STRUCTURES OF CUCUMARIOSIDES C_1 AND C_2 – TWO NEW TRITERPENE GLYCOSIDES FROM THE HOLOTHURIAN Eupentacta fraudatrix

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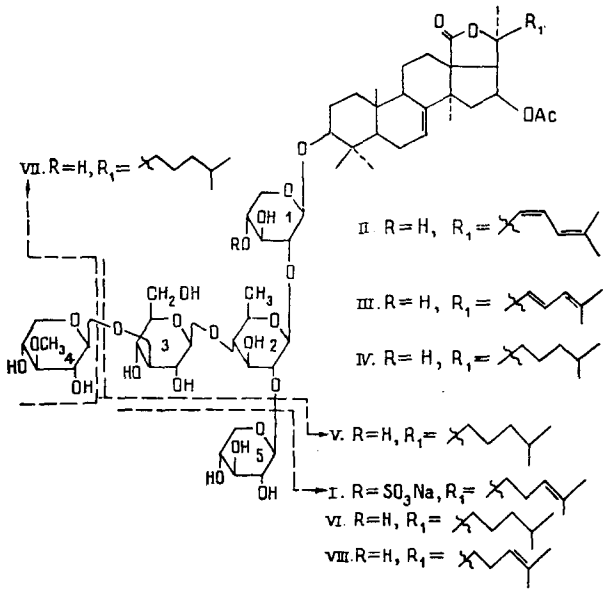
Two new triterpene glycosides – cucmariosides C_1 and C_2 – have been isolated from the Far Eastern holothurian Eupentacta (= Cucumaria) fraudatrix Djakonov et Baranova. Their structures have been established with the aid of ^{13}C NMR and PMR spectroscopy, partial acid hydrolysis, periodate oxidation, and methylation as 16β-acetoxy-3-{[3-O-methyl-β-D-xylopyranosyl-(1→3)-β-D-glucopyranosyl-(1→4)][β-D-xylopyranosyl-(1→2)]-β-D-quinovopyranosyl-(1→2)-β-D-xylopyranosyloxy}holosta-7,23,24(cis)-triene and 16β-acetoxy-3-{[3-O-methyl-β-D-xylopyranosyl-(1→3)-β-D-glucopyranosyl-(1→4)][β-D-xylopyranosyl-(1→2)]-β-D-quinovopyranosyl-(1→2)-β-D-xylopyranosyloxy}holosta-7,22,24(trans)-triene, respectively.

We have previously reported the determination of the structure of the main component of the glycosidic fraction of the Far Eastern holothurian Eupentacta fraudatrix – cucumarinoside G_1 (I) [1]. Continuing investigations of this holothurian, we have isolated two new glycosides – cucumariosides C_1 (II) and C_2 (III).



A comparison of the ^{13}C NMR spectra of cucumariosides C_1 and C_2 (Table 2) showed their considerable structural similarity. The differences consisted only in the signals of the side chain of the aglycon. In actual fact, it was shown from the ^{13}C NMR spectra of the aglyconic moieties of (II) and (III) that they differed from the aglycon of the previously known cucumarioside G_1 (I) by the presence of an additional double bond in the side chain. Thus, the spectrum of (I) had the signals only of a 24(25)-double bond: 123.9 ppm (C-24) and 131.7 ppm (C-25) [1]. At the same time, the spectrum of (II) contained the following signals (ppm): 132.0 (C-22), 120.8 (C-23), 119.7 (C-24) and 136.3 (C-25), and the spectrum of (III): 134.1 (C-22), 121.8 (C-23), 124.9 (C-24) and 134.4 (C-25).

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TABLE 1. ^{13}C NMR Spectra of Cucumariosides C_1 (II) and C_2 (III) (300 K; DMSO-d_6, δ_{DMSO} = 39.6 ppm)

Atom	Compound		Atom	Compound		Atom	Compound	
	II	III		II	III		II	III
C-1	35,6	35,6	C-22	132.0	134,1	C^2-6	17,6	17,5
C-2	26,4	26,4	C-23	120,8	121,8	C^3-1	103,1	103,1
C-3	88,5	88,5	C-24	119,7	124,9	C^3-2	72,9	72,9
C-4	39,6	39,6	C-25	136,3	134,4	C^3-3	86,1	86,0[a]
C-5	47,0	47,2	C-26	26,4	25,8	C^3-4	68,3	68,3
C-6	22,6	22,6	C-27	17,6	17,6	C^3-5	76,5[a]	76,5[a]
C-7	119,7	119,7	C-30	17,1	17,0	C^3-6	60,9	60,9
C-8	145,4	145,3	C-31	28,3	28,3	C^4-1	104,5[a]	104,6
C-9	46,8	46,7	C-32	32,7	32,2	C^4-2	73,5	73,5
C-10	35,0	35,0	OAc	21,3	21,3	C^4-3	86,2[a]	86,1[a]
C-11	21,9	21,8		169,5	169,8	C^4-4	69,0	69,0
C-12	30,0	30,2	C^1-1	104,1[a]	104,1[a]	C^4-5	65,9	65,9
C-13	57,9	58,3	C^1-2	81,3	81 3	OCH_3	60,0	60,0
C-14	47,6	47,2	C^1-3	76,5[a]	76,5[a]	C^5-1	104,3[a]	104,2[a]
C-15	43,2	42,6	C^1-4	69,3	69,3	C^5-2	74,1	74,1
C-16	72,1	72,4	C^1-5	65,5	65,5	C^5-3	75,7[a]	75,7[a]
C-17	56,2	55,4	C^2-1	101,5	101,4	C^5-4	69,0	69,1
C-18	179,1	179,1	C^2-2	81 6	81,6	C^5-5	65,5	65,9
C-19	23,7	23,7	C^2-3	74,8	74 8			
C-20	83,8	83,2	C^2-4	85,7	85,7			
C-21	28,8	30,0	C^2-5	69,9	69,9			

a — ambiguous assignment of the signals.

The UV spectra of (II) and (III) each contained an absorption maximum at 240 nm, which showed the presence of a conjugated dienic system in the side chain of each aglycon. Signals in the ^1H NMR spectra of (II) and (III) at 1.70 and 1.74 ppm (CH_3-26 and -27; 6 H) showed the 22(23),24(25)-position of the conjugated dienic grouping in each of them. This permitted the assumption that cucumarioside C_1 and C_2 differed from one another by the configuration of the 22(23) double bond in the dienic system of the side chain of the aglycon. In actual fact, the spin-spin coupling constant of H-22 and H-23 in the ^1H NMR spectrum of glycoside (II) (J = 12.5 Hz) indicated the cis-configuration, while the corresponding constant in the spectrum of (III) (J = 15.6 Hz) indicated the trans-configuration of this double bond.

On the catalytic hydrogenation of each of cucumarioside C_1 and C_2 we obtained the tetrahydro derivative (IV), in the ^1H NMR spectrum of which the signals of the protons of the methyl groups at 1.70 and 1.74 ppm had disappeared and a doublet had appeared in the strong field at 0.83 ppm (J = 6.6 Hz), which is characteristic for a saturated side chain [2, 3]. The acid hydrolysis of (IV) gave 3-O-methylxylose, quinovose, xylose, and glucose in a ratio of 1:1:2:1, the sugars being identified by GLC-MS in the form of the corresponding aldonitrile peracetates.

The methylation of (IV) and the methanolysis and subsequent acetylation of the reaction products gave a mixture of methyl 2-O-acetyl-3,4-di-O-methyl-α- and -β-xylopyranosides, methyl 2,4-di-O-acetyl-3-O-methyl-α- and -β-quinovopyranosides, methyl 3-O-acetyl-2,4,6-tri-O-methyl-α- and -β-glucopyranosides, and methyl 2,3,4-tri-O-methyl-α- and -β-xylopyranosides, which were identified by the GLC-MS and GLC methods. The methylation results indicated the presence of branching in the carbohydrate chains of glycoside (II) and (III) at the quinovose residue and also the fact that the xylose and 3-O-methylxylose residues or a second xylose occupied the terminal positions.

The periodate oxidation followed by acid hydrolysis of (IV) led to the destruction of both xylose residues, which agreed with the methylation results.

In order to determine the sequence of the monosaccharide residues in the carbohydrate chain of each glycoside we performed partial hydrolysis with 2 N sulfuric acid. After separation of the hydrolysis products by column chromatography on silica gel, we obtained the progenins (V), (VI), and (VII). The structures of the progenins were determined from their ^{13}C and ^1H NMR spectra, and also from their monosaccharide compositions. The acid hydrolysis of progenin (V) gave xylose, quinovose, and glucose in a ratio of 1:1:1. The ^1H NMR spectrum had the signals of three anomeric protons at 4.84, 5.03, and 5.21 ppm (doublets, J = 7.5 Hz). According to the results of acid hydrolysis, progenin (VI) contained xylose, quinovose, glucose, and 3-O-methylxylose residues (1:1:1:1). Its ^1H NMR spectrum showed an additional (in comparison with the spectrum of (V)) signal of an anomeric proton at 5.26 ppm (J = 7.5 Hz) and a three-proton singlet of a methoxy group at 3.88 ppm.

TABLE 2. ^{13}C NMR Spectrum of the Carbohydrate Moiety of the Tetrahydro Derivative (IV) (300 K, C_5D_5N)

C^1-1	105,3	C^3-1	105,0	C^5-1	106,0[c]
C^1-2	82,8	C^3-2	73,9	C^5-2	75,7
C^1-3	78,0	C^3-3	87,8[b]	C^5-3	77,2
C^1-4	70,6[a]	C^3-4	69,5	C^5-4	70,4[a]
C^2-1	103,2	C^3-5	78,0	C^5-5	67,1
C^2-2	83,5	C^3-6	62,1		
C^2-3	75,7	C^4-1	106,1[c]		
C^2-4	86,9	C^4-2	74,8		
C^2-5	71,2[a]	C^4-3	87,2[b]		
C^2-6	18,3	C^4-4	70,1[a]		
		C^4-5	67,1		

a, b, c – assignment of the signals ambiguous.

TABLE 3. ^{13}C NMR Spectra of the Carbohydrate Moieties of Progenins (V), (VI), and (VII) (300 K, C_5D_5N)

Atom	Compound			Atom	Compound	
	V	VI	VII		VI	VII
C^1-1	105,5	105,6	105,3	C^4-1	106,0	
C^1-2	84,4	84,2	83,4[a]	C^4-2	74,7	
C^1-3	78,3	78,0	78,2	C^4-3	87,7[a]	
C^1-4	70,8	70,8	70,5	C^4-4	70,0	
C^1-5	66,7	66,7	66,7	C^4-5	67,1	
C^2-1	105,5	105,6	103,2	OCH_3	60,1	
C^2-2	76,4	76,3	82,8	C^5-1		106,0
C^2-3	76,0	75,9	74,9	C^5-2		75,7
C^2-4	87,4	87,3	86,7	C^5-3		77,1[a]
C^2-5	71,7	71,7	71,2	C^5-4		70,6
C^2-6	18,3	18,2	18,2	C^5-5		67,0
C^3-1	105,3	104,9	105,3			
C^3-2	75,0	73,9	74,9			
C^3-3	78,3	87,3[a]	78,2			
C^3-4	71,7	69,6	71,6			
C^3-5	78,3	78,0	77,9[a]			
C^3-6	62,4	62,3	62,4			

a – assignment of the signals ambiguous.

A comparison of the ^{13}C NMR spectra of progenin (VI) (see Table 3) and of the desulfated derivative of cucumarioside G_1 (VIII) studied previously [1] revealed good agreement of all the signals with the exception of the C-24 and C-25 signals, which, in the spectrum of (VIII) were shifted downfield (the C-24 signal from 39.7 to 124.4 ppm and the C-25 signal from 28.3 to 131.9 ppm). This showed that progenin (VI) was the 24(25)-dihydro derivative of compound (VIII). In actual fact, after (VIII) had been hydrogenated over Adams catalyst, we obtained a product identical with the progenin (VI) according to a comparison of ^{13}C NMR spectra and physical constants.

Thus, the positions of four of the monosaccharide residues in the carbohydrate chain of the tetrahydro derivative (IV) had been established. The attachment of the second xylose residue to C-2 of the quinose residue followed from the methylation results. This conclusion was also confirmed by an analysis of the ^{13}C NMR spectrum of the carbohydrate moiety of progenin (VII) (Table 3) containing, according to the results of acid hydrolysis, quinovose, xylose, and glucose residues (1:2:1). Thus, the C-2 signal of the quinovose residue of (VII) was shifted downfield by 6.4-6.5 ppm (α-shift as the result of glycosylation) as compared with the corresponding signals in the spectra of (V) and (VI). At the same time, in the spectrum of (VII) characteristic upfield shifts (β-shifts) were observed for the C-1 and C-3 atoms of the quinovose residue (−2.4 and −1.0 ppm, respectively).

We determined the configurations of all the glycosidic bonds of (IV) as β from the signals of the anomeric carbon atoms in the ^{13}C NMR spectrum at 103.2, 105.0, 105.3, 106.0, and 106.1 ppm [4, 5] (see Table 2).

Thus, the structure of the tetrahydro derivative of cucumariosides C_1 and C_2 was determined as (IV), and the structures of the glycosides themsleves as (II) and (III), respectively.

EXPERIMENTAL

Melting points were determined on a Boëtius stage. Specific rotations were measured on a Perkin-Elmer 141 polarimeter at room temperature. ^{13}C NMR spectra were obtained on a Bruker WM-250 spectrometer. ^1H NMR spectra were taken on the same instrument at 250 MHz. UV spectra were obtained on a Specord UV-Vis spectrophotometer. GLC analysis was conducted on a Tsvet-110 chromatograph using 0.3 × 150 cm glass columns containing 3% of QF-1 on Chromaton N-HMDS with argon as the carrier gas (60 ml/min) at temperatures of 110-220°C, 5°C/min. Chromato-mass-spectrometric analysis was performed on a LKB 9000s instrument using a 0.3 × 300 cm column containing 1.5% of QF-1 on Chromaton N-HMDS with helium as the carrier gas (30 ml/min). The analysis was performed under the following conditions: temperature of the evaporator 275°C, of the column 110-220°C (5 deg/min), of the molecular separator 265°C, and of the ion source 255°C; ionizing voltage 70 eV.

The animals were collected in the Troits inlet, Peter the Great Bay, in August, 1979, at a depth of 0.5-1.0 m.

Cucumarioside C_1 (II) was isolated by the procedure described previously. mp 196-199°C, $[\alpha]_D^{20}$ −12° (c 0.323; methanol). UV spectrum (methanol): λ_{max} 240 nm. ^1H NMR spectrum (C_5D_5N, ppm, 250 MHz): 1.17 (CH_3-30, 3 H, s), 1.12 (CH_3-31, 3 H, s), 1.25 (CH_3-19, 3 H, s), 1.34 (CH_3-32, 3 H, s), 1.72 (CH_3-21, 3 H, s), 1.70; 1.74 (CH_3=-26,27, 6 H), 3.35 (H-3, 1 H, dd, J = 12.5 Hz, J = 3.8 Hz), 5.70 (H-7, 1 H, m), 3.48 (H-9, 1 H, s), 2.52 (H-15α, 1 H, dd, $J_{15\alpha,15\beta}$ = 12.5 Hz, $J_{15\alpha,16}$ = 8.6 Hz), 5.82 (H-22, 1 H, d), 6.14 (H-23, 1 H, t, $J_{23,22}$ = 12.5 Hz, $J_{23,24}$ = 11.6 Hz, 6.5 (H-24, 1 H, dm, 2.00 (CH_3COO, 3 H, s), 4.88; 4.98; 5.22; 5.29 and 5.43 (signals of anomeric protons, 1 H each, d, J = 7.5 Hz), 1.73 (CH_3 group of quinovose, 3 H, J = 6.1 Hz). For the ^{13}C NMR spectrum, see Table 1.

Cumarioside C_2 (III) was isolated by the same method [1]. mp 192-194°C, $[\alpha]_D^{20}$ −48° (c 0.1; pyridine). UV spectrum (methanol): λ_{max} 240 nm. ^1H NMR spectrum (C_5D_5N, ppm, 250 MHz): 1.17 (CH_3-30, 3 H, s), 1.16 (CH_3-31, 3 H, s), 1.25 (CH_3-19, 3 H, s), 1.34 (CH_3-32, 3 H, s), 1.60 (CH_3-21, 3 H, s), 1.70; 1.74 (CH_3-26, 27, 6 H), 3.37 (H-3, 1 H, dd, J = 12.5 Hz, J = 3.8 Hz), 5.70 (H-7, 1 H, m), 3.52 (H-9, 1 H, m), 2.46 (H-15, 1 H, dd, $J_{15\alpha,15\beta}$ = 12.5 Hz, $J_{15\alpha,16}$ = 7.5 Hz), 6.00 (H-16, 1 H, m), 2.82 (H-17, 1 H, d, $J_{16,17}$ = 8.8 Hz), 5.93 (H-22, 1 H, d), 6.57 (H-23, 1 H, dd, $J_{23,22}$ = 15.0 Hz, $J_{23,24}$ = 10.7 Hz, 5.87 (H-24, 1 H, dm), 2.00 (CH_3COO), 3 H, s), 4.87; 4.96; 5.21; 5.27 and 5.42 (signals of anomeric protons, each 1 H, d, J = 7.5 Hz), 1.71 (CH_3 group of quinovose, 3 H, d, J = 6.2 Hz). For the ^{13}C NMR spectrum, see Table 1.

Hydrogenation of Cucumariosides C_1 and C_2. Glycosides (II) and (III) (100 mg each) were hydrogenated in methanol over Adams catalyst at room temperature for 20 h. The hydrogenation product was isolated by chromatography on a column of Polykhrom-1 in the water–ethanol (100 → 65:35) system. This gave 32 and 40 mg, respectively, of the tetrahydro derivative (IV). mp 221-223°C, $[\alpha]_D^{20}$ −23.5° (c 0.323; methanol). ^1H NMR spectrum (250 MHz, $(CD_3)_2SO$, ppm): 0.99 (CH_3-30, 3 H, s), 0.85 (CH_3-31, 3 H, s), 0.90 (CH_3-19, 3 H, s), 1.18 (CH_3-32, 3 H, s), 1.41 (CH_3-21, 3 H, s), 0.84 (3 H, d), 0.82 (3 H, d, CH_3-26, 27, J = 6.6 Hz), 5.48 (H-7, 1 H, m), 2.38 (H-15α, 1 H, dd, $J_{15\alpha,15\beta}$ = 12.5 Hz, $J_{15\alpha,16}$ = 7.5 Hz), 5.68 (H-16, 1 H, m), 2.72 (H-17, 1 H, d, $J_{16,17}$ = 8.8 Hz), 2.00 (CH_3COO, 3 H, s) 4.26; 4.36; 4.42; 4.57 and 4.67 (signals of anomeric protons, 1 H each, d, J = 7.5 Hz), 1.22 (CH_3 group of quinovose, 3 H, d, J = 6.1 Hz).

Acid Hydroliysis of the Derivative (IV). A solution of 5 mg of (IV) in 2 ml of 12% HCl was heated at 90-100°C for 2 h. The reaction mixture was extracted with chloroform, and the aqueous layer was neutralized with Dowex anion exchange resin in the HCO_3 form. The resin was separated off by filtration and was washed with water. The aqueous layer and the wash waters were combined and concentrated in vacuum to dryness. The residue was dissolved in 1 ml of dry pyridine, 5 ml of hydroxylamine hydrochloride was added, and the mixture was heated at 100°C for 1 h. Then 1 ml of acetic anhydride was added to the reaction mixture and it was heated at 100°C for another 1 h. After this it was evaporated and the residue was analyzed by GLC-MS. The peracetates of the aldononitrile derivatives of O-methylxylose, quinovose, xylose, and glucose were identified (1:1:2:1).

Methylation of the Derivative (IV). A solution of 10 mg of (II) in 2 ml of dry dimethyl sulfoxide (DMSO) was added to a solution of the methylsulfinyl anion (prepared from 100 mg of NaH and 2 ml of DMSO), and the mixture was stirred in an atmosphere of argon at 50°C for 1 h. Then 1 ml of CH_3I was added to the reaction mixture and it was left at room temperature

for 2 h. After this, it was diluted with water (10 ml) and extracted with chloroform (3 × 2 ml). The extract was washed with 2 ml of saturated sodium thiosulfate solution and with 2 ml of water and was evaporated. The residue obtained was boiled with 1 ml of anhydrous methanol saturated with HCl for 2 h. The solution was evaporated, the residue was covered with a mixture of pyridine and acetic anhydride, the mixture was heated at 100°C for 1 h and was evaporated, and the residue was analyzed by GLC-MS to identify the methyl glycosides.

Periodate Oxidation of the Tetrahydro Derivative (IV). A solution of 6 mg of (IV) in 2 ml of water was treated with 10 mg of sodium periodate, and the mixture was left at 20°C for 12 h. The reaction product was extracted with butanol (2 ml). The butanolic extract was washed with water (2 × 1 ml) and evaporated in vacuum. The residue was hydrolyzed and was worked up as described above for the analysis of the monossaccharides in the form of aldonitrile peracetates. Quinovose, glucose, and 3-O-methylxylose were identified (1:1:1).

Partial Acid Hydrolysis of the Tetrahydro Derivative (IV). Compound (IV) (120 mg) was hydrolyzed with 30 ml of 2 N H_2SO_4 at 90-100°C for 5 min. The reaction mixture was diluted with water and deposited on a column of Polychrome-1. The excess of acid was washed out with water until the eluate was neutral, and the combined progenins were eluted with 50% ethanol. The aqueous ethanolic solution was evaporated in vacuum and the residue was chromatographed on a column of silica gel in the chloroform–methanol–water (65:15:1.5) system. This gave 14 mg of progenin (V), 16 mg of progenin (VI), and 21 mg of progenin (VII).

Progenin (V), mp 276-278°C, $[\alpha]_D^{20}$ −11.3°, (c 0.15; $CHCl_3$:MeOH, 1:1). Acid hydrolysis of the progenin gave xylose, quinose, and glucose (1:1:1). ^1H NMR spectrum (250 MHz, C_5D_5N, ppm): 1.18 (6 H, s), 1.20 (6 H, s), 1.37 (6 H, s) (CH_3-19, 26, 27, 30, 31, 32), 1.52 (CH_3-21, 3 H, s), 3.37 (H-3, 1 H, dd, J = 12.5 Hz, J = 3.8 Hz, 3.52 (H-9, 1 H, m), 2.65 (H-17, 1 H, d, $J_{16,17}$ = 8.8 Hz, 2.06 (CH_3COO, 3 H, s), 4.84; 5.03; 5.21 (signals of anomeric protons, 1 H each, d, J = 7.5 Hz), 1.79 (CH_3 group of quinovose, 3 H, d, J = 6.3 Hz). For the ^{13}C NMR spectrum of the carbohydrate moiety, see Table 3.

Progenin (VI), mp 181-183°C, $[\alpha]_D^{20}$ −14.1° (c 0.60; $CHCl_3$:MeOH, 1:1). Acid hydrolysis of the progenin gave xylose, quinovose, glucose, and 3-O-methylxylose (1:1:1:1). ^1H NMR spectrum (250 MHz, C_5D_5N, ppm): 1.18 (6H, s), 1.20 (6 H, s), 1.37 (6 H, s), (CH_3-19, 26, 27, 30, 31, 32), 1.52 (CH_3-21, 3 H, s), 3.37 (H-3, 1 H, dd, J = 12.5 Hz, J = 3.8 Hz), 3.51 (H-9, 1 H, m), 2.66 (H-17, 1 H, d, $J_{16,17}$ = 10 Hz, 2.06 (CH_3COO, 3 H, s), 4.82; 4.98; 5.18; 5.26 (signals of anomeric protons, 1 H each, d, J = 7.5 Hz), 1.78 (CH_3 group of quinovise, 3 H, d, J = 6.3 Hz). For the ^{13}C NMR spectrum of the carbohydrate moiety, see Table 3.

Progenin (VII), mp 196-198°C, $[\alpha]_D^{20}$ − 12.0° (c 0.50; $CHCl_3$:MeOH, (1:1). Acid hydrolysis of the progenin gave xylose, quinose, and glucose (2:1:1). ^1H NMR (250 MHz, C_5D_5N, ppm): 1.16 (6 H, s), 1.18 (6 H, s), 1.32 (6 H, s), (CH_3-19, 26, 27, 30, 31, 32), 1.50 (CH_3-21, 3 H, s), 3.36 (H-3, 1 H, dd, J = 12.5 Hz, J = 3.8 Hz, 3.51 (H-9, 1 H, m), 2.65 (H-17, 1 H, d, $J_{16,17}$ = 10 Hz, 2.05 (CH_3COO, 3 H, s), 4.87, 4.98, 5.21, 5.42 (signals of anomeric protons, 1 H each, d, J = 7.5), 1.72 (CH_3 group of quinovose, 3 H, d, J = 5.8 Hz). For the ^{13}C NMR spectrum of the carbohydrate moiety, see Table 3.

Hydrogenation of the Desulfated Derivatve of Cumuraioside G_1 (VIII). Derivative (VIII) was dehydrogenated in methanol over Adams catalyst for 6 h. The reaction product was isolated by chromatography on silica gel in the chloroform–methanol–water (65:15:1.5) system. Compound (VI) was obtained.

SUMMARY

It has beeen shown that cucumarioside C_1 and C_2 from the holothurian Eupentacta fraudatrix are, respectively, 16β-acetoxy-3-{[3-O-methyl-β-D-xylopropanosyl-(1→3)-β-D-glucopyranosyl-(1→4)][β-D-xylopyranosyl-(1→2)]-β-D-quinovopyranosyl-(1→2)-β-D-xylopyranosyloxy}holosta-7,22,24(cis)-triene. and 16β-acetoxy-3-{[3-O-methyl-β-D-xylopyranosyl-(1→3)-β-D-gluco--pyranosyl-(1→4)][β-D-xylopyranosyl-(1→2)]-β-D-xylopyranosyloxy}holosta-7,22,24(trans)-triene.

LITERATURE CITED

1. Sh. Sh. Afiyatullov, L. Ya. Tishchenko, V. A. Stonik, A. I. Kalinvoskii, and G. B. Elyakov, Khim. Prir. Soedin., 244 (1985).
2. J. D. Chanley and C. Rossi, Tetrahedron, 25, 1897 (1969).
3. J. D. Chanley and C. Rossi, Tetrahedron, 25, 1911 (1969).
4. A. S. Shashkov and O. S. Chizhov, Bioorg. Khim., 2, 437 (1976).

5. A. I. Kalinovskii, I. I. Mal'tsev, A. S. Antonov, and V. A. Stonik, Bioorg. Khim., 10, 1655 (1984).

TRITERPENE GLYCOSIDES OF Astragalus AND THEIR GENINS.

XXIV. CYCLOORBICOSIDE G FROM Astragalus orbiculatus

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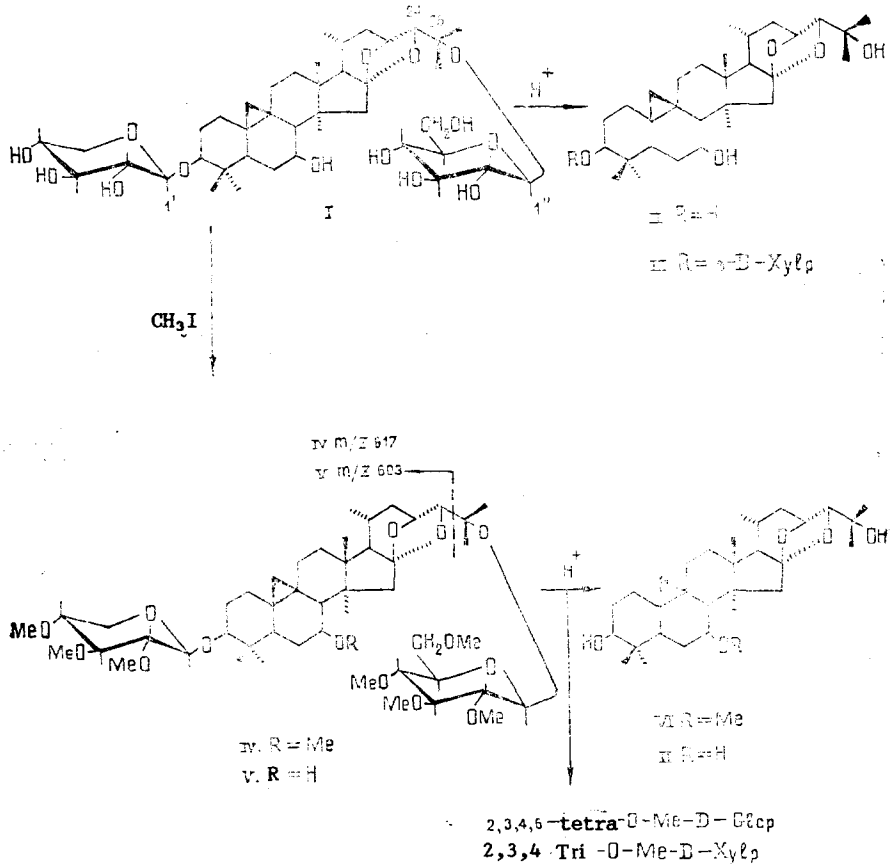
UDC 547.918:547.926

A bisdesmosidic glycoside – cycloorbicoside G – has been isolated from the epigeal parts of the plant Astragalus orbiculatus Ledeb. (Leguminosae), and on the basis of chemical transformations and spectral characteristics its structure has been established as (23R,24S)-16β,23;16α,24-diepoxycycloartane-3β,7β,25-triol 25-O-β-D-glucopyranoside 3-O-β-D-xylopyranoside.

We have previously reported the determination of the structure of cycloorbingenin [1] and cycloorbicoside A [2] – the main glycoside and its genin that were isolated from the epigeal part of Astragalus orbiculatus Ledeb. (Leguminosae).

Extracts of the epigeal part of this plant [1] contained eight substances of triterpene nature numbered in increasing order of polarity 1-8. Substance 1 corresponded to cycloorbicoside A. Column chromatography on silica gel of a butanolic fraction yielded substance 7. In the present paper we consider the structure of this glycoside, which we have called cycloorbicoside G ((I), Scheme).



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