TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS.

XV. CYCLOSIVERSIOSIDES B AND D FROM *Astragalus basineri*

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Two new glycosides have been isolated from the roots of the plant *Astragalus basineri* Trautv. — cyclosiversiosides B and D. It has been shown that cyclosiversioside B is cyclosiversigenin 3-O-(2',3'-di-O-acetyl-β-D-xylopyranoside)-6-O-β-D-glucopyranoside. Cyclosiversioside D is cyclosiversigenin 3-O-(2'-O-acetyl-β-D'-xylopyranoside)-6-O-β-D-glucopyranoside.

Continuing a study of the methylsteroids of plants of the genum *Astragalus* [1], from the roots of *Astragalus basineri* Trautv. we have isolated eight glycosides which have been designated in order of increasing polarity as A, B, C, D, E, F, G, and H. Compounds A, C, E, F, G, and H have been identified with the cyclosiversiosides with the same designations isolated previously from *Astragalus sieversianus* Pall. [1-5]. In the present paper we consider the structures of two new glycosides — cyclosiversiosides B and D. They are identical with substances B and D from *Astragalus sieversianus* [2].

The absorption bands at 1752 and 1260 cm^{-1} observed in the IR spectrum of cyclosiversioside D (I) and also a three-proton singlet at 2.05 ppm in the PMR spectrum show the presence of one acetate group in the molecule of glycoside (I). The treatment of cyclosiversioside D (I) with a 0.25% methanolic solution of potassium hydroxide led to the formation of the known glycoside cyclosiversioside F (III) — cyclosiversigenin 6-O-β-D-glucopyranoside-3-O-β-D-xylopyranoside [3].

Information on the position of attachment of the acetyl group in glycoside (I) was obtained as the result of an analysis of the characteristics of the ^{13}C NMR spectra of cyclosiversioside D (I) and cyclosiversioside F (III). The chemical shifts of the signals of the C-16 and C-25 carbon atoms, bearing free hydroxy groups, in the ^{13}C NMR spectrum of cyclosiversiosides D (I) and F (III) were identical at 73.4 and 71.2 ppm, respectively. This means that the acetyl group in the molecule of compound (I) can be located only in one of the sugar residues.

We have shown previously [1] that in the ^{13}C NMR spectrum of cyclosiversioside F (III) the anomeric carbon atoms of the xylopyranoside and glucopyranoside residues (C-1' and C-1", respectively) resonate at 107.4 and 105.0 ppm, respectively.

In the spectrum of cyclosiversioside D (I), the signals of the anomeric C-1' and C-1" carbon atoms of the xylo- and glucopyranoside residues are located at 104.6 and 10.50 ppm. Consequently, on passing from compound (III) to (I) the chemical shift of the anomeric atoms of the glucopyranoside ring (C-1") was retained, while the signal of the C-1' carbon underwent a diamagnetic shift by 2.8 ppm [$\Delta\delta = \delta(C\text{-}1')_{III}$ 107.4 − $\delta(C\text{-}1')_{I}$ 104.6 = 2.8 ppm]. It is characteristic that the same diamagnetic shift is observed on comparing the ^{13}C NMR spectra of cyclosiversigenin 3,6-di-O-β-D-xylopyranoside and cyclosiversigenin 3-O-(2'-O-acetyl-β-D-xylopyranoside) 6-O-β-D-xylopyranoside [4].

Thus, the upfield shift of the C-1' atom by 2.8 ppm is evidence in favor of the location of the acetyl group at the C-2' carbon atom in cyclosiversioside D (I). In this case, the signal from the C-3' atom of the xylopyranoside residue of compound (I) should also undergo a diamagnetic shift. In actual fact, in the ^{13}C NMR spectrum of cyclosiversioside F (III), the signal from C-3' is located at 78.2 ppm, while in cyclosiversioside D (I) it appears in a stronger field, at 76.1 ppm.

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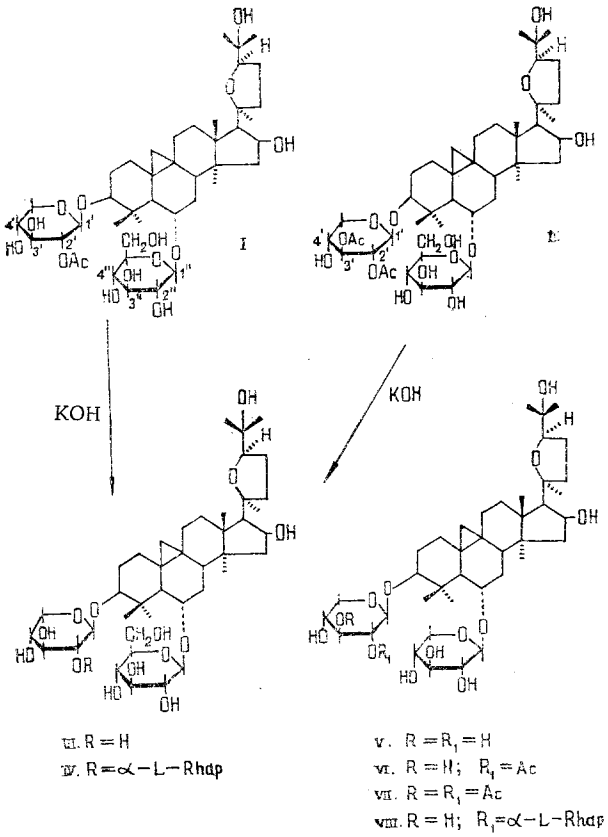

III. R = H
IV. R = α-L-Rhap

V. R = R₁ = H
VI. R = H; R₁ = Ac
VII. R = R₁ = Ac
VIII. R = H; R₁ = α-L-Rhap

The experimental results permit the conclusion that cycloversioside D (I) has the structure of cyclosiversigenin 3-O-(2'-O-acetyl-β-D-xylopyranoside) 6-O-β-D-glucopyranoside.

The molecule of cyclosiversioside B (II) also contains an ester function. Bands at 1760, 1750, and 1260-1250 cm^{-1} in the IR spectrum, and the presence in the PMR spectrum of two three-proton singlets at 1.97 and 2.05 ppm show that cyclosiversioside (II) contains two acetate groups.

The saponification of glycoside (II) with a 0.25% methanolic solution of potassium hydroxide led to cyclosiversioside F (III).

A comparison of the ^{13}C NMR spectra of cyclosiversioside D (I) and B (II) showed that they differ only by the values of the chemical shifts of the signals belonging to the carbon atoms of the xylopyranoside residue. In the spectrum of glycoside (I) the carbon atoms of the xylopyranoside ring are characterized by signals at (ppm): 104.6 (C-1'); 75.4 (C-2'); 76.1 (C-3'); and 71.2 (C-4'). In the case of compound (II) they are characterized by signals at (ppm): 104.0 (C-1'); 73.1 (C-2'); 76.8 (C-3'); and 68.7 (C-4').

It can be seen from these figures that the signal of the C-1 atom in glycoside (II) has undergone an upfield shift by 0.6 ppm. Diamagnetic shifts have also been experienced by the resonance lines of the C-2' and C-4' atoms, amounting to 2.3 and 2.5 ppm, respectively, while the signal of the C-3' atom in the diacetate (II) has been shifted downfield by 0.7 ppm.

These changes caused by the presence of two acetyl groups in the molecule of cyclosiversioside B (II) show, with a high degree of probability, their location on carbon atoms C-2' and C-3'.

Consequently, the bioside (II) is cyclosiversioside 3-O-(2'-3'-di-O-acetyl-β-D-xylopyranoside) 6-O-β-D-glucopyranoside.

This completes our publication of papers on the glycosides of the cycloartane series from the related plants *A. sieversianus* and *A. basineri* belonging to the subgenus *Caprinus* Bge. In the qualitative respect, the compositions of the glycosides of these plants are identical. All the glycosides isolated are derivatives of a single aglycone — cyclosiversigenin [6].

Characteristic for the glycosides of both plants is a bisdesmosidic structure, and, as in the majority of steroid glycosides, one of the sugar residues is attached to the hydroxy group at C-3 while, in the cyclosiversiosides, the other is bound to the hydroxyl at C-6.

The main glycosides in terms of amount and, obviously, the key glycosides are cyclosiversiosides E (V) and F (III). In the case of cyclosiversioside E (V), the hydroxy groups at C-3 and C-6 are glycosylated by D-xylose, while in cyclosiversioside F (III) there is again D-xylose at C-3 hydroxyl but a D-glucose residue substitutes the C-6 hydroxy group.

The other glycosides can be considered as derivatives of the key compounds (III) and (V). In particular, the acetylated glycosides — cyclosiversiosides C and A and cyclosiversiosides B and D, considered in the present paper — have similar structures. To the monoacetate C (VI) corresponds a parallel compound, cyclosiversioside D (I) (a derivative of cyclosiversioside F (III)), and to the diacetate A (VII) corresponds the diacetate B (II).

We can trace the same links in the case of the triglycosides G (IV) and H (VIII). Common to them is the fact that a L-rhamnose residue is attached to the hydroxyl at C-2' of the D-xylose molecule. The difference is in the sugar residue at C-6 of the steroid ring: triglycoside (VIII) belongs to the cyclosiversioside E (V) series, and compound (IV) to the F (III) series.

We have detected no monoglycosides in the plants studied.

EXPERIMENTAL

For general observations, see [6]. PMR spectra were taken in C_5D_5N on a XL-200 instrument (Varian) (δ, 0 — TMS), and ^{13} NMR spectra on a CFT-20 instrument (Varian) in C_5D_5N (0 — TMS).

Isolation of the Glycosides. The air-dried comminuted roots of *A. basineri* (5 kg) gathered at the beginning of the vegetation period (in the environs of Kyzyl-Arvata, Turkm. SSR) were exhaustively extracted with methanol at room temperature. After the methanol had been distilled off, 260 g of total extractive compounds was obtained. Part of the dry residue (60 g) was chromatographed on a column of silica gel using the chloroform—methanol—water (70:22.5:4) system. Rechromatography on silica gel with the same mixture of solvents of the fractions obtained yielded the following compounds: A — 3 g (0.26; yield here and below given on the air-dry raw material); B — 100 g (0.008%); C — 150 mg (0.013%); D — 140 mg (0.012%); E — 4 g (0.35%); F — 5 g (0.43%); G — 800 mg (0.06%); and H — 300 mg (0.02%).

Cyclosiversioside A (VI), $C_{44}H_{70}O_{15}$, mp 230-232°C (from methanol), $[\alpha]_D^{20}$ +24.0 ± 2° (c 0.90; methanol) [4].

Cyclosiversioside B (II), $C_{45}H_{72}O_{16}$, mp 198-200°C (from methanol), $[\alpha]_D^{20}$ +19.7 ± 2° (c 0.88; methanol). ν_{max}^{KBr}, cm^{-1}: 3350-3500 (OH); 1750, 1760, 1250-1260 (ester groups). PMR spectrum (δ, pp,): 0.21 (H at C-19, d, J = 4.4 Hz); 0.56 (H at C-19, d, J = 4.4 Hz), 0.95 (CH_3, s); 1.28 (CH_3, s); 1.31 (2 CH_3, s); 1.42 (CH_3, s); 1.59 (CH_3, s); 1.79 (CH_3, s); 1.97, 2.05 (2 CH_3CO, s).

Cyclosiversioside C (VII), $C_{42}H_{68}O_{14}$, mp 253-255°C (from methanol), $[\alpha]_D^{20}$ +30.0 ± 2° (c 0.90; methanol) [4].

Cyclosiversioside D (I), $C_{43}H_{70}O_{15}$, mp 266-268°C (from methanol), $[\alpha]_D^{22}$ +46.0 ± 2° (c 0.82; methanol). ν_{max}^{KBr}, cm^{-1}: 3300-3500 (OH), 1752, 1250 (ester group). PMR spectrum (δ, ppm: 0.20 (H at C-19, d, J = 4.4 Hz); 0.56 (H at C-19, d, J = 4.4 Hz); 0.95 (CH_3, s); 1.29 (CH_3, s); 1.31 (2 CH_3, s); 1.41 (CH_3, s); 1.59 (CH_3, s); 1.82 (CH_3, s); 2.05 (CH_3CO, s).

Cyclosiversioside E (V), $C_{40}H_{66}O_{13}$, mp 256-258°C (from methanol), $[\alpha]_D^{20}$ +30.0 ± 2° (c 0.70; methanol) [2].

Cyclosiversioside F (III), $C_{41}H_{68}O_{14}$, mp 247-249°C (from methanol), $[\alpha]_D^{20}$ +37.0 ± 2° (c, 0.50; methanol) [3].

Cyclosiversioside G (IV), $C_{46}H_{76}O_{17}$, mp 222-224°C (from methanol), $[\alpha]_D^{20}$ —5.5 ± 2° (c 1.40; methanol) [5].

Cyclosiversioside H (VIII), $C_{47}H_{78}O_{18}$, mp 262-264°C (from methanol), $[\alpha]_D^{20}$ —30.0 ± 2° (c 1.05; methanol) [1].

Alkaline Hydrolysis of Cyclosiversioside D (I). A solution of 65 mg of cyclosiversioside D in 20 ml of methanol was treated with 20 ml of a 0.5% solution of KOH in the same

solvent. The reaction mixture was left at room temperature for 2 days. Then 200 ml of water was added, the methanol was distilled off, and the reaction products were extracted with n-butanol. After the butanolic extract had been washed with water and evaporated to dryness, 20 mg of the glycoside (III) was obtained, with mp 248-249°C (from methanol), $[\alpha]_D^{20}$ + 34.0 ± 2° (c 0.60; methanol), identical with an authentic sample of cyclosiversioside F [3].

Alkaline Hydrolysis of Cyclosiversioside B (II). A solution of 80 mg of cyclosiversioside B in 80 ml of methanol was treated with 80 ml of a 0.5% solution of KOH in the same solvent. The reaction mixture was left at room temperature for 2 days. After a working up procedure similar to that described in the preceding experiment, 37 mg of glycoside (III) was obtained with mp 248-249°C (from methanol), $[\alpha]_D^{22}$ +34.3 ± 2° (c 0.64; methanol), identical with an authentic sample of cyclosiversioside F [3].

SUMMARY

The compositions of the cycloartane glycosides of the plants *Astragalus sieversianus* and *A. basineri* are identical in the qualitative respect. Two new glycosides have been isolated from the roots of *A. basineri* — cyclosiversiosides B and D. It has been shown that cyclosiversioside B is cyclosiversigenin 3-O-(2',3'-di-O-acetyl-β-D-xylopyranoside) 6-O-β-D-glucopyranoside and cyclosiversioside D is cyclosiversigenin 3-O-(2'-O-acetyl-β-D-xylopyranoside) 6-O-β-D-glucopyranoside.

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CATALYTIC REARRANGEMENT OF α-D-GLUCOSE 1,2-ORTHOACETATE DERIVATIVES OF PREGNENOLONE AND 16-DEHYDROPREGNENOLONE

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The rearrangement of pregnenolone and 16-dehydropregnenolone α-D-glucose orthoacetates in the presence of mercuric bromide is, because of the high specific selectivity and satisfactory yields of the desired β-D-glucosides, the most effective method of glycosylating the steroids mentioned.

The glycosylation of steroid alcohols is opening up possibilities both for the creation of convenient water-soluble forms of hormone preparations and for the modification of their biological activities. The known methods of glycosylating the alcohols of the title have, however, a number of deficiencies. Thus the glycosylation of (I) by the Koenigs-Knorre method [1, 2] was accompanied by the formation of a mixture of acetylated α- and β-glucosides, and the trans-glycosylation of (II) by the direct orthoester method [3] was accompanied by considerable amounts of 16-dehydropregnenolone acetate with a low yield of the desired

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