progenin (II), in addition to the peak of an ion with m/z 721 $(M + H - H_2O)^+$ of the main component there were the peaks of ions with m/z 735, 737, 753 (with glycerol as the matrix), and, together with the peak of the $(M + Na)^+$ ion with m/z 761 there were the peaks of ions with m/z 775, 777, and 793 (with glycerol + NaCl as the matrix). Their intensities amounted to 40-70% of the intensity of the peak of the ion with m/z 761. This fact showed the presence of impurities with molecular masses of 752, 754, and 770.

The auxiliary compounds are products of the oxidation of aglycon moiety of progenin (II), since in the central part of the spectrum of this compound there are the peaks of the corresponding ions with m/z 427, 429, and 445, the first of which is the strongest. This agrees with the presence in the EI spectrum of progenin (II) of the peak of an ion with m/z 426 in the composition of which there are four hydrogen atoms fewer than in the M^+ ion of pennogenin. Consequently, this ion may be the product of the dehydration of the aglycon part of a molecule containing a larger number of OH groups than pennogenin.

EXPERIMENTAL

The LSIMS mass spectra were obtained on a Hitachi M-80A mass spectrometer (Japan) at a resolving power of the instrument of 1000, with an accelerating voltage of 3 kV. The collection of the results and their processing were performed with the aid of a M-003 computer system. Glycerol and glycerol with the addition of trace amounts of an aqueous solution of NaCl were used as the matrices. The target was bombarded with a beam of Xe^+ ions having an energy of 8 keV.

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TRITERPENE GLYCOSIDES OF Astragalus AND THEIR GENINS

XXXIX. CYCLOARALOSIDE D FROM Astragalus amarus

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The structure of a triterpene glycoside of the cycloartane series – cycloaraloside D, isolated from the roots of Astragalus amarus Pall. (Leguminosae) – has been established on the basis of chemical transformations and spectral characteristics. Cycloaraloside D is 20R,24S-epoxycycloartane-3β,6α,16β,25-tetraol 3-O-[O-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranoside].

Continuing a study of glycosides of Astragalus amarus Pall. (Leguminosae), we have established the structure of substance 7 [1], which we have called cycloaraloside D (I).

The presence in the PMR spectra of glycoside (I) of two one-proton doublets interconnected in the manner of an AB system, at 0.19 and 0.55 ppm, permitted the glycoside under consideration to be assigned to the triterpenoids of the cycloartane series [2, 3]. This conclusion was confirmed by the formation of cyclosieversigenin (II) on the acid hydrolysis of glycoside (I).

In the carbohydrate fraction of a hydrolysate, D-glucose and L-rhamnose were detected by PC and GLC [4]. GLC showed the glycoside (I) contained one residue each of these monosaccharides.

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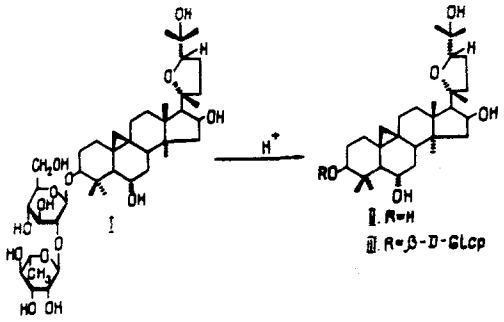
TABLE 1. Chemical Shifts of the Carbon Atoms of Compounds (I)-(III) (δ, ppm, 0 – TMS, C_5D_5N)

C Atom	Compound			C Atom	Compound		
	I	II	III		I	II	III
1	32,72	32,72	32,41	23	26,24	26,29[a]	26,37[a]
2	30,25	31,30	30,16	24	82,03	81,57	81,64
3	88,55	78,21	88,96	25	71,19	71,19	71,26
4	42,61	42,28	42,56	26	27,08*	27,04*	27,04*
5	54,31	53,86	53,93	27	28,40*	28,09*	28,53*
6	67,99	68,27	67,97	28	20,23	20,17	20,09
7	38,36	38,69	38,54	29	28,69	29,28	28,91
8	46,96	47,21	47,06	30	16,71	16,16	16,66
9	21,06	20,84	20,84		β-D-Glcp residue		
10	29,66	29,80	29,51	1	105,09		106,82
11	26,48	26,29[a]	26,37[a]	2	79,57		75,82
12	33,66	33,31	33,31	3	78,42		78,66
13	45,38	44,89	44,97	4	72,60		71,78
14	46,35	46,09	45,91	5	77,51		78,06
15	46,87	46,69	46,09	6	63,21		62,97
16	73,40	73,35	73,43		α-L-Rhap residue		
17	58,56	58,26	58,26	1	101,51		
18	21,35	21,51	21,51	2	72,22		
19	30,51	31,0	30,55	3	72,55		
20	87,20	87,17	87,17	4	74,28		
21	27,99	28,46	28,41	5	69,41		
22	35,21	34,81	34,88	6	18,47		

The signals marked with the same letters are superposed upon one another, and the assignments of those marked with an asterisk are not definite.



Cycloaraloside D was subjected to partial hydrolysis. In addition to cyclosieversigenin, progenin (III) identical with cycloaraloside A [5], was isolated from the products obtained. Consequently, the D-glucose residue was attached to the hydroxy group at C-3 of cyclosieversigenin and had the β-configuration and the C1 conformation.

Analysis of the ^{13}C NMR spectra of compounds (I)-(III) (Table 1) showed that only one carbinol carbon atom of the genin moiety of the cycloaraloside B molecule experienced the effect of glycosylation and resonated at 88.55 ppm (C-3). This means that the L-rhamnose residue was attached to the D-glucose residue, and glycoside (I) had the nature of a monodesmoside. The position of the L-rhamnose residue was revealed by a comparative study of the ^{13}C NMR spectra of glycosides (I) and (II).

Attention is attracted by the upfield displacement of the signal of the anomeric carbon atom of the D-glucose residue on passing from glycoside (III) to cycloaraloside D (I), by −1.73 ppm (105.09-106.82), and also by the downfield shift of the signal of the D-glucose C-2 atom by +3.75 ppm (79.57-75.82). This fact unambiguously determines the position of the L-rhamnose residue at C-2 of the D-glucose residue. The chemical shifts of the carbon atoms of the L-rhamnose residue showed the pyranose form, the 1C conformation, and the α-configuration of the terminal monosaccharide [6]. The molecular rotation difference also showed the α-configuration of the anomeric center of the L-rhamnose residue [7].

Thus, cycloaraloside D has the structure of 20R,24S-epoxycycloartane-3β,6α,16β,25-tetraol 3-O-[O-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranoside].

EXPERIMENTAL

For general observations see [8]. The following solvent systems were used: 1) chloroform–methanol (15:1); 2) n-butyl alcohol–pyridine–water (6:4:3); 3) chloroform–methanol–water (70:12:1).

^1H and ^{13}C spectra were taken on a Bruker WM 250 instrument in deuteropyridine, with TMS as internal standard (δ, ppm).

Cycloaraloside (I) – substance 7 [1], $C_{42}H_{70}O_{14}$, mp 226-228°C (from methanol), $[\alpha]_D^{28}$ −11.9 ± 2° (c 0.84; methanol). $[M]_D$ = −106.86°, $\Delta[M]_{D(I-III)}$ = −322°. $[M]_D$ values of methyl glycosides of L-rhamnopyranose: α, −109°; β, + 169° [7]. ν_{max}^{KBr}, cm^{-1}: 3600-3150 (OH). PMR spectrum: 0.19 and 0.55 (2H-19, d, ^2J = 4 Hz); 1.03, 1.31, 1.33, 1.41, 1.55, 1.60, 2.02 (7 × CH_3, s); 1.77 (CH_3 of L-rhamnose, ^3J = 6 Hz); 2.55 (H-17, d.d, ^3J = 7.5 Hz); 3.12 (H-22, q, $^2J = {}^3J_1 = {}^3J_2$ = 10 Hz); 3.60 (H-3, d.d, $^3J_1$ = 11, $^3J_2$ = 4 Hz); 3.77 (H-6, d.d.d, $^3J_1 = {}^3J_2$ = 8.5, $^3J_3$ = 3.5 Hz); 5.03 (anomeric proton of D-glucose, d, ^3J = 7 Hz); 6.62 (anomeric proton of L-rhamnose, br.s).

Cyclosieversigenin (II) from (I). Cycloaraloside D (40 mg) was hydrolyzed with 5 ml of a 0.5% methanolic solution of sulfuric acid at 50°C for 2 h. After the usual working up of the reaction products, the genin moiety, when chromatographed on a column in system 1, yielded 17 mg of cyclosieversigenin (II), mp 239-241°C (from methanol), $[\alpha]_D^{28}$ +52 ± 2° (c 1.1; methanol).

D-Glucose and L-rhamnose were detected in the carbohydrate part of the hydrolysate by (system 2) and GLC [4]. GLC showed the presence of these monosaccharides as components of glycoside (I) in a ratio of 1.00:0.96.

Cyclosieversigenin (II) and cycloaraloside A (III) from (I). Glycoside (I) (60 mg) was subjected to partial acid hydrolysis in 10 ml of a 0.25% methanolic solution of sulfuric acid at 50°C for 1 h. The reaction products after the appropriate working up were chromatographed on a column with elution by system 1. This led to the isolation of 10 mg of cyclosieversigenin (II), mp 239-241°C (from methanol), $[\alpha]_D^{28}$ +52 ± 2° (c 0.8; methanol).

Continued elution of the column with system 3 led to the isolation of 23 mg of glycoside (III) having mp 240-242°C (from system 3), $[\alpha]_D^{28}$ +33 ± 2° (c 1.0; methanol), $[M]_D$ = +215.16°, which was also identified as cycloaraloside A [5] on the basis of its PMR spectrum.

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