Azurogenin A Diacetate (II) from (I). A solution of 200 mg of genin (I) in 5 ml of pyridine was treated with 2 ml of acetic anhydride, and the reaction mixture was left at room temperature for 96 h. After working up by the generally adopted method and recrystallization of the product from aqueous methanol, 143 mg of the diacetate (II), $C_{31}H_{46}O_8$, was obtained with mp 183-186°C, $[\alpha]_D^{24}$ −90.5 ± 2° (c 0.96; chloroform). ν_{max}^{Nujol} (cm^{-1}): 850, 875, 910>930, 960, 970, 990 [spiroketal chain of the (25R) series]; 1240, 1260, 1730, 1745, (CH_3COO−); 1712 (C=O); 3490 (OH). Mass spectrum, m/z (%): M^+ 546(29), 487(14), 477(10), 474(31), 432(16), 417(6), 372(66), 139(100).

CONCLUSIONS

The combined fruit of the cocultivated Allium suvorovii Rgl. and A. stipitatum Rgl. has yielded a new genin of the spirostan series — anzurogenin A, which is 2α,3β,5β-trihydroxy-(25R)-spirostan-6-one.

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TRITERPENEGLYCOSIDES OF Astragalus AND THEIR GENINS.

XXV. CYCLOCANTHOSIDE D FROM Astragalus tragacantha

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The epigeal part of the plant of Astragalus tragacantha Habl. (Leguminosae) has yielded, together with cyclosieversigenin 3-O-β-D-xylopyranoside, a new glycoside of the cycloartane series — cyclocanthoside D, the structure of which has been established on the basis of chemical transformations and spectral characteristics as 24S-cycloartane-3β,6α,16β,24,25-pentaol 16-O-β-D-glucopyranoside 3-O-β-D-xylopyranoside.

The study of cycloartane derivatives isolated from the epigeal part of the plant Astragalus tragacantha (Leguminosae) [1] has continued. Glycoside 5 has been identified as cyclosieversigenin 3-O-β-D-xylopyranoside [2-4]. In the present paper we consider the structure of glycoside 12, which we have called cyclocanthoside D [(I), scheme].

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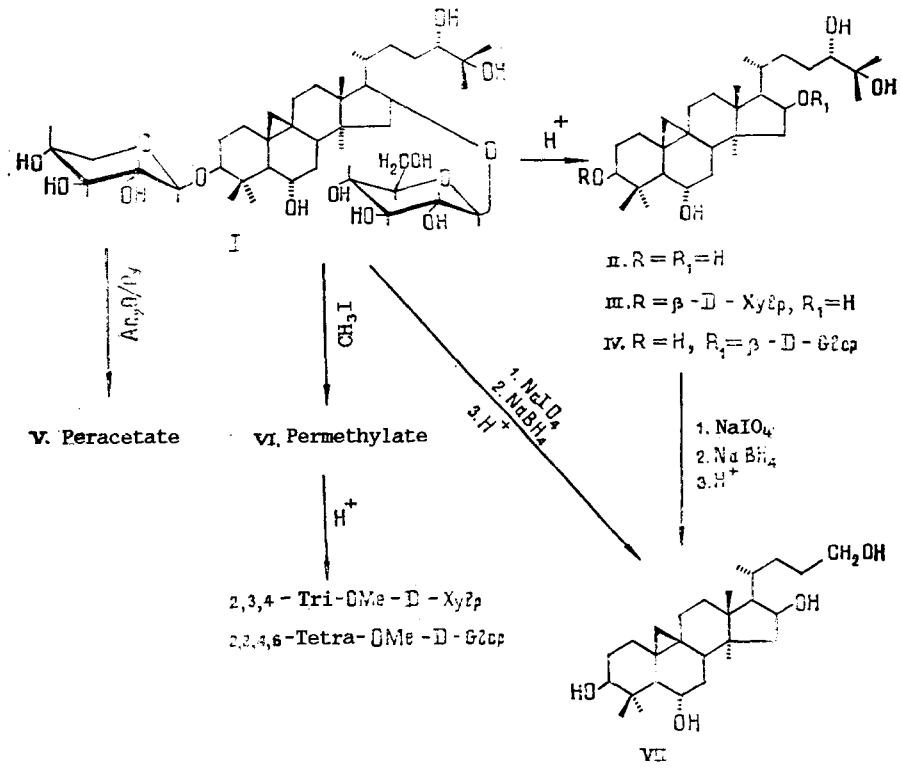

A proof of the structure of cyclocanthogenin (II) which is the genin of glycoside (I) was given in [1]. It was shown with the aid of GLC [5] that cyclocanthoside D contained D-glucose and D-xylose residues in a ratio of 1:1.

The partial hydrolysis of cyclocanthoside D led to the genin (II) and to two progenins (III) and (IV), containing D-xylose and D-glucose residues, respectively. The formation of two progenins showed that bioside (I) was a bisdesmoside.

A study of the product of the methylation of cyclocanthoside D led to a similar conclusion. Glycoside (I) was methylated by Hakomori's method [6]. The deca-O-methyl ether (VI) (M^+ 926) contained, according to GLC [7], residues of 2,3,4-tri-O-methyl-D-xylopyranose and of 2,3,4,6-tetra-O-methyl-D-glucopyranose.

The Smith degradation [8] of glycoside (I) gave the tetraol (VII), which was identified as 25-norcycloartane-3β,6α,16β,24-tetraol [1]. The formation of the tetraol (VII) unambiguously determined the position of one of the monosaccharide residues at C-16 [9]. A similar degradation of progenin (IV) likewise led to the tetraol (VII). Consequently, the D-glucose residue was attached to the hydroxy group at C-16.

Cyclocanthoside D was acetylated with acetic anhydride in pyridine. The PMR spectrum of peracetate (V) (M^+ 1206) showed a one-proton multiplet at 3.18 ppm which was assigned to H-3 [10]. Consequently, the D-xylose residue was present at C-3.

The anomeric protons of the D-glucose and D-xylose residues in the PMR spectra compounds (I) and (III-VI) appeared in the form of doublets with the SSCCs ^3J = 7-8 Hz. This means that the monosaccharide residues had the C1 conformation and the β-configuration of the glycosidic centers [11] (see scheme above).

Thus, cyclocanthoside D is 24S-cycloartane-3β,6α,16β,24,25-pentaol 16-O-β-D-glucopyranoside 3-O-β-D-xylopyranoside.

EXPERIMENTAL

For general observations see [1]. The following solvent systems were used: 1) chloroform–methanol (15:1); 2) chloroform–methanol–water (70:12:1); 3) benzene–acetone (7:1); and 4) benzene–ethyl acetate (5:1).

The conditions for performing GLC have been described in [10].

PMR spectra were taken on a Tesla BS-567 A instrument in deuteropyridine or deuterochloroform (δ, ppm, O-HMDS).

Cyclosieversigenin 3-O-β-D-xylopyranoside (substance 5), mp 263-264°C (from methanol), $[\alpha]_D^{24}$ +42 ± 2° (c 0.6; methanol) [2-4]. Glycoside 5 was also identified from the characteristics of its PMR spectrum.

Cyclocanthoside D (I) – substance 12, $C_{41}H_{70}O_{14}$, mp 290-292°C (from methanol), $[\alpha]_D^{21}$ +9.3 ± 2° (c 0.86; pyridine). ν_{max}^{KBr}, cm^{-1}: 3570-3240 (OH); 3055 (CH_2 of a cyclopropane ring). The methanolysis of 5 mg of glycoside (I) in 2 ml of absolute methanol containing 5% of hydrogen chloride for 12 h followed by the analysis of the methanolysis products by GLC [5] showed the presence of D-glucose and D-xylose in a ratio of 1.00:1.01. PMR spectrum (C_5D_5N): 0.08 and 0.46 (2H-19, d, ^2J = 4 Hz), 0.86 (CH_3, s), 0.96 (CH_3-21, d, ^3J = 6 Hz), 1.22 (CH_3, s), 1.26 (CH_3, s), 1.34 (2 × CH_3, s), 1.84 (CH_3, s), 4.68 and 4.76 (1H each, d, ^3J = 7 and 8 Hz, respectively; anomeric protons).

Partial Hydrolysis of Cyclocanthoside D (I). A mixture of 3 g of cyclocanthoside D and 500 ml of ethanol containing 0.05% of sulfuric acid was heated at 50°C for 30 days. After the usual treatment, the reaction products were chromatographed on a column with elution by system 1. This gave 600 mg of cyclocanthogenin (II), mp 194-195°C (from methanol, $[\alpha]_D^{23}$ +57.5 ± 2° (c 0.87, methanol). Further washing of the column with system 2 led to the isolation of 70 mg of progenin (III) and 450 mg of progenin (IV).

Cyclocanthogenin 3-O-β-D-xylopyranoside (III), $C_{35}H_{60}O_9$, mp 154-155°C (from ethyl acetate), $[\alpha]_D^{20}$ +26.6 ± 2° (c 0.75; methanol); ν_{max}^{KBr}, cm^{-1}: 3550-3300 (OH); 3050 (CH_2 of a cyclopropane ring). According to GLC, glycoside (III) contained one D-xylose residue. PMR spectrum (C_5D_5N): 0.14 and 0.44 (2H-19, ^2J = 4 Hz, 0.90 (CH_3, s), 0.96 (CH_3-21, d, ^3J = 6 Hz), 1.20, 1.26, 1.32, 1.34, 1.84 (each 3H, 5 × CH_3, s), 4.77 (1H, d, ^3J = 8 Hz, anomeric proton of the D-xylopyranose residue).

Cyclocanthogenin 16-O-β-D-glucopyranoside (IV), $C_{36}H_{62}O_{10}$, mp 254-255°C (from ethyl acetate–methanol), $[\alpha]_D^{21}$ +40.6 ± 2° (c 1.27; methanol). ν_{max}^{KBr}, cm^{-1}: 3580-3200 (OH); 3050 (CH_2 of a cyclopropane ring). GLC showed the presence of one D-glucose residue in glycoside (IV). PMR spectrum (C_5D_5N): 0.12 and 0.50 (2H-19, d, ^2J = 4 Hz), 0.83 (CH_3, s), 0.94 (CH_3-21, d, ^3J = 6 Hz), 1.23 (CH_3, s), 1.26 (CH_3, s), 1.32 (2 × CH_3, s), 1.76 (CH_3, s), 4.75 (1H, d, ^3J = 7.5 Hz, anomeric proton of the D-glucopyranose residue).

25-Norcycloartane-3β,6α,16β,24-tetraol (VII) from (I). A solution of 100 mg of cyclocanthoside D in 15 ml of methanol was treated with 200 mg of sodium periodate in 2 ml of water, and the mixture was stirred for 3 h. Then 0.5 ml of ethylene glycol was added to the reaction mixture to decompose the excess of oxidant. The solution was diluted with water, and the product was extracted with chloroform. The residue after the chloroform had been evaporated off was dissolved in 15 ml of methanol. To this solution, 200 mg of sodium tetrahydroborate was added in portions and the mixture was left at room temperature for 1 h. After this, it was acidified by the addition of 5 ml of methanol containing 0.5 ml of sulfuric acid, and was then left at the same temperature for 3 h. The reaction products were poured into a double volume of water and were extracted with chloroform. The chloroform extract was washed with water and evaporated. The residue was chromatographed on a column with elution by system 1. This yielded 40 mg of a product with mp 192-194°C (from ethanol), $[\alpha]_D^{23}$ +43.5 ± 2° (c 0.46; methanol) which was identified as the tetraol (VII) [1] by spectral characteristics, as well.

25-Norcycloartane-3β,6α,16β,24-tetraol (VII) from (IV). Under conditions similar to those described in the preceding experiment, 20 mg of glycoside (IV) was subjected to Smith degradation [8], which led to 7 mg of the tetraol (VII) with mp 191-194°C (from ethanol), $[\alpha]_D^{24}$ +43 ± 2° (c 0.4; methanol) which was identified by the usual means.

Deca-O-methyl Ether (VI) from (I). With constant stirring, 100 mg of sodium hydride was added in portions to a solution of 100 mg of the glycoside (I) in 25 ml of dimethyl sulfoxide. After this, 1 ml of methyl iodide was added to the solution dropwise. The reaction was performed at room temperature for 4 h. Then the reaction mixture was poured into 100 ml of a 2% aqueous sodium hyposulfite solution and was extracted with chloroform. The chloroform extract was washed with water and evaporated. The reaction products were chromatographed on a column with elution by system 3. This gave 60 mg of the methyl ether (VI), $C_{51}H_{90}O_{14}$, mp 148-150°C (from methanol), $[\alpha]_D^{21}$ 0 ± 3° (c 1.0; benzene). ν_{max}^{KBr}, cm^{-1}: 3050 (CH_2 of a cyclopropane ring). M^+ 926. PMR spectrum ($CDCl_3$): 0.18

and 0.46 (2H-19, d, ^2J = 4 Hz), 0.82 (d, CH_3-21), 0.86, 0.92, 1.01, 1.04, 1.10, 1.18 (each 3H, s, 6 × CH_3), 3.11, 3.16, 3.34, 3.40, 3.42 (each 3H, s, 5 × OCH_3), 3.46 (s, 2 × OCH_3), 3.56 (s, 3 × OCH_3), 4.20 and 4.23 (each 1H, d, ^3J = 8 and 7 Hz, respectively, anomeric protons).

Identification of the Methylated Monosaccharides. The methyl ether (VI) (10 mg) was subjected to methanolysis in 3 ml of absolute methanol containing 5% of hydrogen chloride for 12 h, and the products were analyzed with the aid of GLC [7]. The presence of 2,3,4,6-tetra-O-methyl-D-glucopyranose (T_{rel} 1.00, 1.18) and of 2,3,4-tri-O-methyl-D-xylopyranose (T_{rel} 0.38, 0.43) was established.

Cyclocanthoside D Decaacetate (V) from (I). Glycoside (I) (106 mg) was acetylated with 2 ml of acetic anhydride in 2.5 ml of pyridine at room temperature for 15 days. After evaporation of the solvents, the residue was chromatographed on a column with elution by system 4. This yielded 100 mg of the peracetate (V), $C_{61}H_{90}O_{24}$, mp 221-223°C (from methanol), $[\alpha]_D^{21}$ 0 ± 3° (c 1.0, benzene). ν_{max}^{KBr}, cm^{-1}: 3055 (CH_2 of a cyclopropane ring); 1770-1740, 1270-1210 (ester groups). M^+ 1206. PMR spectrum (C_5D_5N): 0.08 and 0.40 (2H-19, d, ^2J = 4 Hz, 0.86-0.95 (3 × CH_3), 1.09, 1.14, 1.44, 1.48 (each 3H, 4 × CH_3, s), 1.85-2.06 (10 × CH_3COO), 3.18 (1H, H-3, m), 4.73 and 4.86 (each 1H, d, ^3J = 7 and 8 Hz, respectively; anomeric protons).

CONCLUSIONS

The epigeal part of the plant Astragalus tragacantha Habl. (Leguminosae) has yielded a new cycloartane glycoside – cyclocanthoside D, which has the structure of 24S-cycloartane-3β,6α,16β,24,25-pentaol 16-O-β-D-glucopyranoside 3-O-β-D-xylopyranoside.

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