SUMMARY

The composition of the products of the hydrogenation of 3,7,7-trimethylcyclohepta-1,3,5-triene on platinum black has been studied.

It has been established that the products of incomplete hydrogenation contains 2- and 3-carenes and caranes, together with compounds having a seven-membered ring. This is confirmation of the tautomeric equilibrium between 3,7,7-trimethylcycloheptatriene and cara-2,4-diene.

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TRITERPENE GLYCOSIDES OF *Climacoptera transoxana*.

II. THE STRUCTURE OF COPTEROSIDE D

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UDC 547.918:547.914.4

A new tripterpene glycoside, copteroside D, has been isolated from the epigeal part of *Climacoptera transoxana* (Iljin) Botsch. On the basis of chemical transformations and physicochemical characteristics, copteroside D has been ascribed the structure of hederagenin 28-O-β-D-glucopyranoside 3-O-[O-β-D-xylanopyranosyl-(1→ 2)-β-D-glucopyranosiduronic acid].

Continuing a study of the triterpene glycosides of the epigeal part of *Climacoptera transoxana* (Iljin) Botsch. (family Chenopodiaceae), we have isolated from the total extractive substances [1] a compound which we have called copteroside D (II). Quantitatively, it is one of the main glycosides of the plant.

The acid hydrolysis of glycoside (II) yielded the genin (I) which was identified from its physicochemical constants as hederagenin. With the aid of TLC and GLC [2] it was established that the carbohydrate moiety of the copteroside D molecule included residues of D-glucose, D-glucuronic acid, and D-xylose in a ratio of 1:1:1. As has been shown previously [1], copteroside D contains an acylosidic component. To determine the nature of the O-acylosidic moiety, glycoside (II) was subjected to alkaline hydrolysis, as a result of which glycoside (V) was obtained. Acid hydrolysis of the latter showed that it included D-glucuronic

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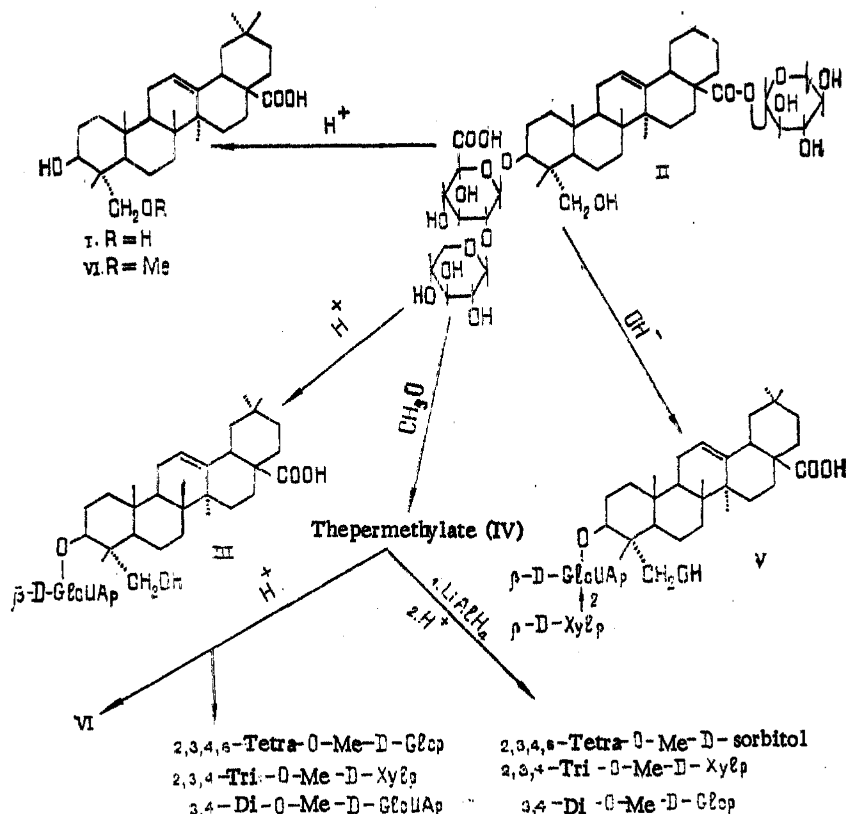
acid and D-xylose residues. Consequently, the acylosidic moiety of copteroside D is D-glucose.



The stepwise acid hydrolysis of copteroside D led to glycoside (III), which was found to be identical with copteroside B [1]. This fact shows that the second terminal monosaccharide residue of the triglyceride (II) is D-xylose.

To determine the position of attachment of the D-xylose residue, copteroside D was methylated by Hakomori's method [3]. Acid hydrolysis of the permethylate (IV) (M^+ 1096) gave 23-O-methylhederagenin (VI) and a mixture of methylated carbohydrates. Among the methylated sugars, 2,3,4,6-tetra-O-methyl-D-glucopyranose, 2,3,4-tri-O-methyl-D-xylopyranose, and 3,4-di-O-methyl-D-glucopyranuronic were detected by TLC in comparison with authentic samples. As was to be expected, reduction of the permethylate (IV) with lithium tetrahydroaluminate followed by acid hydrolysis led to 3,4-di-O-methyl-D-glucopyranose, 2,3,4-tri-O-methyl-D-xylopyranose, and 2,3,4,6-tetra-O-methyl-D-sorbitol. It can be seen from the facts given that the D-xylose residue is attached to the D-glucuronic acid through the hydroxyl at C-2.

A calculation of molecular rotation differences showed that all the glycosidic bonds have the β configuration.

Thus, glycoside (V) is copteroside C [1], and copteroside D has the structure of hederogenin 28-O-β-D-glucopyranoside 3-O-[O-β-D-xylopyranosyl-(1 → 2)-β-D-glucopyranosiduronic acid].

EXPERIMENTAL

For general observations, see [1]. The following solvent systems were used: 1) chloroform—methanol—water (65:35:8); 2) butanol—ethanol—25% ammonia (10:2:5); 3) chloroform—methanol, a) (20:1), b) (50:1); 4) benzene—acetone (2:1); 5) butanol—acetic acid—water (4:1:5); and 6) butanol—methanol—water (5:3:1).

Isolation of Copteroside D. The fractions enriched with glycoside D were rechromatographed on a column of silica gel in system 1. The process was monitored in systems 1 and 2. Fractions containing glycoside D alone were evaporated to small volume. On the addition of acetone, acicular crystals precipitated from the aqueous methanol. The yield of glycoside on the weight of the air-dry raw material was 0.72%.

Copteroside D, $C_{47}H_{74}O_{19}$, is readily soluble in water, mp 234-236°C (from aqueous acetone), $[\alpha]_D^{20}$ +14 ± 3° (c 1.1; 30% aqueous methanol), ν_{max}^{KBr} 3640-3250 (OH), 1740 (C=O of an ester group).

Hederagenin (I) from (II). Glycoside (II) (250 mg) was hydrolyzed with 5% sulfuric acid at 100°C for 8 h. The reaction mixture was diluted with water and the resulting precipitate was filtered off, washed with water, and dried. After purification by column chromatography in system 3b, 30 mg of hederagenin (I) was obtained with mp 326-328°C (from ethanol), $[\alpha]_D^{20}$ +78 ± 2° (c 1.0; pyridine).

The hydrolysate was neutralized with $BaCO_3$ and was then filtered and evaporated. D-glucose, D-xylose, and D-glucuronic acid were detected in the residue by TLC in system 6. GLC [2] showed the presence of the same monosaccharides in a ratio of 1:1:1.

Hederagenin 3-O-β-D-glucopyranosiduronic Acid (III) from (II). Glycoside D (540 mg) was hydrolyzed with 0.5% sulfuric acid at 100°C for 6 h. The reaction mixture was diluted with water and exhaustively extracted with n-butanol. The butanolic extract was washed with water and evaporated to dryness. The residue (310 mg) was separated on a column, and elution with system 3b yielded hederagenin (I). Elution with system 1 gave a progenin with mp 190-195°C (from ethanol), $[\alpha]_D^{20}$ +31 ± 2° (c 1.4; ethanol). The R_f values of this glycoside on TLC in systems 1 and 2 were identical with those of an authentic sample of hederagenin 3-O-β-D-glucopyranosiduronic acid [1].

Copteroside C (V) from (II). A solution of 300 mg of glycoside D in 20 ml of water was treated with 30 ml of 10% KOH solution and the mixture was heated at 100°C for 6 h. Then it was neutralized with a dilute solution of sulfuric acid. The neutralized solution was repeatedly extracted with butanol. The butanolic extract was washed with water and evaporated. The dry residue, after chromatographic purification on a column, yielded 215 mg of a hederogenin bioside with mp 220-224°C (from ethanol), $[\alpha]_D^{20}$ +19 ± 2° (c 1.2; methanol), which was identical with copteroside C [1].

Bioside (V) (60 mg) was subjected to acid hydrolysis with 8% sulfuric acid. D-Xylose and D-glucuronic acid were detected in the neutralized and evaporated hydrolysate by TLC in system 6.

The Permethylate (IV) from (II). In small portions, 0.8 g of sodium hydride was added to a solution of 0.7 g of glycoside (II) in 80 ml of dimethyl sulfoxide. The mixture was stirred at room temperature for 2 h and then 6 ml of methyl iodide was added to it dropwise and it was stirred for another 3 h. It was then poured into 250 ml of 5% sodium hyposulfite solution and extracted with chloroform. The chloroform extract was washed with water and dried with anhydrous sodium sulfate. After the solvent had been distilled off, the residue was chromatographed on a column with elution by benzene. This gave, in amorphous form, 550 mg of the permethylate (IV), $C_{58}H_{96}O_{19}$. $[\alpha]_D^{20}$ +30 ± 3° (c 1.3; methanol), the IR spectrum of which lacked the absorption due to hydroxy groups. Mass spectrum, m/z (%): M^+ 1096 (0.16), 8.32 (25.5), 686 (2.6), 393 (14.6), 220 (15.0), 219 (18.9), 187 (100.0), 175 (73.5).

23-O-Methylhederagenin (VI) from (IV). The permethylate (IV) (200 mg) was heated in 20 ml of 7% methanolic sulfuric acid at the boiling point of the mixture for 6 h. Then the reaction mixture was diluted with three volumes of water and the resulting precipitate was filtered off and dried. Purification on a column yielded 23-O-methylhederagenin (38 mg), identified by TLC in system 3a. After the elimination of the methanol, the hydrolysate was heated at 100°C for another 4 h. Then it was neutralized with $BaCO_3$ and evaporated, and the residue was found by TLC in system 4 with markers to contain 2,3,4,6-tetra-O-methyl-D-glucopyranose, 2,3,4-tri-O-methyl-D-xylopyranose, and 3,4-di-O-methyl-D-glucuronic acid.

Reductive Cleavage of the Permethylate (IV). A solution of 300 mg of the permethylate (IV) in 50 ml of tetrahydrofuran was treated with 0.4 g of lithium tetrahydroaluminate. The mixture was stirred at the boiling point for 6 h. The excess of reducing agent was decomposed by the addition of ethyl acetate, and then 10 ml of dilute sulfuric acid solution was added. The organic layer was separated from the aqueous layer. The aqueous layer was washed with ether. The combined organic extracts were evaporated. The dry residue was hydrolyzed with 5% sulfuric acid in methanol. The reaction mixture was diluted with water and the resulting precipitate was filtered off. The genin was shown to be identical with an authentic sample of 28-hydroxy-23-methoxy-β-amyrin [4].

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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