TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS. XIII. THE STRUCTURE OF CYCLOSIVERSIOSIDE H — A TRIGLYCOSIDE FROM *Astragalus sieversianus*

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A new triglycoside of the cycloartane series has been isolated from the roots of *Astragalus sieversianus* Pall.; it is cyclosiversigenin 6-O-β-D-glucopyranoside 3-O-[O-α-L-rhamnopyranosyl-(1 → 2)-β-D-xylopyranoside].

We have previously [1] established the structure of cyclosiversioside G — a triglycoside isolated from the roots of *Astragalus sieversianus* Pall. (family Leguminosae). In the present paper we consider the structure of cyclosiversioside H (I) (substance H) which we have isolated from the roots of the same plant [2].

It was established by GLC [3] that cyclosiversioside H (I) is a triglycoside containing D-xylose, D-glucose, and L-rhamnose residues in a ratio of 1:1:1. The products of the hydrolysis of triglycoside (I) were found to contain cyclosiversioside F (cyclosiversigenin 6-O-β-D-glucopyranoside 3-O-β-D-xylopyranoside) (II) [4], the monoglycosides (IV) and (V) [4], and cyclosiversigenin (III) [5].

Consequently, cyclosiversioside H (I) is likewise a glycoside of the cycloartane series and contains one additional L-rhamnose residue as compared with cyclosiversoiside F (II).

The position of the L-rhamnose residue in cyclosiversioside H was determined in the following way. (See formula at top of following page).

In the ^{13}C NMR spectrum of cyclosiversigenin (III), the signals of the C-3, C-6, C-16, and C-25 carbinol carbon atoms appear at 78.2, 68.3, 73.43, and 71.2 ppm, respectively. In the case of cyclosiversioside H, these carbon atoms are characterized by signals at 87.9 ppm (C-3); 78.6 ppm (C-6), 73.3 ppm (C-16), and 71.2 ppm (C-25). Thus, on passing from the genin (III) to the triglycoside (I) a glycosylation effect was suffered by the atoms C-3 (+9.7 ppm) and C-6 (+10.3 ppm). At the same time, the chemical shifts of the C-16 and C-25 signals remained unchanged. It follows from this that the L-rhamnose molecule is not bound directly to the genin moiety but is attached to one of the sugar residues.

In the ^{13}C NMR spectrum of triglycoside (I), the signal of an anomeric carbon atom at 101.6 ppm must be assigned to C-1''' of the L-rhamnopyranoside group [6, 7]. The signals of the C-1' and C-1" anomeric carbon atoms of the xylo- and glucopyranoside rings have very close values and appear at 105.5 and 105.0 ppm.

We may note that in the ^{13}C NMR spectrum of cyclosiversioside F (II) the anomeric carbon atom C-1' and C-1" of the xylopyranoside and glycopyranoside residues resonate at 107.4 and 105.0 ppm, respectively, and therefore it is obvious that in the spectrum of cyclosiversioside H (I) the signal corresponding to the C-1' atom has undergone a diamagnetic shift by 1.9 ppm ($\delta_{II(C-1')}$ = 107.4 ppm; $\delta_{I(C-1')}$ = 105.5 ppm; $\Delta\delta$ = 1.9 ppm).

The diamagnetic nature and the magnitude of the change in the chemical shift of the C-1' anomeric carbon atom that has been found unambiguously shows that the L-rhamnose residue is attached to the C-2' atom of the D-xylose residue.

On the basis of a calculation of the molecular rotation difference [8] between the triglycoside (I) and the diglycoside (II), the α configuration was assigned to the glycosidic center of the L-rhamnose residue.

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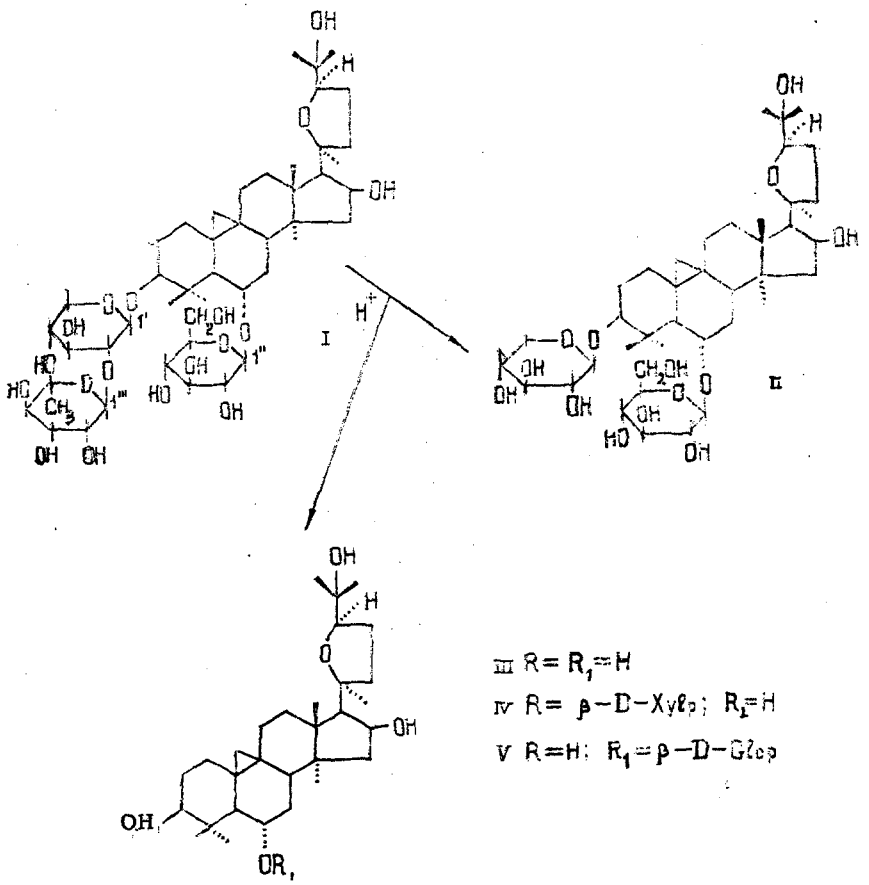

Thus, cyclosiversioside H (I) is 20S,24R-epoxycycloartane-3β,6α,16β,25-tetraol 6-O-β-glucopyranoside 3-O-[O-α-L-rhamnopyranosyl-(1 → 2)-β-D-xylopyranoside].

EXPERIMENTAL

For general observations and methods of isolation, see [1, 2]. PMR spectra were recorded on a JNM-4H-100/100 MHz instrument (δ, 0 — HMDS) and ^{13}C NMR spectra on a CFT-20 instrument (Varian) in C_5D_5N (0 — TMS).

Cyclosiversioside H ((I), substance H [2]), $C_{47}H_{78}O_{18}$, mp 262-264°C (from methanol), $[\alpha]_D^{20}$ −30.0 ± 2° (c 1.05; methanol). ν_{max}^{KBr}, cm^{-1}: 3300-3500 (OH), 3040 (CH_2 of cyclopropane ring). PMR spectrum (δ, ppm): 0.48 (H at C-19, d, J = 4 Hz), 0.90-1.70 (8 CH_3). By the GLC method [3], D-glucose, D-xylose, and L-rhamnose residues were found in cyclosiversioside H in a ratio of 1.00:0.90:0.98.

Partial Hydrolysis of Cyclosiversioside H. To a solution of 300 mg of cyclosiversioside H (I) in 30 ml of methanol was added 30 ml of a 0.5% methanolic solution of sulfuric acid, and the mixture was heated on the boiling bath for 1.5 h. After cooling, 50 ml of water was added to the reaction mixture, and the methanol was distilled off. The reaction products were extracted with butanol, and then the solvent was evaporated off and the residue was chromatographed on a column of silica gel. Elution with chloroform–methanol–water (70:22.5:4) yielded 2 mg of the genin (III), which was identified as cyclosiversigenin [5] (TLC, ethyl acetate), and 3 mg of the monoside (IV), identical with cyclosiversigenin 3-O-β-D-xylopyranoside [4] (TLC; chloroform–methanol–water (70:22.5:4)).

On continuing the washing of the column with the same system of solvents, two more substances were isolated. A monoglycoside (V) (12 mg) with mp 240-243°C from methanol, $[\alpha]_D^{20}$ +32.0 ± 2° (c 0.66; methanol) proved to be identical with cyclosiversigenin 6-O-β-D-glucopyranoside [4]. A diglycoside (II) (30 mg) with mp 260-261°C (from methanol), $[\alpha]_D^{20}$ +33.3 ± 2° (c 0.54; methanol) was identified by comparison with an authentic sample from the nature of its IR spectrum and its mobility on TLC as cyclosiversioside F [4].

SUMMARY

A new triglycoside of the cycloartane series has been isolated from the roots of *Astragalus sieversianus* Pall.; it is cyclosiversigenin 6-O-β-D-glucopyranoside 3-O-[O-α-L-rhamnopyranosyl-(1 → 2)-β-D-xylopyranoside].

LITERATURE CITED

1. A. N. Svechnikova, P. U. Umarov, M. B. Gorovits, N. A. Abdullaev, and N. K. Abubakirov, Khim. Prir. Soedin., 312 (1983).
2. A. N. Svechnikova, R. U. Umarova, M. B. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 204 (1982).
3. T. T. Gorovits, Khim. Prir. Soedin., 263 (1970).
4. A. N. Svechnikova, R. U. Umarova, M. B. Gorovits, N. D. Abdullaev, and N. K. Abubakirov, Khim. Prir. Soedin., 208 (1982).
5. A. N. Svechnikova, R. U. Umarova, M. B. Gorovits, K. L. Seitanidi, Ya. V. Rashkes, M. R. Yagudaev, and N. K. Abubakirov, Khim. Prir. Soedin., 67 (1981).
6. K. Tori, S. Seo, Y. Yashimura, M. Nakamura, Y. Tomita, and H. Ishii, Tetrahedron Lett., 4167 (1967).
7. L. I. Strigina and V. V. Isakov, Khim. Prir. Soedin., 847 (1980).
8. W. Klyne, Biochem. J., 47, XLI (1950).

^{13}C NMR SPECTRA OF STEROID GLYCOSIDES.

III. ACETATES OF PENNOGENIN TRIOSIDES

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The ^{13}C NMR spectra of two pennogenin trioside acetates have been measured and an assignment has been made of the signals of the C atoms. The mutual influence of the aglycone and of the acetylated carbohydrate chains, and also of the acetylated monosaccharides composing the carbohydrate chains, have been determined.

One of the promising methodological approaches to determining the structures of natural spirostanol glycosides is ^{13}C NMR spectroscopy. Investigations in this direction have been successfully developed in recent years [1-7]. However, the great complexity of the ^{1}H NMR spectra of the free glycosides prevents the unambiguous assignment of the signals in the ^{13}C NMR spectra by using the method of selective decoupling from protons. The spectroscopy of the acetates of glycosides has a number of advantages due to the lesser complexity of the ^{1}H NMR spectra and the good solubility of the acetates of the glycosides in a large number of nonpolar solvents.

We have studied the ^{13}C NMR ($CDCl_3$) spectra of two acetates of spirostanol glycosides — polygonatosides C^1 (I) and C^2 (II) [8]. We report the assignment of the resonance signals of the C atoms in the spectra.

The assignment of the signals of the C atoms in the ^{13}C NMR spectra of (I) and (II) was carried out on the basis of results for pennogenin [9] and those given in the literature for the corresponding methyl glycosides [10].

To illustrate the mutual influence of the aglycone and the component carbohydrate chains, we calculated the glycosylating shifts $\Delta\delta = \delta_C$ of the glycoside acetate $- \delta_C$ of the aglycone (for the aglycone), and $\Delta\delta = \delta_C$ of the glycoside acetate $- \delta_C$ of the acetate of the methyl glycoside (for the acetylated monosaccharides) [4]. The glycosylation shifts for the $(OAc)_3$-α-L-Araf residues of (I) are not given because of the absence from the literature of informa-

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