methanol). When 50 mg of this substance was hydrolyzed with 6% sulfuric acid at 100°C for 7 h, D-glucuronic acid and D-xylose were detected by TLC in system 6.

The Permethylate (IX) from Copteroside H (VIII). The glycoside (200 mg) was methylated by Hakomori's method (40 ml of dimethyl sulfoxide, 150 mg of sodium hydride, and 4 ml of CH_3I). This gave 145 mg of the permethylate (IX) in amorphous form, $C_{58}H_{94}O_{20}$, $[\alpha]_D^{20}$ +10 ± 2° (c 0.5; methanol). Mass spectrum, m/z (%): M^+ 1110 (0.02), 846 (16.6), 701 (0.6), 483 (41.6), 393 (0.4), 248 (30.5), 219 (25.0), 175 (91.6), 101 (100.0).

Reductive Cleavage of the Permethylate (IX). Compound (IX) (100 mg) was reduced with lithium tetrahydroaluminate (80 mg) by the usual procedure. The product of the reaction was hydrolyzed with a 6% solution of sulfuric acid in methanol. According to TLC in system 4, the sugar fraction consisted of 2,3,4,6-tetra-O-methyl-D-sorbitol, 2,3,4-tri-O-methyl-D-xylose, and 3,4-di-O-methyl-D-glucose. The last-mentioned methylated sugar was also identified with the aid of GLC [7], and its reaction for an α-diol group was positive.

The genin of the reduced product was characterized as 23,28-dihydroxy-β-amyrin (XI), mp 198-200°C (hexane—acetone (10:2)) mass spectrum, m/z (%): M^+ 458 (3.0), 234 (40.0), 223 (5.0), 216 (25.0), 203 (100.0).

SUMMARY

From the epigeal part of *Climacoptera transoxana* (Iljin). Botsch. have been isolated two new triterpene glycosides — copterosides G and H, which are bisdesmosidic glycosides.

Copteroside G had the structure of gypsogenic acid 28-O-β-D-glucopyranoside 3-O-β-D-glucuronopyranoside, and copteroside H is gypsogenic acid 28-O-β-D-glucopyranoside 3-O-[O-β-D-xylopyranosyl-(1 → 2)-β-D-glucuronopyranoside].

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TRITERPENE GLYCOSIDES OF *Salsola micranthera*.

II. THE STRUCTURE OF SALSOLOSIDE E

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A new triterpene glycoside — salsoloside E — has been isolated from the epigeal part of the plant *Salsola micranthera* Botsch. family Chenopodiaceae. On the basis of chemical transformations and physicochemical characteristics its structure has been established as oleanolic acid 28-O-β-D-glucopyranoside 3-O-{[O-β-D-glucopyranosyl-(1 → 2)][O-β-D-xylopyranosyl-(1 → 4)]-β-D-glucuronopyranoside}.

From the combined glycosides of the epigeal part of *Salsola micranthera* Botsch. (family Chenopodiaceae) we have isolated an individual glycoside — salsoloside E (I) [1]. This is quantitatively the main glycoside of the plant. Gas—liquid chromatography [2] showed the presence in the sugar moiety of salsoloside E of D-glucuronic acid, D-glucose, and D-xylose residues in a ratio of 1:2:1. The aglycone of the new compound is oleanolic acid (II). In an acid hydrolysate of compound (V) obtained by the alkaline saponification of glycoside E, the same monosaccharides were detected with the aid of PC and TLC.

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The progenin (V) was methylated by Hakomori's method [3]. The resulting permethylate (VI) (M^+ 1066), on hydrolysis by sulfuric acid, gave 2,3,4-tri-O-methyl-D-xylose, 2,3,4,6-tetra-O-methyl-D-glucose, and a monomethyl derivative of D-glucuronic acid. In the genin fraction, methyl oleanolate (VII) was identified. Glycoside E itself was also methylated. In a hydrolysate of the product of the reduction of the permethylate (III) (M^+ 1270), in addition to 1,3,4-tri-O-methyl-D-xylose and 2,3,4,6-tetra-O-methyl-D-glucose we detected 2,-3,4,6-tetra-O-methyl-D-sorbitol and a monomethyl derivative of D-glucose. The genin after this reaction was identified as erythrodiol (IV) (M^+ 442).

It follows from the results given above that both D-glucose residues and the D-xylose residue are terminal and the carbohydrate chain is branched at D-glucuronic acid.

Further information on the structure of glycoside E (I) was obtained by comparing the mass spectra of the permethylates (III) and (VI). The mass spectra of both compounds (III) and (VI) had the peak of an ion with m/z 219, corresponding to a terminal methylated hexose (in this case, D-glucose), and the peak of an ion with m/z 597, corresponding to a methylated trisaccharide containing one residue each of D-xylose, D-glucose, and D-glucuronic acid. A fragment with m/z 1006 showed that the trisaccharide residue was attached to the C-3 hydroxyl of the aglycone. In the mass spectrum of the permethylate (III), in addition to the peaks mentioned there was the characteristic peak of an ion with m/z 657 arising on the detachment of the trisaccharide units from the molecular ion. This fragment unambiguously showed that the substituent at C-28 was a methylated hexose. In the mass spectrum of the permethylate (VI) there was no fragment with m/z 656, but there was a peak of an ion from retrodiene decomposition with m/z 262.

To determine the nature of the branching in the carbohydrate chain at C-3, the glycoside (V) was subjected to partial hydrolysis. The progenins (VIII-X) were isolated.

From its physicochemical constants, progenin (VIII) was identified as oleanolic acid 3-O-β-D-glucuronopyranoside [4].

Progenin (IX) proved to be an oleanolic acid bioside. The carbohydrate chain consisted of D-glucose and D-glucuronic acid residues. This compound was identical with a bioside obtained by the alkaline hydrolysis of salsoloside C [1].

Progenin (X), which was obtained in the largest yield, also proved to be a bioside, with a carbohydrate chain consisting of D-glucose and D-glucuronic acid residues. In an acid hydrolysate of the reduced permethylate (XI) (M^+ 906) of this bioside, 2,3,4,6-tetra-O-methyl-D-glucose and a dimethylglucose were detected. The second methylated sugar gave a positive reaction for the presence of an α-diol grouping [5], while for the methyl glycoside of the monomethylglucose this reaction was negative. Consequently, the dimethyl derivative was 3,4-di-O-methyl-D-glucose, and the monomethylglucose and monomethylglucuronic acid mentioned above each had a substituent at the C-3 hydroxyl.

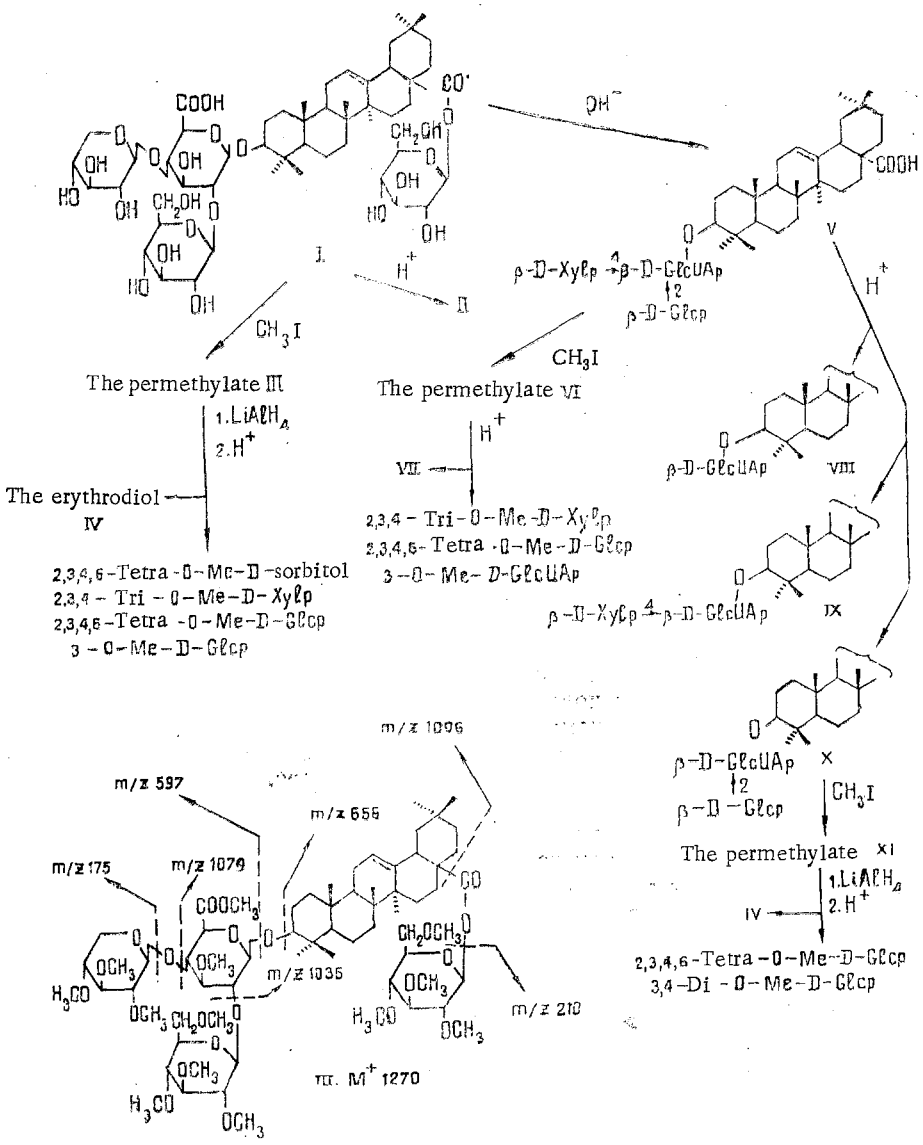
The results of a study of the products of the stepwise hydrolysis of salsoloside E (I) showed that the genin bore at the C-3 hydroxyl a D-glucuronic acid residue, and to the latter were attached two sugar residues: D-xylose by a 1 → 4 bond and D-glucose by a 1 → 2 bond.

A molecular rotation difference calculation [6] showed that all the anomeric centers had the β configuration (see scheme 1).

Thus salsoloside E (I) is a bisdesmosidic glycoside of oleanolic scid that has the structure of oleanolic acid 28-O-β-D-glucopyranoside 3-O-{[O-β-D-glucopyranosyl-(1 → 2)][O-β-D-xylopyranosyl-(1 → 4)]-β-D-glucuronopyranoside}.

On comparing the glycoside compositions of *Salsola micranthera* and *Climacoptera transoxana* [7], it is not difficult to observe the taxonomic closeness of the genera *Salsola* and *Climacoptera*. A common structural element in the glycosides is that they are all 3-O-β-D-glucuronopyranosides of oleanolic acid or of its analogs oxidized at C-23. The growth of the carbohydrate chain takes place by the addition of D-xylose and D-glucose residues to the D-glucuronic acid residue. The acylosidic moiety consists of a D-glucose residue. The molecular masses of the compounds that we have described are comparatively low — the maximum number of monosaccharide residues does not exceed four.

Scheme 1



EXPERIMENTAL

General Observations. The following solvent systems were used: 1) chloroform–methanol–water [a – (65:35:8); b – (35:15:3); 2) 1-butanol-ol–ethanol–25% ammonia (10:2:5); 3) chloroform–methanol (15:3); 4) benzene–acetone (10:2); 5) chloroform–ethanol (25:1); 6) 1-butanol–acetic acid–water (4:1:5); 7) 1-butanol–methanol–water (5:3:1).

Other information is given in our previous papers [1, 7].

Salsoloside E (I). Acid and Alkaline Hydrolysis. Fractions containing only glycoside E were purified on a column of silica gel with elution by methanol. The yield on the weight of air-dry raw material amounted to 1.1%; $C_{53}H_{84}O_{23}$, mp 224-226°C (from aqueous acetone), $[\alpha]_D^{20}$ +19 ± 2° (c 0.8; aqueous methanol).

Glycoside (I) (50 mg) was hydrolyzed with 6% sulfuric acid at 100°C for 4 h. The precipitate that deposited was separated off and was washed several times with water. On TLC in system 5, oleanolic acid (II) was identified. The filtrate was neutralized with barium carbonate and evaporated. In the residue, D-glucose, D-glucuronic acid, and D-xylose were detected by PC (system 6) and TLC (system 7). The ratio of the sugars according to GLC was 1.0:0.39:0.45.

Glycoside E (I) (1.9 g) was saponified with an 8% solution of KOH at 100°C for 5 h. The reaction mixture was neutralized with dilute sulfuric acid, and the reaction product was extracted with n-butanol. The butanolic extract was washed with water and evaporated to dryness. The residue was deposited on a column of silica gel. Elution with system 1b

yielded 1.4 g of the triglycoside (V), $C_{47}H_{74}O_{18}$, mp 192-196°C (from aqueous acetone), $[\alpha]_D^{20}$ +10 ± 2° (c 0.8; methanol). When product (V) was subjected to acid hydrolysis with 6% sulfuric acid under the conditions described above, oleanolic acid (II), D-glucose, D-glucuronic acid, and D-xylose were detected (TLC, system 7).

Methylation of Salsoloside E (I) and the Trioside (V). Glycoside (E) (700 mg) was dissolved in 50 ml of dimethyl sulfoxide, and 750 mg of sodium hydride was added in small portions. The mixture was stirred at room temperature for 1.5 h. Then 6 ml was added dropwise and the resulting mixture was stirred for another 3 h. After the usual working up and chromatography on a column of silica gel (system 4), 620 mg of the amorphous permethylate (III) was obtained: $C_{66}H_{110}O_{23}$, $[\alpha]_D^{20}$ −15 ± 2° (c 0.6; methanol). Mass spectrum, m/z (%): M^+ 1270 (0.03), 1079 (0.18), 1035 (0.17), 1006 (2.0), 656 (1.0), 597 (0.26), 219 (17.0), 187 (100.0), 175 (17.0).

By the method described above (3 ml of dimethyl sulfoxide, 280 mg of sodium hydride, and 4 ml of methyl iodide), 300 mg of the glycoside (V) yielded 270 mg of the permethylate (VI): amorphous powder, $C_{57}H_{94}O_{18}$, $[\alpha]_D^{20}$ −12 ± 3° (c 0.7; chloroform). Mass spectrum, m/z (%): M^+ 1066 (0.1), 1006 (0.07), 875 (0.5), 831 (0.5), 597 (0..24), 453 (59.0), 262 (24.0), 219 (21.4), 187 (100.0), 175 (28.6).

Reductive Cleavage of the Permethylate (III). Compound (III) (300 mg) was reduced with lithium tetrahydroaluminate (450 mg) by the usual procedure. The reaction product was hydrolyzed with a 6% solution of sulfuric acid in methanol. The sugar fraction consisted (according to TLC, system 3) of 2,3,4,6-tetra-O-methyl-D-sorbitol, 2,3,4-tri-O-methyl-D-xylose, 2,3,4,6-tetra-O-methyl-D-glucose, and 3-O-methyl-D-glucose. The methyl glycoside of the last-mentioned methylated carbohydrate did not exhibit the Bonner reaction. Erythrodiol (IV) was detected in the genin fraction of the hydrolysate; $C_{30}H_{50}O_2$. Mass spectrum, m/z (%): M^+ 442 (9.0), 234 (50.0), 203 (100.0).

Partial Hydrolysis of the Glycoside (V). A solution of 0.6 g of the glycoside (V) in 100 ml of 1% sulfuric acid was heated at 100°C for 3 h. After this, the reaction mixture was exhaustively extracted with n-butanol. The butanolic extracts were washed with water and were evaporated to dryness. The residue obtained (400 mg) was fractionated on a column of silica gel (using system 1b as eluent). The monoside (VIII) (40 mg), the bioside (IX) (20 mg), and the bioside (X) (110 mg) were isolated.

After recrystallization from ethanol, the monoside (VIII), $C_{36}H_{56}O_9$, had mp 206-210°C, $[\alpha]_D^{20}$ +20 ± 3° (ethanol). On hydrolysis with 6% sulfuric acid it formed oleanolic acid (II) and D-glucuronic acid. It was shown to be identical with an authentic sample of oleanolic acid 3-O-β-D-glucuronopyranoside [8] with the aid of TLC (systems 1a and 2).

The bioside (IX), $C_{41}H_{64}O_{13}$, mp 208-212°C (from ethanol), $[\alpha]_D^{20}$ +14 ± 2° (c 1.0; methanol), did not differ in its TLC behavior from the compound obtained by the alkaline hydrolysis of salsoloside C [1].

The bioside (X), $C_{42}H_{66}O_{14}$, had mp 215-217°C (from ethanol) $[\alpha]_D^{20}$ +6 ± 2° (c 0.9; methanol). The acid hydrolysis of this product led to the formation of oleanolic acid (II), D-glucose, and D-glucuronic acid. Compound (X) (70 mg) was methylated by Hakomori's method, which gave the permethylate (XI) (60 mg), $C_{50}H_{82}O_{14}$, $[\alpha]_D^{20}$ −9 ± 2° (c 0.5; chloroform). Mass spectrum, m/z (%): M^+ 906 (0.14), 846 (0.2), 453 (50.0), 437 (2.5), 405 (28.1), 393 (11.0), 368 (3.75), 262 (34.6), 219 (19.0), 203 (60.0), 187 (100.0).

The permethylate (XI) (40 mg) was reduced with lithium tetrahydroaluminate (35 mg) by the usual procedure. In the sugar fraction of the reduced product TLC (in system 3) showed the presence of 2,3,4-tetra-O-methyl-D-glucose (the reaction for the presence of an α-diol grouping was positive). Erythrodiol (IV) was identified as the genin (TLC, system 5).

In addition to the compounds described, oleanolic acid (II) and the initial glycoside (V) were isolated.

Acid Hydrolysis of the Permethylate (VI). The permethylate (VI) (200 mg) was hydrolyzed with a 6% solution of sulfuric acid in methanol at the boil for 5 h. After the usual working up, 2,3,4-tri-O-methyl-D-xylose, 2,3,4,6-tetra-O-methyl-D-glucose, and 3-O-methyl-D-glucuronic acid (giving the Bonner reaction) were detected by TLC in system 3 in the presence of authentic samples. Methyl oleanolate (VII) was identified as the genin (TLC, system 5).

SUMMARY

A new triterpene glycoside — salsoloside E, which is a bisdesmosidic glycoside — has been isolated from the epigeal part of *Salsola micranthera* Botsch.

Salsoloside E has the structure of oleanolic acid 28-O-β-D-glucopyranoside 3-O-{[O-β-D-glucopyranosyl-(1 → 2)][O-β-D-xylopyranosyl-(1 → 4)]-β-D-glucuronopyranoside}.

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STEROID SAPONINS AND SAPOGENINS OF *Allium*.

XX. STRUCTURE OF KARATAVIOSIDES E AND F

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The structures of two new steroid glycosides of the spirostan series isolated from inflorescences of the plant *Allium karataviense* Rgl. (family Alliaceae) — karataviosides E and F — have been shown on the basis of chemical transformations and spectral characteristics.

We have previously reported that the inflorescences of *Allium karataviense* Rgl. (family Alliaceae) contain, in addition to karataviosides A [1], B [2], and C [3], two minor glycosides — karataviosides E and F [4]. In the present paper we present experimental information to prove the structures of the last two compounds.

The Smith degradation [5] of karataviosides E (I) and F (IV) led to the formation of karatavigenin C (II) [4].

Analysis of the product of the methanolysis of karatavioside E (I) by TLC and GLC showed that the molecule of the glycoside (I) contained D-glucose, D-galactose, and D-xylose residues in a ratio of 2:1:1. For karatavioside F (IV) using the same methods the sugars mentioned were found in a ratio of 3:1:1.

As a result of the treatment of karatavioside F (IV) with the gastric juice of the snail *Helix plectotropis* a glycoside identical with karatavioside E (I) was isolated. This shows that enzymatic hydrolysis split off one D-glucose residue.

The Hakomori methylation [6] of karatavioside F (IV) led to a permethylate (III) the IR spectrum of which did not include the band of hydroxylic absorption.

In the PMR spectrum of the permethylate (III) there were five doublets in the 4.22-5.00 ppm region corresponding to the resonance of anomeric protons of sugars. The SSCC values of the signals under discussion (^3J = 7-8 Hz) indicate the β configuration of all the glycosidic bonds [7, 8]. At the same time, it can be seen that all the carbohydrate rings are present in the C1 confirmation [9].

When the permethylate (II) was subjected to complete acid hydrolysis, a mixture of methylated sugars was isolated from the reaction mixture. After separation into individual compo-

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