The methanol was driven off from the filtrate and it was heated for another 3 h. The resulting solution was neutralized with $BaCO_3$ and evaporated to dryness. The residue was shown by TLC in system 4 in the presence of markers to contain 2,3,4-tri-O-methyl-D-xylopyranose, 3,4-di-O-methyl-D-glucopyranose, and 2,3,4,6-tetra-O-methyl-D-sorbitol. These results were also confirmed by GLC [5].

SUMMARY

A new triterpene glycoside, copteroside D, has been isolated from the epigeal part of *Climacoptera transoxana* (Iljin) Botsch. and it has been identified as hederagenin 28-O-β-D-glucopyranoside 3-O-[O-β-D-xylopyranosyl-(1 → 2)-β-D-glucuronopyranosiduronic acid].

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TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS.

XII. ASKENDOSIDE B FROM *Astragalus taschkendicus*

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On the basis of chemical transformations and with the aid of physicochemical characteristics it has been established that a new glycoside of the cycloartane series — askendoside B (I) — isolated from the roots of *Astragalus taschkendicus* Bge., is 20S,24R-epoxycycloartane-3β,6α,16β,25-tetraol 3-O-[O-α-L-arabinopyranosyl-(1 → 2)-(3'-O-acetyl-β-D-xylopyranoside)] 6-O-β-D-xylopyranoside, $C_{47}H_{76}O_{18}$, mp 215-218°C, $[\alpha]_D^{20}$ −45.5° (c 1.1; pyridine). The acid hydrolysis of (I) yielded cyclosiversigenin (II) with mp 239-241°C, $[\alpha]_D^{20}$ +54.5° (c 1.2; MeOH), and cyclosiversigenin 3-O-β-D-xylopyranoside (III) with mp 262-264°C, $[\alpha]_D^{20}$ +41° (c 0.4; MeOH). The periodate oxidation of glycoside (I) followed by acid hydrolysis likewise led to (II) and to D-xylose. The alkaline hydrolysis of (I) yielded askendoside D (IV), with mp 235-236°C, $[\alpha]_D^{23}$ −8.5° (c 1.0; pyridine). The Smith degradation of (I) led to (III). The IR and PMR spectra of (I) are given.

We have previously reported the structure of two genins, cycloasgenin A [1] and cycloasgenin C [2] and of two glycosides, askendosides C [3] and D [4] of the cycloartane series isolated from the roots of *Astragalus taschkendicus* Bge. (family Leguminosae). In the present paper we consider the structure of substance D [1], which we have called askendoside B (I). (Formula, top, following page.)

The presence in the PMR spectrum of glycoside (I) of a one-proton doublet at 0.46 ppm permitted this compound to be assigned to the methylsteroids of the cycloartane series [5]. A confirmation of this was the formation of cyclosiversigenin (II) and cyclosiversigenin 3-O-β-D-xylopyranoside (III) when askendoside B (I) was hydrolyzed [4, 6].

The presence in glycoside (I) of D-xylose and L-arabinose residues, in a ratio of 2:1, respectively, was found by TLC and GLC [7].

Absorption bands in the IR spectrum at 1730 and 1260 cm^{-1} show that the substance under consideration contains an ester function. Analysis of its PMR spectrum, having a three-pro-

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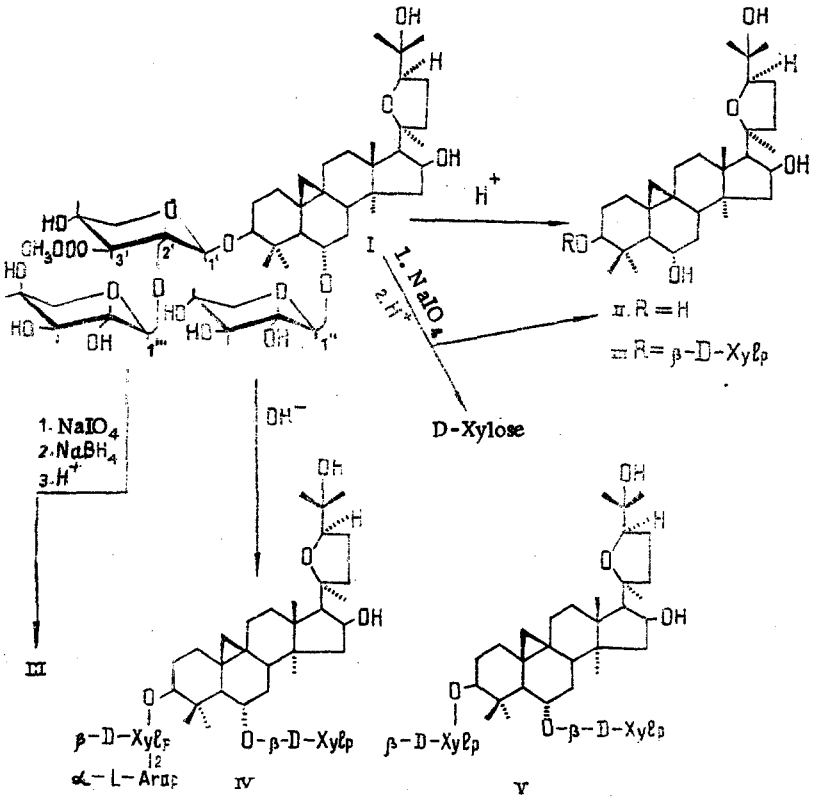

ton singlet at 2.02 ppm, shows the presence in the glycoside (I) molecule of one acetate group. The alkaline hydrolysis of askendoside B led to compound (IV), which was identical with askendoside D [4] according to its physicochemical constants and a comparison of IR and PMR spectra.

In the PMR spectrum of askendoside B, the signal of a proton geminal to an acetyl group appears at 5.50 ppm in the form of a triplet with $\Sigma^3 J$ = 15 Hz. The same spectrum shows resonance lines of the 4.6-4.9 ppm region of three anomeric protons of carbohydrate residues and the signal of a proton geminal to a hydroxy group at C-16 [1, 8]. Consequently, the acetyl group must be attached not to the genin but to the sugar moiety of the molecule.

The periodate oxidation of askendoside B followed by acid hydrolysis led to cyclosiversigenin (II) and D-xylose. The formation of D-xylose shows that the acetyl group is located in one of the two D-xylopyranoside residues of the askendoside B molecule.

The Smith degradation of askendoside B [9] led to the glycoside (III). The latter was identified as cyclosiversigenin 3-O-β-D-xylopyranoside [4, 6] by its physicochemical constants and a comparison of IR spectra.

The formation of glycoside (III) on the Smith degradation of askendoside B in combination with the triplet resonance lines of the proton geminal to the acetate group unambiguously determines the position of the acetyl group at C-3' of the D-xylopyranose residue attached to cyclosiversigenin at C-3. This conclusion was confirmed by a comparative analysis of the ^{13}C NMR spectra of the compound (I) under consideration, askendoside D (IV), and cyclosiversioside E (V) [10].

In the ^{13}C NMR spectra of askendoside B (I) and askendoside D (IV) the signals of the anomeric carbon atoms appear at (the figures for glycoside (IV) are given in parentheses) 103.8 (105.5) ppm – C-1'; 104.9 (105.1) ppm – C-1"; and 105.6 (106.5) ppm – C-1"', while the values of the chemical shifts of the anomeric carbon atoms of the cyclosiversioside E (V) molecule are, as shown previously [11] 107.3 ppm (C-1') and 105.3 ppm (C-1"). It follows from a comparison of these facts that on passing from cyclosiversiode E (V) to the trioside (IV), the C-1' signal undergoes a diamagnetic shift by 1.8 ppm. An additional diamagnetic shift of this signal by 1.7 ppm is observed on passing from askendoside D (IV) to askendoside B (I). Consequently, the total magnitude of the diamagnetic shift of the signal after consideration amounts to 3.5 ppm and can be due only to the influence on the chemical shift of C-1' of the L-arabinopyranose residue and an acetyl group located at C-2' and C-3', respectively, of the askendoside B molecule.

The facts given permit the conclusion that askendoside B has the structure of 20S,24R-epoxycycloartane-3β,6α,16β,25-tetraol 3-O-[O-α-L-arabinopyranosyl-(1 → 2)-(3-O-acetyl-β-D-xylopyranoside)] 6-O-β-D-xylopyranoside.

EXPERIMENTAL

For general observations, see [1, 3]. The following solvent systems were used: 1) chloroform–methanol (15:1); 2) chloroform–methanol (10:1); 3) chloroform–methanol–water (70:23:4); 4) benzene–ethyl acetate (2:1); 5) butanol–methanol–water (5:3:1); and 6) ethyl acetate–acetic acid–water (6:3:2).

The PMR spectra were taken on a JNM-4H-100 spectrometer in deuteropyridine (δ, 0 – HMDS) and the ^{13}C NMR spectra on a Varian CFT-20 instrument in deuteropyridine (δ, 0 – TMS). For the isolation of the isoprenoids of *Astragalus taschkendicus* Bge., see [1, 2].

Askendoside B (I) – substance D [1], $C_{47}H_{76}O_{18}$, mp 215-218°C (from methanol), $[\alpha]_D^{25}$ –45.5 ± 2° (c 1.1; pyridine). ν_{max}^{KBr}, cm^{-1} 3485-3315 (OH), 1730, 1260 (ester group). GLC [7] showed the presence of D-xylose and L-arabinose residues in the askendoside B molecule in a ratio of 1.00:0.56. PMR (C_5D_5N): 0.46 (1 H at C-19, d, ^2J = 4 Hz); 1.01 (3 H, s, CH_3); 1.17 (9 H, s, 3 CH_3); 1.24 (3 H, s, CH_3); 1.47 (6 H, s, 2 CH_3); 2.02 (3 H, s, $OCOCH_3$ at C-3'); 4.6-4.9 (4 H, three anomeric protons and 1 H at C-16); 5.50 ppm (1 H, t, Σ^3J = 15 Hz, H at C-3').

Cyclosiversigenin (II) and Cyclosiversigenin 3-O-β-D-Xylopyranoside (III) from (I). A solution of 213 mg of askendoside B in 50 ml of 0.5% methanolic sulfuric acid was boiled for 1.5 h. Then the reaction mixture was diluted with water to a volume of 200 ml and the methanol was evaporated off. The precipitate that had deposited was filtered off, washed with water, and dried. The residue (97 mg) was chromatographed on a column with elution by system 1. This gave 64 mg of cyclosiversigenin (II) with mp 239-241°C (from methanol), $[\alpha]_D^{20}$ +54.5 ± 2° (c 1.2 methanol), also identified by comparison of its IR and PMR spectra with those of an authentic sample [2, 4, 8].

On the continuing elution of the column with system 2, 30 mg of glycoside (III) was isolated with mp 262-264°C (from methanol), $[\alpha]^{20}$ +41 ± 2° (c 0.4; methanol) which was identified as cyclosiversigenin 3-O-β-D-xylopyranoside [4, 6] likewise from its R_f values in TLC (systems 2 and 3) and the characteristics of its IR spectrum.

Askendoside D (IV) from (I). A solution of 400 mg of potassium hydroxide in 10 ml of methanol was added to 50 mg of askendoside B (I) in 70 ml of methanol, and the mixture was stirred at room temperature for 2 h. Then it was diluted with water to a volume of 200 ml and the methanol was evaporated off. The aqueous solution was neutralized with dilute sulfuric acid and extracted with butanol. The butanolic extract was washed with water and evaporated. The residue after recrystallization from aqueous methanol gave 32 mg of glycoside (IV) with mp 235-236°C, $[\alpha]_D^{23}$ –8.5 ± 2° (c 1.0; pyridine), likewise shown to be identical with askendoside D from its chromatographic mobility on TLC and the features of its PMR and IR spectra [4].

Cyclosiversigenin (II) and D-Xylose from (I). A solution of 200 mg of sodium periodate in 10 ml of water was added to 55 mg of askendoside B in 25 ml of methanol, and the mixture was left at room temperature for 20 days. After this, to decompose the excess of oxidant, 15 ml of water containing 1.5 ml of glycerol was added to the reaction mixture. The reaction products were extracted with chloroform (40 ml). The chloroform extract was washed with water, dried over anhydrous sodium sulfate, and evaporated. The dry residue was dissolved in 10 ml of 0.5% methanolic sulfuric acid and the solution was boiled on the water bath for 3 h. Then it was diluted with water to a volume of 50 ml and the methanol was evaporated off. The precipitate that deposited was filtered off and chromatographed on a column with elution by system 4. This gave 14 mg of cyclosiversigenin (II) with mp 239-241°C (from methanol).

The filtrate after the removal of the precipitate was separated into two aliquot parts. To the first part was added 1 ml of concentrated sulfuric acid and it was boiled on the water bath for 5 h. After cooling, the reaction mixture was neutralized with type ARA-8p anion-exchange resin, and then resin was filtered off. The aqueous solution was evaporated to dryness. The residue was found by TLC in systems 3, 5, and 6 in the presence of an authentic sample to contain D-xylose. The second portion of the filtrate was neutralized with the same

type of anion-exchange resin. After the removal of the resin the aqueous solution was evaporated to dryness. Methyl D-xyloside was detected in the residue by the GLC method.

Smith Degradation of Askendoside D. A solution of 800 mg of sodium periodate in 50 ml of water was added to 210 mg of askendoside B in 100 ml of methanol. The reaction was carried out at room temperature with stirring for 16 h. To decompose the excess of oxidant, 2 ml of ethylene glycol was added to the reaction mixture. Then the solution was diluted with 150 ml of water, the reaction products were extracted with chloroform (200 ml), and the chloroform extract was evaporated to dryness. The residue was dissolved in methanol, and to this solution 800 mg of sodium tetrahydroborate was added in small portions and the mixture was left at room temperature for 3 h. Then 50 ml of a 6% methanolic solution of sulfuric acid was added to it and it was left at the same temperature for another 1.5 h. After this, the reaction mixture was diluted with 2 volumes of water and extracted with chloroform (200 ml). The chloroform extract was washed with water, and the solvent was distilled off. The residue was chromatographed on a column with elution by system 2. This gave 115 mg of glycoside (III) with mp 262-264°C (from methanol), $[\alpha]_D^{29}$ +42 ± 2° (c 0.45; methanol), which was identified as cyclosiversigenin 3-O-β-D-xylopyranoside [4, 6] also on the basis of its chromatographic behavior in TLC (systems 2 and 3) and from the nature of its IR spectrum.

SUMMARY

A new glycoside of the cycloartane series, askendoside B, has been isolated from the roots of the plant *Astragalus taschkendicus* Bge.; it is cyclosiversigenin 3-O-[0-α-L-arabinopyranosyl-(1 → 2)-(3'-O-acetyl-β-D-xylopyranoside)] 6-O-β-D-xylopyranoside.

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