

The hydrolysate after the extraction of the aglycone was treated with 1.5 ml of concentrated H₂SO₄ and boiled for 4 h and was then neutralized with BaCO₃. 2,3,4,6-Tetra-O-methyl-D-glucopyranose, 2,3,6-tri-O-methyl-D-galactopyranose, and 4,6-di-O-methyl-D-glucopyranose were identified in the aqueous fraction by TLC (system 4b) in comparison with authentic samples.

SUMMARY

A new steroid glycoside of the spirostan series — eruboside B — has been isolated from a methanolic extract of the inflorescences of *Allium erubescens*; eruboside B is (25R)-5 α -spirostan-3 β ,6 β -diol 3-O-[[O- β -D-glucopyranosyl-(1 \rightarrow 3)]-[O- β -D-glucopyranosyl-(1 \rightarrow 2)]-O- β -D-glucopyranosyl-(1 \rightarrow 4)- β -D-galactopyranoside].

LITERATURE CITED

1. Yu. S. Vollerner, M. B. Gorovits, T. T. Gorovits, and N. K. Abubakirov, *Khim. Prir. Soedin.*, 740 (1978).
2. M. E. Wall, C. R. Eddy, M. L. McClennan, and M. E. Klump, *Anal. Chem.*, 24, 1337 (1952).
3. J. Romo, G. Rosenkranz, and F. Sondheimer, *J. Am. Chem. Soc.*, 76, 5169 (1954).
4. L. I. Eristavi, M. B. Gorovits, and N. K. Abubakirov, *Khim. Prir. Soedin.*, 124 (1973).
5. S. Hakomori, *J. Biochem.*, 55, 205 (1964).
6. T. Okanishi, A. Akahori, and F. Yasuda, *Chem. Pharm. Bull.*, 13, 545 (1965).
7. J. M. Van der Veen, *J. Org. Chem.*, 28, 564 (1963).
8. V. V. Isakov et al., *Khim. Prir. Soedin.*, 78 (1972).
9. N. K. Kochetkov et al., *Chemistry of the Carbohydrates* [in Russian], Moscow (1967), p. 63.
10. C. Sannié, S. Heitz, and H. Lapin. *Compt. Rend.*, 233, 1670 (1951).
11. R. Kuhn, L. Löw, and H. Trischmann, *Chem. Ber.*, 90, 203 (1957).
12. F. Kawasaki et al., *Tetrahedron*, 21, 299 (1965).
13. M. B. Gorovits, A. N. Kel'ginbaev, F. S. Khristulas, and N. K. Abubakirov, *Khim. Prir. Soedin.*, 562 (1973).

STEROID SAPONINS AND SAPOGENINS OF *Allium*.

XVI. TUROSIDE C FROM *Allium turcomanicum*

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From a methanolic extract of the bulbs of *Allium turcomanicum* Rgl. we have isolated a new furostanol glycoside, turoside C (I). An acid hydrolysate was found to contain the aglycone — neoagigenin (II) — and the sugars D-xylose, D-glucose, and D-galactose in a ratio of 1:4:1. The structure of the furostanol (I) has been established by methylation, enzymatic hydrolysis, and oxidative cleavage, and also by the oxidative cleavage of (II), as (25S)-5 α -furostan-2 α ,3 β ,6 β ,22 α ,26-pentaol 26-O- β -D-glucopyranoside 3-O-[[O- β -D-xylopyranosyl-(1 \rightarrow 3)]-[O- β -D-glucopyranosyl-(1 \rightarrow 2)]-O- β -D-glucopyranosyl-(1 \rightarrow 4)- β -D-galactopyranoside].

We have previously reported the isolation from the bulbs of *Allium turcomanicum* Rgl. (family Liliaceae) of a glycoside of the spirostanol series — turoside A — and of turoside A 6-O-benzoate [1, 2]. Continuing the study of the steroid components of this plant, we have isolated from a methanolic extract of the bulbs a new furostanol glycoside, turoside C (Ia).

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The repeated chromatographic purification of the total extractive substances led to a mixture of two compounds (Ia) and (Ib). The substances isolated gave a positive Ehrlich color reaction [3, 4] and on chromatography in a thin layer of silica gel (system 2) they had similar R_f values [Ia) 0.28; Ib) 0.30]. The IR spectrum of the mixture of glycosides (Ia) and (Ib) had no frequencies characteristic for spirostan saponins [5, 6] but had a weak broadened band at 900 cm^{-1} . All these properties are indicative for furostanol compounds [7].

It is known [7] that on contact with methanol furostanol glycosides form 22-O-methyl ethers which in an aqueous medium readily undergo the reverse change. By boiling the mixture of substances (Ia) and (Ib) in methanol we obtained compound (Ib), and heating aqueous solutions of the same mixture gave the pure glycoside (Ia). The PMR spectrum of compound (Ib) had a three-proton signal of a 22-methoxy group at 3.11 ppm [8], which was absent from the PMR spectrum of glycoside (Ia). Thus, the more polar compound (Ia) is the native glycoside and substance (Ib) is its 22-O-methyl ether.

Since compounds (Ia) and (Ib) are very readily converted into one another, subsequent operations were mainly performed with a mixture [the substance (Ia/Ib)] without the isolation of the individual components.

The acid hydrolysis of (Ia/Ib) gave neoagigenin (II) [19], and the hydrolysate was found by the GLC method [10, 11] to contain D-galactose, D-glucose, and D-xylose in a ratio of 1:4:1.

The enzymatic hydrolysis of (Ia/Ib) with the aid of the complex enzyme of the snail *Helix plectotropis* [12] led to the spirostanol glycosides (III) and (IV). From its physico-chemical constants and GLC behavior, glycoside (III) was identified as furoside A [1]. Compound (IV), which was isolated in low yield, proved to be a neoagigenin pentaoside. It is not excluded that this glycoside will be found in the plant in the native form, and we have therefore called it turoside B.

According to GLC, the glycoside (IV) contained D-xylose, D-glucose, and D-galactose in a ratio of 1:3:1, i.e., substance (IV) has one glucose residue less than turoside C. Consequently, turoside C is a hexaoside, one glucose residue being present at C-26 and the other five sugar residues being attached to the steroid part of the molecule.

The Hakomori methylation [13] of the glycosides (Ia/Ib) and of the pentaoside (IV) gave the permethylates (V) and (VI), the hydrolysis of which yielded the same set of methylated sugars: 2,3,4,6-tetra-O-methyl-D-glucopyranose, 2,3,4-tri-O-methyl-D-xylopyranose, 2,3,6-tri-O-methyl-D-galactopyranose, 3,4,6-tri-O-methyl-D-glucopyranose, and 4,6-di-O-methyl-D-glucopyranose.

2,6-Di-O-methylneoagigenin (VII) was also identified in the products of the hydrolysis of the permethylates (V) and (VI) [1]. Thus, in turoside C (Ia) and the pentaoside (IV) a carbohydrate chain containing five monosaccharide residues is attached to the hydroxy group at C-3 of the aglycone. The order of linkage of four of them is determined by the fact that when (Ia/Ib) were subjected to fermentation, the previously described [1] turoside A (III) was identified, and this contained the known tetrasaccharide lycotetraose [1, 14-21]. The detection of 3,4,6-tri-O-methyl-D-glucopyranose among the methylated sugars shows that the third, additional, glucose molecule is attached to the hydroxy group at the second carbon atom of the terminal glucose of lycotetraose.

A calculation of molecular rotation differences [22] showed the β -configurations of all the glycosidic bonds.

The fact that turoside C belongs to the group of furostanol glycosides was also shown by its conversion into pregnenolone (XIII) and into the acetate of the methyl hydroxy(methyl)-valerate glucoside (XI) [7]. For this purpose, substance (Ia/Ib) was acetylated to give the acetate (VIII), which was converted by boiling in acetic acid into the pseudosaponin (IX) [23]. Oxidation of compound (IX) [24] followed by saponification led to the pregnene glycoside (X) and to the glucoside of δ -hydroxy- γ -methylvaleric acid (XII). D-Glucose was detected in a hydrolysate of substance (XII) by GLC and TLC. Without being isolated in the pure form, glycoside (XII) was subjected to acetylation and methylation. This gave the tetraacetate of the glucoside of methyl δ -hydroxy- γ -methylvalerate (XI), which was identified by its mass spectrum [7].

Hydrolysis of the glycoside (X) gave compound (XIII) for which, on the basis of spectral characteristics, the structure of $2\alpha,3\beta,6\beta$ -trihydroxy- 5α -pregn-16-en-20-one is sug-

gested. D-Xylose, D-glucose, and D-galactose were detected in the hydrolysate in a ratio of 1:3:1 (GLC).

To confirm the structure of the pregnenolene (XIII), neoagigenin (II) was subjected to oxidative cleavage. The opening of the side chain of the sapogenin (II), performed in the presence of pyridine hydrochloride [25] with subsequent oxidation and hydration of the ester grouping at C-16, gave 2 α ,3 β ,6 β -trihydroxy-5 α -pregn-16-en-20-one 2,3,6-triacetate (XIV). The constants and special characteristics of the saponification product of the acetate (XIV) agreed completely with those for compound (XIII) obtained in the oxidation degradation of turoside C.

Turoside C has the structure corresponding to formula (Ia).

EXPERIMENTAL

General Observations. For thin-layer chromatography (TLC) we used type KSK silica gel (<56 μ) containing 7% of gypsum. Column chromatography was performed on silica gel of the same type (100 > SiO₂ > 56 μ). The following solvent systems were used: 1) chloroform-methanol-water (65:35:8); 2) chloroform-methanol-water (70:50:10); 3) benzene-acetone (3:1); 4) chloroform-methanol (12:1); and 5) benzene-acetone (50:1).

The glycosides were detected with the Sannié [26] and Ehrlich [3] reagents, the sugars and their derivatives with o-toluidine salicylate, and the other compounds with iodine and with concentrated sulfuric acid.

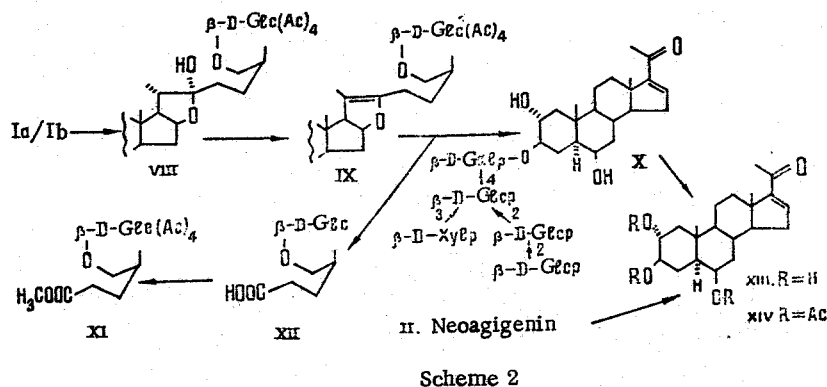
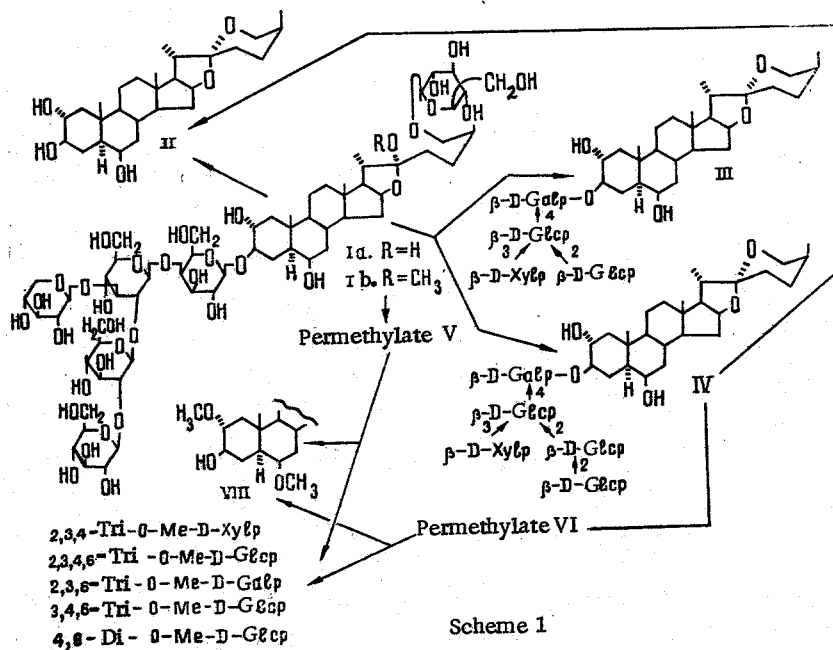
Gas-liquid chromatography (GLC) was performed on a Tsvet-4 chromatography. The mono-saccharides were analyzed in the form of the trimethylsilyl derivatives of the methyl glycosides [10, 11] using a column (3 m \times 4 mm) filled with 5% of the silicone phase SE-30 on Chromaton N-AW; the thermostat temperature was 190°C and the carrier gas here and below was helium at a rate of flow of 45 ml/min. The methyl glycosides obtained by boiling the methyl ethers of the sugars in 5% methanolic HCl (4 h) were chromatographed on a column (1 m \times 4 mm) containing 20% of poly(butane-1,4-diyl succinate) on Celite (phase 1, thermostat temperature 160°C, rate of flow of helium 50 ml/min) or 10% of poly(phenyl ether) on Chromaton N-AW (phase 2, thermostat temperature 180°C, rate of flow of helium 50 ml/min). The retention times (T_{rel}) for the methylated methyl glycosides were calculated in relation to the retention time of methyl 2,3,4,6-tetra-O-methyl- β -D-glucopyranoside [27].

Mass spectra were obtained on a MKh-1303 instrument fitted with a system for the direct introduction of the substance into the ion source and on a MKh-1310 instrument. IR spectra were recorded on a UR-20 spectrometer in KBr or paraffin oil, and PMR spectra were recorded on a JNM-4H-100 (100 MHz) instrument in CDCl₃ or C₅D₅N with HMDS as internal standard (δ scale).

Turoside C (Ia) and Its Methyl Ether (Ib). The sum (150 g) of the extractive substances from the bulbs of *Allium turcomanicum* (for isolation see [1]) was separated by column chromatography using system 1 as eluent. The fractions containing glycosides more polar than turoside A were collected. In this way, 58 g of a resinous mass was obtained the components of which were rechromatographed with system 2 as eluent. The fractions containing a mixture of glycosides (Ia) and (Ib) were dissolved in methanol, and the saponins were precipitated with acetone and rechromatographed on a column (eluent - system 2). This procedure was repeated five times. As a result, 7 g (yield 0.66% calculated on the air-dry raw material) of substance (Ia/Ib) was obtained, which gave two spots in system 2. The glycosides isolated were colored by the Ehrlich and Sannié reagents red and greenish yellow, respectively.

A mixture of 100 mg of saponins (Ia/Ib) and 10 ml of water was boiled for 5 h. Then 100 ml of acetone was added to the cooled solution and the resulting precipitate was filtered off. This gave 75 mg of turoside C (Ia), C₆₃H₁₀₄O₃₅, mp 192-196°C, $[\alpha]_D^{22}$ -69.5 \pm 3° (c 0.46; chloroform-methanol (1:1)); ν_{max}^{KBr} , cm⁻¹: 3300-3500 (OH) and a weak broadened band at 900 cm⁻¹. There was no absorption characteristic for spirostan compounds. In the PMR spectrum there were no signals of protons of methoxy groups.

A mixture of 100 mg of substance (Ia/Ib) and 10 ml of methanol was boiled for 5 h. Part of the methanol was evaporated off and the residual solution was treated with 100 ml of acetone. The precipitate that deposited was filtered off, giving 85 mg of the 22-O-methyl ether of turoside C (Ib), C₅₃H₁₀₆O₃₅, mp 179-182°C, $[\alpha]_D^{22}$ -75.2 \pm 3° (c 0.54; chloroform-methanol (1:1)). PMR spectrum (C₅D₅N, δ , ppm): 3.11 (22-OCH₃, s).



Acid Hydrolysis of the Glycosides (Ia/Ib). A solution of 200 mg of (Ia/Ib) in 70 ml of 50% aqueous methanol containing 6% of HCl was heated at 100°C for 6 h. Then the hydrolysate was diluted with water (500 ml) and the precipitate that deposited after the methanol had been evaporated off was filtered off. Recrystallization of the precipitate from methanol gave 25 mg of neoagigenin (II), $C_{27}H_{44}O_5$, mp 267–268°C, $[\alpha]_D^{20} -71.8 \pm 3^\circ$ (c 0.98; chloroform-methanol (10:1)); ν_{max}^{KBr} , cm^{-1} : 3300–3500 (OH), 855, 900<930, 990 (spiroketal chain of the 25S series); M^+ 448 [1, 9].

D-Xylose, D-glucose, and D-galactose were found in the hydrolysate in a ratio of 1.0:4.0:1.0 (GLC).

Enzymatic Hydrolysis of the Glycosides (Ia/Ib). A solution of 2.0 g of substance (Ia/Ib) in 100 ml of water was treated with 25 ml of a complex enzyme of the snail *Helix plectotropis* (for preparation, see [12]) and the mixture was left at room temperature. The course of the reaction was monitored by TLC in system 1. After 48 h, the reaction mixture was extracted with butanol, and the extract was evaporated. The total material so obtained (1.6 g) was separated by column chromatography using system 1 as eluent. This gave 1.35 g of turoside A (III), $C_{50}H_{82}O_{24}$, mp 278–280°C (from methanol), $[\alpha]_D^{20} -61.3 \pm 3^\circ$ (c 0.92; chloroform-methanol (10:1)); ν_{max}^{KBr} , cm^{-1} : 3200–3500 (OH), 855, 900, 925, 990 (spiroketal chain) [1]. The further elution of the column with the same system gave 70 mg of the neoagigenin pentaoside (IV), $C_{56}H_{92}O_{29}$, mp 261–263°C (from methanol), $[\alpha]_D^{20} -67.5 \pm 3^\circ$ (c 0.36; chloroform-methanol (10:1)); ν_{max}^{KBr} , cm^{-1} : 3200–3600 (OH), 860, 900, 925, 990 (spiroketal chain).

The hydrolysis of the neoagigenin pentaoside (IV) (15 mg) and the treatment of the reaction mixture were performed as described above for the glycosides (Ia) and (Ib). This

gave 3 mg of neoagigenin (II) with mp 265-267°C (methanol), $[\alpha]_D^{20} -69.8 \pm 3^\circ$ (c 0.21; chloroform-methanol (10:1)). The hydrolysate of the glycoside (IV) was found by GLC to contain D-xylose, D-glucose, and D-galactose in a ratio of 0.98:3.00:0.90.

Methylation of Substance (Ia/Ib) and the Pentaoside (IV). A solution of 800 mg of the glycosides (Ia/Ib) in 50 ml of dimethylformamide was treated with 700 mg of sodium hydride, and the mixture was stirred at room temperature for an hour. Then 10 ml of methyl iodide was added in drops and the mixture was stirred for another 4 h, after which it was poured into water (500 ml) and extracted with chloroform. The extract was treated with sodium thiosulfate, washed with water, and dried over anhydrous sodium sulfate. After the solvent had been distilled off, the residue was methylated in the same way twice more. The reaction products were separated by column chromatography using system 3 as eluent. This gave 550 mg of the amorphous permethylate (V) with $[\alpha]_D^{20} -91.7 \pm 3^\circ$ (c 0.92; chloroform). The IR spectrum of this compound lacked absorption in the region of hydroxy groups.

The methylation of 50 mg of the pentaoside (IV) in the same way yielded 24 mg of the permethylate (VI), $[\alpha]_D^{20} -87.5 \pm 3^\circ$ (c 0.62; chloroform). Again, absorption characteristic for hydroxy groups was absent from the IR spectrum of this compound.

Hydrolysis of the Permethylates (V) and (VI). A solution of 500 mg of the permethylate (V) in 50 ml of 60% aqueous methanol containing 5% of H_2SO_4 was heated on the water bath for 7 h. After dilution with water (200 ml) and evaporation of the methanol, the precipitate that had deposited was filtered off. Recrystallization from acetone yielded 18 mg of neoagigenin 2,6-dimethyl ether (VII), $C_{29}H_{48}O_5$, mp 180-181°C, $[\alpha]_D^{22} -108.0 \pm 3^\circ$ (c 0.92; chloroform); ν_{max}^{KBr} , cm^{-1} : 3400-3500 (OH), 855, 900<925, 990 (spiroketal chain of the 25S series); M^+ 476 [1].

The hydrolysis of 20 mg of permethylate (VI) was performed similarly, and the presence of the ether (VII) in the hydrolysis products was likewise established by TLC in system 3.

Separation of the Methylated Sugars. The hydrolyzate of the permethylate (V) after the elimination of the aglycone (VII) and the addition of 5 ml of H_2SO_4 was boiled on the water bath for 5 h. Then the reaction mixture was neutralized with the aid of $BaCO_3$, the precipitate was filtered off, and the filtrate was evaporated to dryness. The residue (220 mg) was separated by column chromatography with elution by system 4. This gave five fractions containing individual methylated carbohydrates. Intermediate fractions proved to be mixtures of them. The methylated sugars were identified with the aid of TLC (system 4) and GLC in comparison with authentic samples obtained in previous work [1, 21].

Below we give the retention times (T_{rel}) of the methylated sugars isolated:

- 2,3,4-Tri-O-methyl-D-xylopyranose, T_{rel} 0.45, 0.56 (phase 1); 0.42, 0.52 (phase 2);
- 2,3,4,6-Tetra-O-methyl-D-glucopyranose, T_{rel} 1.00, 1.46 (phase 1); 1.00, 1.40 (phase 2);
- 2,3,6-Tri-O-methyl-D-galactopyranose, T_{rel} 3.24, 3.72, 4.18, 5.05 (phase 1); 1.63, 2.14, 2.29, 2.63 (phase 2);
- 3,4,6-Tri-O-methyl-D-glucopyranose, T_{rel} 3.13, 3.73 (phase 1); 1.79, 2.40 (phase 2);
- 4,6-Di-O-methyl-D-glucopyranose, T_{rel} 2.54 — main peak; 2.66 — shoulder (phase 2).

These results and also the intensities of the GLC peaks coincided with the corresponding indices of authentic samples.

The TLC (system 4) of the hydrolysate of the permethylate (VI) showed the presence of the same methylated sugars.

Heneicosacetate VIII (from (Ia/Ib)). A solution of 1.6 g of the mixture of glycosides (Ia) and (Ib) in 30 ml of pyridine was treated with 30 ml of acetic anhydride. After the reaction mixture had been left to stand at room temperature for 48 h it was poured into ice water, and the precipitate that deposited was filtered off. Its recrystallization from a mixture of ethanol and water gave 1.4 g of the acetate (VIII), $C_{104}H_{146}O_{56}$, mp 136-138°C, $[\alpha]_D^{22} -91.6 \pm 3^\circ$ (c 0.46; chloroform), ν_{max}^{KBr} , cm^{-1} : 3300 (OH), 1750 (C=O of an acetyl group), 910.

Oxidative Cleavage of the Acetate (VIII). A solution of 1.3 g of the acetate (VIII) in 20 ml of acetic anhydride was heated at 120°C for one hour. After cooling 3 ml of water was added and the reaction mixture was evaporated to dryness. The pseudosaponin (X) so obtained

(1.2 g) was dissolved in 15 ml of acetic acid, and then 250 mg of sodium acetate was added and the solution was cooled to 12°C. With stirring, a solution of 600 mg of CrO₃ in 5 ml of 40% acetic acid was added dropwise over 15 min. The mixture was left overnight at room temperature and then the oxidizing agent was destroyed by the addition of methanol. After this, the reaction mixture was diluted with water (50 ml) and extracted with chloroform. The extract was washed with sodium sulfite and with water and was dried over anhydrous sodium sulfate and evaporated. The syrup so obtained was dissolved in 45 ml of tert-butanol and the solution was treated with 2 g of KOH in 3 ml of water. Saponification was carried out at room temperature with stirring for 3.5 h. The contents of the vessel were diluted with water (50 ml), the solvent was distilled off, and the residue was extracted with butanol. The mixture separated into two phases: aqueous (phase A) and butanolic (phase B).

Tetraacetate of the Glucoside of Methyl δ-Hydroxy-γ-methylvalerate (XI). Phase A was acidified to pH 3, was extracted once each with chloroform and butanol, neutralized with 2 N NaOH, and evaporated to dryness. GLC showed the presence of D-glucose in the amorphous residue (XII). Part of product (XII) (140 mg) was acetylated in 3 ml of pyridine and 3 ml of acetic acid at room temperature for 24 h. The reaction products were poured into ice water and filtered off. The precipitate was dissolved in 3 ml of methanol and was methylated with diazomethane. The methyl ether was purified by column chromatography using system 5 for elution. This gave 8 mg of the chromatographically pure syrupy compound (XI) the mass spectrum of which had peaks characteristic for glucose tetraacetate with m/e 331, 243, 242, 200, 169, 157, 141, 140, 115, 109, 105, and 98 [28, 29], and ions with m/e 129 and 97 corresponding to the decomposition of the aglycone part of the tetraacetate of the glucoside of methyl δ-hydroxy-γ-methylvalerate [7].

2α,3β,6β-Trihydroxy-5α-pregn-16-en-20-one 3-O-β-pentaoside (X). The butanolic extract (phase B) was evaporated and chromatographed on a column using system 1 as eluent. This yielded 150 mg of glycoside (X), C₅₀H₈₀O₂₈, mp 225-227°C (from methanol), [α]_D²² -57.8 ± 3° (c 1.12; methanol); ν_{max}^{KBr}, cm⁻¹: 3300-3600 (OH), 1660, 1595 (Δ¹⁶-20-keto grouping) [30]; λ_{max}^{C₂H₅OH} 239 nm (log ε 3.84).

2α,3β,6β-Trihydroxy-5α-pregn-16-en-20-one (XIII) from (X). Glycoside (X) (130 mg) was heated at 80°C in a mixture of 15 ml of 2 N HCl and 10 ml of benzene for 3 h. After cooling, the reaction mixture separated into two layers. GLC showed the presence of the aqueous fraction of the hydrolysate of D-xylose, D-glucose, and D-galactose in a ratio of 1.02:3.00:1.02. The benzene layer was washed with water and evaporated in vacuum. Recrystallization of the residue obtained from methanol gave 12 mg of compound (XIII), C₂₁H₃₂O₄, mp 190-192°C, [α]_D²² -50.0 ± 3° (c 0.36; chloroform); ν_{max}^{KBr}, cm⁻¹: 3300-3500 (OH), 1665, 1590 (Δ¹⁶-20-keto grouping); λ_{max}^{C₂H₅OH} 239 nm (log ε 3.97); M⁺ 348.

2α,3β,6β-Triacetoxy-5α-pregn-16-en-20-one (XIV) from (II). A solution of 800 mg of neogigenin (II) and 600 mg of pyridine hydrochloride in 10 ml of acetic anhydride was boiled for 4 h. The resulting pseudosapogenin acetate was treated with a solution of 700 mg of chromium trioxide in 7 ml of 90% acetic acid, and the mixture was left at room temperature for 4 h. Then 700 mg of sodium bisulfite and 1.0 g of sodium acetate in 5 ml of water were added and the reaction mixture was boiled for one hour. After this, it was poured into ice water and extracted with chloroform. The chloroform solution was washed with dilute sulfuric acid and with water to neutrality, and was dried over anhydrous Na₂SO₄. After the solvent has been distilled off, 340 mg of compound (XIV) was obtained, C₂₇H₃₈O₇, mp 238-240°C (from methanol), [α]_D²² -66.6 ± 3° (c 0.34; chloroform); ν_{max}^{KBr}, cm⁻¹: 1740 (C=O of an acetyl group), 1660, 1590 (Δ¹⁶-20-keto grouping); λ_{max}^{C₂H₅OH}: 239 nm (log ε 4.10). PMR spectrum (CDCl₃, δ, ppm): 0.86 (3H at C-18, s), 1.08 (3H at C-19, s), 1.90, 1.92, 1.96 (3 × OAc at C-2, C-3, and C-6, s), 4.93 (3 H at C-2, C-3, and C-6, m), 6.62 (H at C-16, d, J = 4 Hz); M⁺ 474.

The saponification of 100 mg of the acetate (IV) with a 2% solution of KOH in tert-butanol (5 ml) at room temperature for 24 h led to the formation of 8 mg of a compound with mp 192-194°C (methanol), [α]_D²² -52.6 ± 3° (c 0.24; chloroform); ν_{max}^{KBr}, cm⁻¹: 3300-3500 (OH), 1665, 1590 (Δ¹⁶-20-keto grouping); M⁺ 348. According to the constants given and its R_f value in TLC (system 4), this substance was identical with the 2α,3β,6β-trihydroxy-5α-pregn-16-en-20-one (XIII) obtained from the pentaoside (X).

SUMMARY

From a methanolic extract of the bulbs of *Allium turcomanicum* Rgl. a new furostanol glycoside has been isolated - turoside C, which is (25S)-5α-furostan-2α,3β,6β,22α,26-pentaol

26-O-β-D-glucopyranoside 3-O-[[O-β-D-xylopyranosyl-(1→3)]-[O-β-D-glucopyranosyl-(1→2)-O-β-D-glucopyranosyl-(1→2)]-O-β-D-glucopyranosyl-(1→4)-β-D-galactopyranoside].

LITERATURE CITED

1. G. V. Pirtskhaleva, M. B. Gorovits, T. T. Gorovits, and N. K. Abubakirov, *Khim. Prir. Soedin.*, 355 (1978).
2. G. V. Pirtskhalava, M. B. Gorovits, and N. K. Abubakirov, *Khim. Prir. Soedin.*, 532 (1978).
3. E. Stahl, *Thin-Layer Chromatography*, first ed., Allen and Unwin, London (1969).
4. S. Kijosawa, M. Huton, T. Komori, T. Nohara, J. Hosokawa, and T. Kawasaki, *Chem. Pharm. Bull.*, 16, 1162 (1968).
5. M. E. Wall, C. R. Eddy, M. L. MacClennan, and M. E. Klumpp, *Anal. Chem.*, 24, 1337 (1952).
6. C. R. Eddy, M. E. Wall, and M. K. Scott, *Anal. Chem.*, 25, 266 (1953).
7. R. Tschesche, G. Ludke, and G. Wulff, *Chem. Ber.*, 102, 1253 (1969).
8. T. Kawasaki, T. Komori, K. Mijahara, T. Nohara, J. Hosokawa, and K. Mihashi, *Chem. Pharm. Bull.*, 22, 2164 (1974).
9. A. N. Kel'ginbaev, M. B. Gorovits, and N. K. Abubakirov, *Khim. Prir. Soedin.*, 801 (1974).
10. G. Wulff, *J. Chromatogr.*, 18, 285 (1965).
11. T. T. Gorovits, *Khim. Prir. Soedin.*, 263 (1970).
12. N. K. Abubakirov, V. A. Maslennikova, and M. B. Gorovits, *Zh. Obshch. Khim.*, 29, 1235 (1959).
13. S. Hakomori, *J. Biochem.*, 55, 205 (1964).
14. R. Kuhn, J. Low, and H. Trischmann, *Chem. Ber.*, 90, 203 (1957).
15. T. Kawasaki, J. Nishioka, T. Komori, T. Yamauchi, and K. Mijahara, *Tetrahedron*, 21, 299 (1965).
16. T. Kawasaki and J. Nishioka, *Chem. Pharm. Bull.*, 12, 1311 (1964).
17. K. Mijahara, Y. Ida, and T. Kawasaki, *Chem. Pharm. Bull.*, 20, 2506 (1972).
18. Y. Mori and T. Kawasaki, *Chem. Pharm. Bull.*, 21, 244 (1973).
19. R. Tschesche, A. M. Jawellana, and G. Wulff, *Chem. Ber.*, 107, 2828 (1974).
20. A. N. Kel'ginbaev, M. B. Gorovits, T. T. Gorovits, and N. K. Abubakirov, *Khim. Prir. Soedin.*, 480 (1976).
21. Yu. S. Vollerner, M. B. Gorovits, T. T. Gorovits, and N. K. Abubakirov, *Khim. Prir. Soedin.*, 740 (1978).
22. W. Klyne, *Biochem. J.*, 47, xli (1950).
23. H. Hirschmann and F. B. Hirschmann, *Tetrahedron*, 3, 243 (1958).
24. M. E. Wall, H. E. Kenny, and E. S. Rothmann, *J. Am. Chem. Soc.*, 77, 5665 (1955).
25. W. G. Dauben and G. J. Fonken, *J. Am. Chem. Soc.*, 76, 4619 (1954).
26. C. Sannié, S. Heitz, and H. Lapin, *Compt. Rend.*, 233, 1670 (1951).
27. A. O. Aspinall, *J. Chem. Soc.*, 1676 (1963).
28. K. Heyns and H. Scharmann, *Ann. Chem.*, 667, 183 (1963).
29. K. Beimann, D. C. de Jong and H. K. Schnoes, *J. Am. Chem. Soc.*, 85, 1763 (1963).
30. R. N. Jones, P. Humphries, and K. Dobriner, *J. Am. Chem. Soc.*, 71, 241 (1949).