The new glycoside of the cycloartane series has been isolated from the roots of Astragalus sieversianus Pall. and has been shown to be cyclosiversigenin 3-O-[α-L-rhamnopyranosyl-(1→2)-β-D-xylopyranoside]-6-O-β-D-xylopyranoside.

In the present paper we consider the structure of cyclosiversioside G (substance G) which we isolated from the roots of Astragalus sieversianus Pall. [1-3].

It was established by the GLC method [4] that cyclosiversioside G (I) contained D-xylose and L-rhamnose residues in a ratio of 2:1. In the products of the Smith degradation of the trioside (I) [5], cyclosiversigenin (II) [6] was detected, which showed that the glycoside under investigation belonged to the cycloartane series.

The Hakomori methylation [7] of glycoside (I) gave the deca-O-methyl ether (III), the acid hydrolysis of which led to 2,3,4-tri-O-methyl-D-xylopyranose, 2,3,4-tri-O-methyl-L-rhamnopyranose, and 3,4-di-O-methyl-D-xylopyranose. In addition, from products we isolated the dimethyl ether (V), shown to be identical with the authentic 16,25-dimethyl ether of siversigenin [1].

Thus, the structure of the derivatives obtained in the acid cleavage of the deca-O-methyl ether (III) shows that cyclosiversigenin G(I) is a bisdesmosidic glycoside in which the sugar residues are attached to cyclosiversigenin at the C-3 and C-6 hydroxy groups.

Hydrolysis of the glycoside (I) in 0.25% sulfuric acid yielded a diglycoside (IV), identical with the 3,6-di-O-β-D-xylopyranoside of cyclosiversigenin - cyclosiversioside E (IV) [1]. Consequently, in the glycoside (I), the disaccharide moiety contains D-xylose and L-rhamnose residues and the monosaccharide moiety D-xylose. The formation of 3,4-di-O-methyl-D-xylopyranose on the acid cleavage of the methyl ether (III) shows that the L-rhamnose is attached to the hydroxy group on the second carbon atom of one of the D-xylose molecules.

The position of the bioside residue in the genin was established on the basis of the results of a comparative analysis of the chemical shifts of the signals of the anomeric carbon atoms in the $^{13}$C NMR spectra of cyclosiversioside E (IV) and the triglycoside (I) (see Scheme on following page).

It has been established previously [3] that in the $^{13}$C NMR spectrum of compound (IV) the signals of the C-1' and C-1'' anomeric carbon atoms of the two xylopyranose residues appears at 107.3 and 105.3 ppm, respectively.

In the $^{13}$C NMR spectrum of the triglycoside (I) under investigation, one of the three anomeric carbon atoms resonated at 101.6 ppm. From the value of its chemical shift, this signal was assigned to C-1'' of the L-rhamnose residue [8, 9].

The chemical shifts of the C-1' and C-1'' anomeric carbon atoms of the two xylopyranose residues of compound (I) are extremely close and in the spectrum a single common signal at 105.4 ppm corresponds to
them. Consequently, in the spectrum of glycoside (I) the signal corresponding to the C-1' carbon atom has undergone a diamagnetic shift by 1.9 ppm (δ\textsubscript{IV}(C-1') = 107.3 ppm; δ\textsubscript{I}(C-1') = 105.4 ppm, Δδ = 1.9 ppm).

The upfield shift of the C-1' anomeric carbon atom \[8\] shows that the molecule of L-rhamnose is attached to the C-2' atom of the D-xylose residue which, in its turn, is attached to the hydroxy group at C-3 of the aglycone.

A calculation of molecular rotation differences \[10\] between the triglycoside (I) and the diglycoside (IV) showed that the L-rhamnose residue has the α configuration of the glycosidic center. Thus, cyclosiversioside G (I) is cyclosiversigenin 3-O-[O-α-L-rhamnopyranosyl-(1 → 2)-β-D-xylopyranosyl]-6-O-β-D-xylopyranoside.

**EXPERIMENTAL**

For general observations and methods of isolation, see \[1, 6\]. PMR spectra were taken in \(\text{C}_2\text{D}_2\text{N}\) on a JMN-4H-100/100 MHz instrument (δ, 0 – HMDS), and \(^{13}\text{C}\) NMR spectra on a Varian CFT-20 instrument in \(\text{C}_2\text{D}_2\text{N} (0 – \text{TMS})\).

The sugars were chromatographed in the form of the trimethylsilyl ethers of their methyl glycosides \[4\] on a column (3.7 m × 3 mm) containing Chromaton N-AW impregnated with 5% of the silicone phase SE-30. The temperature of the thermostat was 190°C and the carrier gas here and below was helium, at a rate of flow of 45 ml/min.

The methyl ethers of the sugars were identified in the form of their methyl glycosides \[11\]. The chromatography of the latter was carried out on a column (1.2 m × 3 mm) containing Celite impregnated with 20% of poly-(butane-1,4-diyl succinate) (phase 1) at a thermostat temperature of 180°C and on a column (1.2 m × 3 mm) containing Chromaton N-AW impregnated with 10% of poly(phenyl ether) 5 F-4 E (phase 2) at a thermostat temperature of 190°C. The retention times (\(\text{Trel}\)) of the methylated methyl glycosides were calculated with respect to the retention time of methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside.

Cyclosiversioside G (I, substance G) \[1\], \(\text{C}_{64}\text{H}_{76}\text{O}_{17}\), mp 222-224°C (from methanol), [\(\alpha\)]\textsubscript{D}\textsuperscript{20} = -5.42 + 2° (c 1.34 methanol); \(\nu\textsuperscript{\text{KBr}}\), cm\textsuperscript{-1}: 3350-3430 (OH). PMR spectrum (δ, ppm): 0.49 (H at C-19, d, G = 4.0 Hz), 1.04-1.49 (CH\(\text{3}×8\)). By the GLC method \[4\], D-xylose and L-rhamnose in a ratio of 2.19:1.00 were detected in cyclosiversioside G.