to solution in C_6D_6, and a series of experiments to determine Overhauser effects on the irradiation of the anomeric protons was performed (Table 4).

Preirradiation of the H-1 proton of the rhamnopyranose residue caused in the difference spectrum an enhancement (5-6%) of the H-4 signal of the glucopyranose (2) residue for both glycosides. Thus, both glycosides containing the disaccharide fragment Rhap-(1 → 4)-Glcp. Preirradiation of the H-1 proton of the glucopyranose (3) residue in glycoside I caused an enhancement (8%) of the H-2 signal of the arabinopyranose residue. Preirradiation of the H-1 protons of the arabinopyranose and glucopyranose (2) residues did not lead to the appearance of signals in the difference NOE spectrum, even for the protons closest to the anomeric protons in the residues concerned. The zero NOE is obviously due to the long correlation time of the "internal," in comparison with the "terminal," residues.

For a definitive elucidation of the structures of glycosides G and I, they were subjected to alkaline hydrolysis, as a result of which progenins and oligosaccharide fractions were isolated, as described above. The structures of the progenins followed unambiguously from an analysis of their ^1H and ^{13}C NMR spectra (Tables 5 and 6). The oligosaccharide fractions proved to be completely identical. Analysis of the ^{13}C NMR and PMR spectra showed that each of the oligosaccharides consisted of three residues, two of which were those of rhamnopyranose and glucopyranose, while the third was a six-carbon fragment with a deoxy unit (Tables 7 and 8). The presence of a six-carbon fragment with a deoxy unit at the C-3 carbon atom can apparently be explained by the modification, during alkaline hydrolysis, of a glucopyranose residue initially substituted in the C-6 position to form a metasaccharinic acid. As is known from the literature, under the action of acids and bases monosaccharides are converted as the result of a series of transformations into, as the final products, metasaccharinic acids or their lactones [4].

TABLE 7. ^{13}C NMR Chemical Shifts of the Carbohydrate Residues in the Oligosaccharide from Glycosides G and I (δ, ppm, pyridine, 40°C)

Carbon atom	Monosaccharide residue		
	Rha_p	Glc_p (2)	Glc_p (1)*
1	102,82	104,90	—
2	72,84	74,04	75,36
3	72,59	77,27	32,4
4	74,04	78,67	71,07
5	70,49	77,15	76,78
6	18,53	61,57	68,67

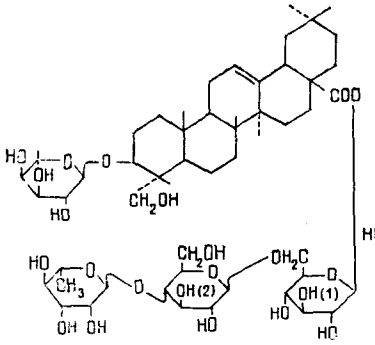
*The chemical shifts given are for the product of the modificaiton of Glcp (1), apparently consisting of the lactone of the corresponding metasaccharinic acid.

TABLE 8. Parameters of the PMR Spectrum of the Oligosaccharide from Glycosides G and I [chemical shifts (δ, ppm) and SSCCs (J, Hz), D_2O, 40°C]

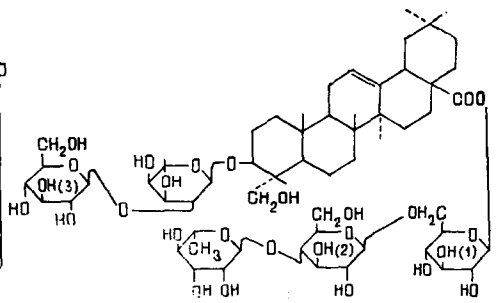
H	Monosaccharide residue		
	Rha_p	Glc_p (1)	Glc_p (2)
1	4,87 d $J_{1,2}$=1,8		4,46 d $J_{1,2}$=8,0
2	3,98 dd $J_{2,3}$=3,6	4,74 dd $J_{2,3a}$=8,5 $J_{2,3B}$=10,6	3,33 dd $J_{2,3}$=9,1
3	3,76 dd $J_{3,4}$=9,2		3,57 m
3a		2,68 ddd $J_{3a,3B}$=12,6 $J_{3a,4}$=5,5	
3B		2,14 dt $J_{3B,4}$=10,6	
4	3,48 t $J_{4,5}$=9,2	4,63 ddd $J_{4,5}$=3,6	3,57 m
5	4,02 dq $J_{5,6}$=6,3	4,15 dt $J_{5,6A}$=3,6	3,48 m
6	1,27 d		
6_A		4,00 dd $J_{6A,6B}$=11,4	3,87 dd $J_{5,6A}$=2,0 $J_{6A,6B}$=12,3
6_B		3,71 dd $J_{6B,5}$=6,5	3,72 dd $J_{5,6B}$=4,7

The sequences of linkages of the monosaccharide residues in the oligosaccharides were determined with the aid of NOE experiments. The signals in the carbon spectra of the progenins and of the oligosaccharide fragment were assigned with the aid of the selective heteronuclear magnetic resonance procedure. The interpreted ^{13}C NMR spectra of the progenins and the oligosaccharide were the basis for the assignment of the signals in the spectra of the glycosides.

Thus, from the information available the glycosides G and I under investigation may be assigned the following structures:



Glycoside G



Glysocide I

EXPERIMENTAL

GLC analysis was performed on a Chrom-5 instrument using a column with 5% of XE-60 on Chromaton N-AW HMDS, FID, carrier gas helium, rate 40 ml/min; temperature of the column 210°C, of the evaporator 250°C, and of the detector 270°C. IR spectra were taken on a UR-20 instrument (in paraffin oil). PMR and ^{13}C NMR spectra were recorded on Bruker WP-250 and AM-300 instruments with working frequencies for protons and carbon, respectively, of 250 and 63 MHz and 300 and 75 MHz, at various temperatures and with different solvents.

Isolation of Glycosides G and I. Chromatography on a column with silica gel of the purified enriched combined saponins obtained as described previously [1] from the air-dry roots of the great marsh marigold led to the isolation of the individual polar glycosides G (mp 172-173°C) and I (mp 217-218°C) (chloroform–methanol–water (26:14:3) system; revealing agent for TLC at 25% solution of tungstophosphoric acid in ethanol). The IR spectra of gycosides G and I contained a characteristic absorption band in the 1740 cm^{-1} region.

Acid Hydrolysis of Glycosides G and I. Glycosides G and I (50 mg in each case) were hydrolyzed with 2 N HCl (5 ml) at 100°C for 5 h. The aglycon that precipitated was filtered off and washed with distilled water, and it was identified as hederagenin by comparison with an authentic sample (chloroform–methanol (20:1) system). The filtrate was evaporated to dryness and the disappearance of traces of HCl. In both cases, rhamnose, arabinose, and glucose were identified by comparison with authentic samples. After reduction of the monosaccharides followed by acetylation as described previously [1], rhamnitol, arabitol, and sorbitol acetates were identified by GLC in comparison with authentic samples in ratios of 1:1:2 and 1:1:3 for glycosides G and I, respectively.

Alkaline Hydrolysis of Glycosides G and I. Glycosides G and I (100 mg in each case) were subjected to alkaline hydrolysis in 5% KOH solution at 100°C for 1.5 h. The hydrolysates were neutralized with KU-2 cation-exchanger (H^+) and were filtered. The progenins were extracted with butanol, and the butanolic (progenin) and aqueous (oligosaccharide) fractions were evaporated. The progenins from glycosides G and I were hydrolyzed with 2 N HCl as described above. By TLC, arabinose was detected in the first case and arabinose and glucose in the second, these sugars then being identified by GLC in the form of polyol acetates, in comparison with authentic samples, in a ratio of 1:1.

Acetates of Glycosides G and I. Glycosides G and I (100 mg in each case) were acetylated in a mixture of acetic anhydride and pyridine (3 ml each) at room temperature for 12 h, and then the mixture was evaporated to dryness with the addition of methanol and toluene to eliminate traces of acetic anhydride and pyridine. The glycoside acetates obtained were purified on a column with silica gel (benzene–ethyl acetate (1:1) system; revealing agent a 5% ethanolic solution of H_2SO_4). The completeness of acetylation was checked by IR spectroscopy.

SUMMARY

Two triterpene glycosides, a tetraoside and a pentaoside of hederagenin, have been isolated from the roots of the great marsh marigold and their chemical structures have been determined.

Glycoside G is hederagenin 3-O-α-L-arabinoside 28-O-[O-α-L-rhamnopyranosyl-(1 → 4)-O-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside].

Glycoside I is hederagenin 3-O-[O-β-D-glucopyranosyl-(1 → 2)-α-L-arabinoside] 28-O-[O-α-L-rhamnopyranosyl-(1 → 4)-O-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside].

LITERATURE CITED

1. M. M. Vugal'ter, G. E. Dekanosidze, O. D. Dzhikiya, and É. P. Kemertelidze, Khim. Prir. Soedin., 712 (1986).
2. H. Kizu and T. Tomimori, Chem. Pharm. Bull, 30, No. 3, 859 (1982).
3. M. M. Benidze, O. D. Dzhikiya, T. A. Pkheidze, É. P. Kemertelidze, and A. S. Shashkov, Khim. Prir. Soedin., 537 (1987).
4. N. K. Kochetkov, A. F. Bochkov, B. A. Dmitriev, A. I. Usov, O. S. Chizhov, and V. N. Shibaev, The Chemistry of the Carbohydrates [in Russian] (1967), p. 102.

ALKALOIDS OF Aconitum barbatum.

STRUCTURE OF BATACONINE

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The epigeal part of Aconitum barbatum gathered in the early vegetation period in the environs of Ulan-Bator has yielded delcosine, lycoctonine, songorine, and the new base bataconine. The structure of bataconine has been shown on the basis of spectral characteristics (IR, NMR, and mass spectra) and also of a correlation with the known alkaloid neoline.

We have investigated the alkaloids of the epigeal part of Aconitum barbatum Pers gathered in the early vegetation period in the environs of Ulan Bator (Mongolian People's Republic). The amount of combined alkaloids was 1.5% on the weight of the air-dry plant. By separating the combined alkaloids, we isolated delcosine, lycoctonine, songorine, and a new base with the composition $C_{23}H_{37}NO_6$, which has been named cataconine (I).

The IR spectrum of the alkaloid had absorption bands of hydroxy groups at 3525, 3480, and 3365 cm^{-1} and of ether bonds at 1120 and 1090 cm^{-1}. According to its PMR spectrum, the alkaloid contained one N-ethyl and two methoxy groups. The mass spectrum of the alkaloid was characteristic for the spectra of C_{19} diterpene alkaloids and contained the peak of the $M^+ - 17$ ion (100%), which is due to a hydroxy group at C-1 [1]. The presence in the mass spectrum of the peaks of the ions $M^+ - 15$ (26%), $M^+ - 17$ (100%), $M^+ - 56$ (4.5%), and $M^+ - 87$ (7%) showed that it belonged to the alkaloids of the aconitine type, containing hydroxy groups at C-1 and C-8 and a methoxymethyl group at C-4 [2].

When the alkaloid was acetylated with acetic anhydride in pyridine a triacetyl derivative (II) was obtained, which indicated the presence of three secondary hydroxy groups in the alkaloid. The PMR spectrum of the triacetate had the signals of one N-ethyl, three acetoxy, and two methoxy groups and the signals of protons geminal to the three acetoxy groups: a one-proton doublet with a splitting constant of 7 Hz at 5.93 ppm assigned to H-6; a quartet at 4.93 ppm with splitting constants of 10 and 7 Hz assigned to 1-β-H; and a triplet with a spin–spin coupling constant of 5 Hz, assigned to 14-β-H [4, 5].

The facts given permit structure (I) to be proposed for bataconine. To confirm this hypothesis we methylated (I) with methyl iodide in the presence of sodium hydride, and obtained the 6,14-dimethyl derivative (I), which proved to be identical with the product of the methylation of neoline (III) under similar conditions. Consequently, bataconine has the structure (I).

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