TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS.

VI. CYCLOASGENIN C FROM *Astragalus taschkendicus*

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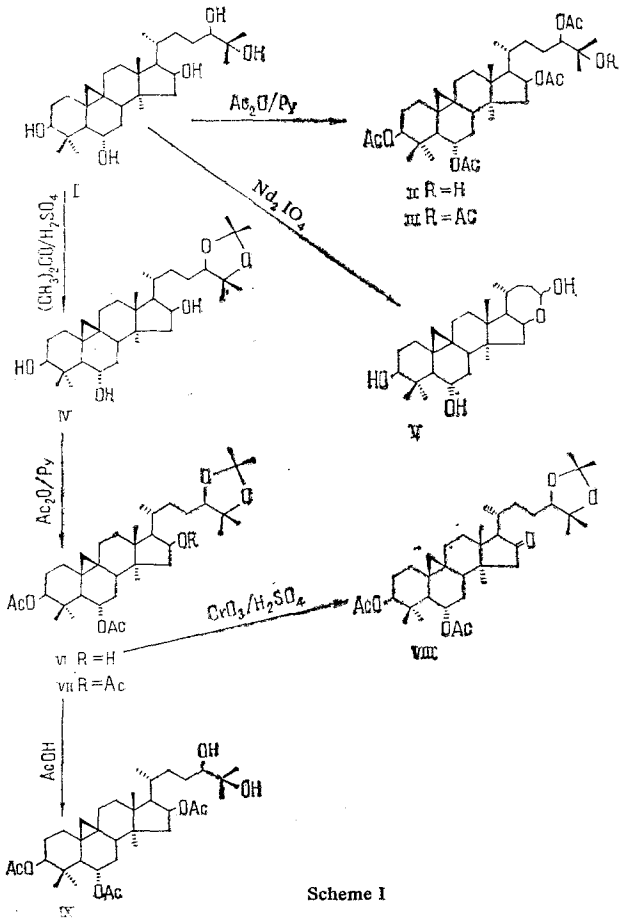
UDC 547.587+581.192

A new isoprenoid — cycloasgenin C — has been isolated from the roots of the plant *Astragalus taschkendicus* C. Bge, and on the basis of chemical transformations and spectral characteristics its structure has been established as 24(R)-cycloartane-3β,6α,16β,24,25-pentaol.

We have reported [1] the structure of cycloasgenin A — an isoprenoid of the cycloartane type isolated from the roots of the plant *Astragalus taschkendicus* Bge. Continuing the investigation of the methylsteroids of this plant, we have isolated from the roots of *Astragalus taschkendicus* collected in 1980 not only the substances mentioned previously but two other compounds of genin nature. One of them has been identified as cyclosieversigenin [2], and the other has proved to be new and has been called cycloasgenin C (I, scheme 1). Cyclosieversigenin and cycloasgenin C have also been isolated from the products of the methanolysis of the combined glycosides E and F [1].



Scheme I

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TABLE 1. Chemical Shifts of the Protons of Cycloasgenin C(I) and of Its Derivatives (δ, ppm, O — HMDS)

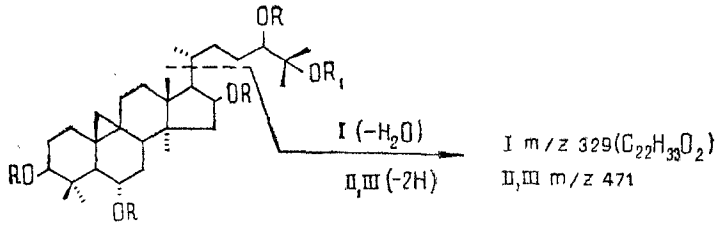
Compound	Positions of the protons						
	H-3	H-6	H-16	2H-19	H-24	CH_3 group	OAc
I	[~3,60 m]*	[~3,60 m]*	[4,54 m]	[0,21; 0,48 d]	[~3,60 m]*	[0,91; 0,98 d; 1,21; 1,27; 1,35; 1,36; 1,73]	—
II	~4,56 m*	~4,56 m*	5,19 m	0,28; 0,53 d	~4,56 m*	0,78; 0,85 d; 0,87; 0,92; 1,04; 1,11×2CH_3	1,90; 1,93; 1,97; 2,00
III	4,52 q ^3J=10,8 and 4,5 Hz	4,64 sx ^3J=9,0; 9,0 4,4 Hz	5,22 sx ΣJ=22,6 Hz	0,29; 0,52 d ^2J=4,7 Hz	4,98 q ^3J=11,0 and 2,1 Hz	0,78; 0,86 d; 0,87; 0,92; 1,04; 1,37; 1,41	1,90; 1,93; 1,97; 1,99; 2,01
IV	~3,40 m	3,54 m	4,35 m	0,30; 0,47 d	3,20 q	0,88; ~0,91 d, 0,92; 1,05; 1,10; 1,20× ×2CH_3; 1,27; 1,35	—
V	3,25 q ^3J=10,8 and 4,5 Hz	3,50 sx ^3J=9,4; 9,4; 3,6 Hz	4,15 q ΣJ=23,2 Hz	0,31; 0,45 d ^2J=4,7 Hz	4,58 q ^3J=9,3 and 2,3 Hz	0,87; 0,88 d; 0,91; 1,07; 1,20	—
	[~3,53 m] *	[~3,53 m] *	[4,13 m]	[0,20; 0,45 d]	[4,73 q ^3J=8,0 and 2,7 Hz]	[0,83 d; 0,88; 1,15; 1,19; 1,70]	
VI	~4,38 m*	4,65 m	~4,38 m*	0,29; 0,55 d	3,58 q	0,79; 0,86; 0,91 d; 0,94; 1,04; 1,08; 1,19; 1,26; 1,34	1,91; 1,98
VII	~4,53 m*	~4,53 m*	5,16 m	0,30; 0,55 d	3,48 q	0,80; 0,88 d; 0,90; 0,94; 1,01; 1,07; 1,17; 1,24; 1,31	1,90; 1,96; 1,98
VIII	4,54 m*	4,66 m*	—	0,34; 0,59 d	3,59 t	0,80; 0,92 d; 0,94; 1,04; 1,06×2CH_3; 1,19; 1,25; 1,34	1,91; 1,97
IX	~4,54 m*	~4,54 m*	5,24 m	0,30; 0,56 d	3,14 m	0,77; 0,90×2CH_3; 0,95; 1,08×2CH_3; 1,13	1,91; 1,96; 1,98

Note. The spectra were taken in $CDCl_3$ or in C_5D_5N. The indices given in square brackets were obtained when using C_5D_5N. The signals denoted by asterisks are superposed on one another in the horizontal series. The signals of the methyl groups have a singlet nature with the exception of the CH_3 at C-20, which has a doublet nature; d — doublet; t — triplet; q — quartet; sx — sextet; m — multiplet.

The elementary composition of cycloasgenin C (I) is $C_{30}H_{52}O_5$. In the strong-field region of the PMR spectrum of this compound at 0.48 and 0.21 ppm (Table 1), just as in the spectrum of cycloasgenin A [1], two one-proton doublets belonging to the protons of a cyclopropane ring are observed. As was to be expected, the IR spectrum of the new genin (I) has an absorption band at 3040 cm^{-1} due to the CH_2 group of a cyclopropane ring [3]. These facts permit cycloasgenin C to be assigned to isoprenoids of the cycloartane series.

It follows from the PMR spectrum of cycloasgenin C (I) that its molecule contains only four protons geminal to hydroxy groups. These hydrogen atoms are represented by the one-proton multiplet at 4.54 ppm and a multiplet with its center at 3.60 ppm, corresponding to three proton units. This conclusion is confirmed by the fact that these signals shift downfield in the PMR spectra of the tetraacetate (II) and of the pentaacetate (III).

Thus, of the five oxygen atoms of the cycloasgenin C molecule, four belong to secondary hydroxy groups. The formation of the pentaacetate (III) shows that the fifth oxygen atom is included in a tertiary hydroxy group.



I. $R = R_1 = H$, M^+ 492
II. $R = Ac$, $R_1 = H$, M^+ 660
III. $R = R_1 = Ac$, M^+ 702

Scheme 2

In the mass spectrum of the genin (I) there is the peak of an ion with m/z 329 — $C_{22}H_{33}O_2$ — formed as the result of the cleavage of the C-17—C-20 bond and the ejection of one molecule of water from the pentacyclic nucleus [4] (scheme 2). The cleavage of the C-17—C-20 bond is also observed in the mass spectra of the tetraacetate (II) and the pentaacetate (III). The corresponding ions in the spectra of the two acetates are identical, and a peak with m/z 471 relates to them. As we shall see, in this fragment all three acetoxy groups are retained. Consequently, the pentacyclic part of the cycloasgenin C molecule contains three secondary hydroxy groups, and the side chain contains one secondary and one tertiary hydroxy group.

It follows from the molecular formula of the genin (I), $C_{30}H_{52}O_5$, that the side chain of this compound, unlike the side chain of cycloasgenin A [1] and that of cyclosieversigenin [2], has an acyclic structure.

Cycloasgenin C (I) gives a monoacetonide (IV) and undergoes oxidation by sodium periodate. These transformations show the presence of an α-diol grouping in the molecule of the genin (I).

Compound (V), formed as the result of periodate oxidation, has M^+ 432. The loss of 60 units on passing from the genin (I) (M^+ 492) to the product of periodate oxidation (V) (M^+ 432) unambiguously determines the position of the diol grouping in the acyclic part of the molecule, namely, as at C-24—C-25.

It is interesting to note that it was impossible to detect a carbonyl function in compound (V). This fact can be explained by the formation of an internal hemiacetal between the C-24 aldehyde group on a hydroxyl located in the cyclic nucleus.

The acetylation of the acetonide (IV) gave the diacetate (VI) and the triacetate (VII). The Jones oxidation of the diacetate (VI) [5] led to the keto derivative (VIII). The IR spectrum of compound (VIII) shows at 1742 cm^{-1} the absorption characteristic for a five-membered cyclic ketone. Consequently, there is a keto function in compound (VIII), which means that the hydroxy group remaining free in the diacetate (VI) is located in ring D.

The circular dichroism curve of substance (VIII) with a negative Cotton effect at 305 nm ($\Delta\varepsilon = -5.09$) shows the position of the keto group under consideration at C-16 [6]. This determines the position of one of the secondary hydroxy groups located in the pentacyclic part of the molecule.

It may be concluded from a comparison of the PMR spectra of the diacetate (VI) and of the keto derivative (VIII) that in the former compound one of the multiplets of the two-proton signal at 4.38 ppm belongs to the proton at C-16. As was to be expected, in the triacetate (VII) the signal of this proton is shifted downfield and appears at 5.16 ppm.

The molecular rotation increment between the triacetate of the acetonide (VII) and the diacetate of the acetonide (VI), $[M]_{D\text{-}VII} = +601°$, $[M]_{D\text{-}VI} = +395°$ $\{\Delta[M]_D = +206°\}$ shows the β-orientation of the C-16 hydroxy group [7].

The positions and configurations of the two remaining unidentified hydroxy groups were found by a comparative study of the PMR spectra of compound (V), of cycloasgenin C (I), of cycloasgenin A [1], and of cyclosieversigenin [2].

The PMR spectrum of the product of the periodate oxidation of (V) ($CDCl_3$) contains a one-proton quartet at 3.25 ppm with $^3J = 10.8$ and 4.5 Hz. The good agreement of the parameters of this signal with the analogous index of the 3α-H atom of cyclosieversigenin and of triterpenoids of the dammarane series [8-10] shows the presence of a 3β-hydroxy group in the molecule of the compound under discussion and, consequently, also in the cycloasgenin C molecule.

In the PMR spectrum of cycloasgenin C (C_5D_5N), just as in the spectra of cycloasgenin A [1] and of cyclosieversigenin [2], thanks to the influence of a closely adjacent hydroxyl, one of the methyl groups experiences a descreening effect and resonates at 1.73 ppm. On this basis, it is possible to arrive at the conclusion that the cycloasgenin C molecule also contains a hydroxy group at C-6. In actual fact, in the PMR spectrum ($CDCl_3$) of substance (V) at 3.50 ppm there is a sextet signal of a proton in the geminal position to this hydroxyl. The values of the chemical shift and the spin-spin coupling constants ($^3J_1 \simeq {}^3J_2 \simeq 9.4$; $^3J_3 = 3.6$ Hz) unambiguously determine the β orientation of this proton, which means the α orientation of the hydroxy group at C-6 [1, 2].

As has been shown, the product of the periodate oxidation of (V) is an intramolecular hemiacetal. This conclusion is confirmed by the PMR spectrum of the compound in question in which the signal of an anomeric proton at C-24 can readily be seen at 4.73 ppm (C_5D_5N). Furthermore, the H-16 signal undergoes a diamagnetic shift by −0.41 ppm as compared with the corresponding signal in the spectrum of cycloasgenin C. All this permits compound (V) to be determined as 16β,24ξ-epoxy-25-norcycloartane-3β,6α,24-triol.

The absolute configuration of the C-24 chiral center was established by a modification of Nakanishi's method [11]. For this purpose, the 3,6,16-triacetate-24,25-acetonide (VII) was treated with acetic anhydride, giving the 3,6,16-triacetate-24,25-diol (IX). The circular dichroism spectrum of this compound taken in the presence of $Eu(fod)_3$ showed a negative Cotton effect at 320 nm ($\Delta\xi = -6.05$). This fact leads to the conclusion that compound (IX) has the 24R absolute configuration [12].

Summarizing the discussion, we are justified in concluding that cycloasgenin C is 24(R)-cycloartane-3β,6α,16β,24,25-pentaol.

EXPERIMENTAL

General Observations (see [1]). The following solvent systems were used: 1) benzene—ethyl acetate (1:1); 2) chloroform—methanol (15:1); 3) chloroform—ethyl acetate (1:3); 4) benzene—chloroform—ethyl acetate (5:1:1); 5) chloroform—ethyl acetate (1:1); 6) chloroform—methanol—water (70:23:4). For column chromatography we used type L silica gel with grain dimensions of 50-100 μm.

Isolation of the Isoprenoids. The dried and ground roots (5.3 kg) of the plant *Astragalus taschkendicus* Bge., collected on May 20, 1980 (Tadzh. SSR, valley of R. Shar-Shar, Babatag range) were exhaustively extracted with methanol (100 liters) at room temperature. The combined isoprenoids were obtained from the methanolic extract as described previously [1]. Part of the total material (100 g) was chromatographed in system 2, and a fraction of weakly polar compounds was collected. Continuing the elution of the column with system 6, the individual substances C, D, E, F were isolated [1]. The repeated rechromatography of the total weakly polar components led to the isolation of 50 mg (0.0024%) of cyclosieversigenin [2] and 100 mg (0.0048%) of cycloasgenin C.

Cyclosieversigenin, $C_{30}H_{50}O_5$, mp 239-241°C (from methanol), $[\alpha]_D^{29}$ +50.6 ± 2° (c 1.59; methanol) [2].

methanol); ν_{max}^{KBr} (cm^{-1}): 3480-3350 (OH), 3040 (CH_2 of a cyclopropane ring). Mass spectrum, m/z (%):

Cycloasgenin C (I), $C_{30}H_{52}O_5$, mp 244-246°C (from acetone), $[\alpha]_D^{23}$ +33.7 ± 2° (c 1.18; methanol); ν_{max}^{KBr} (cm^{-1}): 3480-3350 (OH), 3040 (CH_2 of a cyclopropane ring). Mass spectrum, m/z (%): M^+ 492 (7.0), 474 (100), 459 (44.2), 456 (72.1), 441 (46.5), 438 (14.0), 430 (16.3), 423 (40.7), 415 (39.6), 405 (22.1), 397 (48.8), 379 (25.6), 355 (7.0), 329 (25.6), 311 (34.9).

The 3,6,16,24,25-Pentaacetate (III) and the 3,6,16,24-Tetraacetate (II) of Cycloasgenin C from (I). Cycloasgenin C (I) (150 mg) was acetylated with 2 ml of acetic anhydride in 4 ml of pyridine at room temperature for 36 h. The reaction mixture was poured into ice water, and the precipitate that deposited was filtered off. The reaction products were separated on a column with elution by system 1. This gave 9 mg of the 3,6,16,24,25-pentaacetate (III), $C_{40}H_{62}O_{10}$, mp 200-202°C (from ethanol), $[\alpha]_D^{25}$ +120.0 ± 2° (c 0.1; methanol), ν_{max}^{KBr} (cm^{-1}): 3040 (CH_2 of a cyclopropane ring), 1730-1720, 1260-1230 (ester group). Mass spectrum, m/z (%): M+ 702 (3.0), 642 (69.7), 582 (100), 567 (60.6), 522 (45.5), 507 (45.5), 471 (9.1), 463 (24.2), 447 (18.2), 413 (33.3), 375 (33.3), 353 (30.3), 315 (71.2), 293 (62.1).

Continuing the elution of the column with the same mixture of solvents led to the isolation of 140 mg of cycloasgenin C 3,6,16,24-tetraacetate (II), $C_{38}H_{60}O_9$, mp 213°C (from ethanol), $[\alpha]_D^{25}$ +91.9 ± 2° (c 0.74; methanol), ν_{max}^{KBr} (cm^{-1}): 3510 (OH), 3045 (CH_2 of a cyclopropane ring), 1730, 1280-1240 (ester group). Mass spectrum, m/z (%): M+ 660 (0.4), 642 (5.5), 600 (28.1), 558 (7.3), 540 (100), 525 (46.9), 480 (100), 471 (12.5), 465 (93.8), 447 (9.4), 437 (12.5), 420 (21.9), 405 (68.8), 353 (37.5), 333 (50.0), 315 (31.3), 293 (81.3), 273 (100), 245 (18.8).

16β,24ξ-Epoxy-25-norcycloartane-3β,6α,24-triol (V) from (I). A solution of 135 mg of cycloasgenin C (I) in 10 ml of methanol was treated with a solution of 140 mg of sodium periodate in 6 ml of water. The reaction was carried out at room temperature with stirring for 5 h. Then the reaction mixture was poured into water and the precipitate that deposited was filtered off. Chromatography of the reaction products on a column with elution by system 2 gave 76 mg of 16β,24ξ-Epoxy-25-norcycloartane-3β,6α,24-triol (V) from (I). $C_{27}H_{44}O_4$, mp 203-204°C (from ethyl acetate), $[\alpha]_D^{22}$ +30.55 ± 2° (c 0.59; methanol), ν_{max}^{KBr} (cm^{-1}): 3740-3340 (OH), 3032 (CH_2 of a cyclopropane ring). Mass spectrum, m/z (%): M^+ 432 (18.2), 414 (100), 399 (56.8), 396 (56.8), 381 (40.9), 371 (20.5), 363 (15.9), 355 (31.8), 331 (20.5), 311 (18.2), 293 (9.1), 284 (20.5), 256 (63.6), 249 (25.0), 246 (25.0), 231 (23.9), 228 (23.9), 213 (29.5), 185 (34.1).

Cycloasgenin C 24,25-Acetonide (IV) from (I). Cycloasgenin C (I) (500 mg) was treated with 20 ml of dry acetone containing 0.2% of sulfuric acid. The reaction mixture was stirred at room temperature for 6 h. Then 70 ml of water was added and the reaction products were extracted with chloroform. The chloroform extracts were washed with water to neutrality, dried over anhydrous sodium sulfate, and evaporated to dryness. The residue was chromatographed on a column with elution by system 3. This gave 480 mg of cycloasgenin C 24,25-acetonide (IV), $C_{33}H_{56}O_5$, mp 188-189°C (from ethyl acetate), $[\alpha]_D^{24}$ +59.5 ± 2° (c 0.84; methanol); ν_{max}^{KBr} (cm^{-1}): 3510-3430 (OH), 3040 (CH_2 of a cyclopropane ring). Mass spectrum m/z (%): M^+ 532 (1.2), 517 (66.7), 514 (16.7), 499 (11.1), 496 (11.1), 474 (10.2), 456 (50.0), 441 (50.0), 438 (13.0), 423 (58.3), 405 (25.0), 401 (33.3), 329 (91.7), 311 (100), 201 (41.7).

The 3,6,16-Triacetate 24,25-Acetonide (VII) and 3,6-Diacetate 24,25-Acetonide (VI) of Cycloasgenin C from (IV). The acetylation of 400 mg of cycloasgenin C 24,25-acetonide (IV) was carried out with 3 ml of acetic anhydride in 6 ml of pyridine at room temperature for 6 h. The reaction mixture was poured into ice water and the resulting precipitate was filtered off. The reaction products were separated by chromatography on a column, with elution by system 4. This 205 mg of cycloasgenin C 3,6,16-triacetate 24,25-acetonide (VII), $C_{39}H_{62}O_8$, mp 133-134°C (from methanol), $[\alpha]_D^{24}$ +91.3 ± 2° (c 0.6; methanol); ν_{max}^{KBr} (cm^{-1}): 1740, 1250 (ester group). Mass spectrum, m/z (%): M^+ 658 (0.5), 643 (45.5), 598 (18.2), 583 (1.8),

556 (4.7), 538 (81.8), 523 (22.1), 480 (24.7), 463 (27.3), 421 (29.9), 413 (26.0), 405 (45.5), 353 (24.7), 331 (16.9), 311 (18.2), 293 (63.6), 273 (100).

Continuing the elution of the column with the same system of solvents, we isolated 190 mg of cycloasgenin C 3,6-diacetate 24,25-acetonide (VI), $C_{37}H_{60}O_7$, mp 159-160°C (from methanol, $[\alpha]_D^{23}$ +64.2 ± 2° (c 0.53; methanol); ν_{max}^{KBr} (cm^{-1}): 3540-3510 (OH), 3050 (CH_2 of a cyclopropane ring), 1725, 1255 (ester group). Mass spectrum, m/z (%): M^+ 616 (0.1), 601 (54.5), 556 (53.3), 541 (21.2), 496 (78.8), 481 (36.4), 438 (24.2), 423 (36.4), 413 (30.3), 405 (39.4), 369 (13.6), 353 (21.2), 331 (9.1), 311 (18.2), 293 (45.5), 273 (100), 201 (81.8).

3β,6α,24,25-Tetrahydroxy-24(R)-cycloartan-16-one 3,6-Diacetate 24,25-Acetonide (VIII) from (VI). Cycloasgenin C 3,6-diacetate 24,25-acetonide (VI) (120 mg) was oxidized with 0.3 ml of the Jones reagent [5] in 30 ml of acetone at −10°C for 30 min. Then the reaction mixture was poured into 60 ml of water containing 1 g of Na_2SO_3. The reaction products were extracted with chloroform. The chloroform extract was washed with water, dried over anhydrous sodium sulfate, and evaporated to dryness. The residue was chromatographed on a column with elution by system 4. This yielded 100 mg of 3β,6α,24,25-tetrahydroxy-24(R)-cycloartan-16-one 3,6-diacetate 24,25-acetonide (VIII), $C_{37}H_{58}O_7$, mp 130-131°C (from methanol), $[\alpha]_D^{27}$ 0 + 3° (c 0.23; methanol); ν_{max}^{KBr} (cm^{-1}): 3042 (CH_2 of a cyclopropane ring), 1742 (C=O at C-16), 1730, 1260-1240 (ester group). CD (c 0.1; methanol), $\Delta\varepsilon$ = −5.09 (305 nm). Mass spectrum, m/z (%): M^+ 614 (0.6), 599 (58.3), 557 (25.0), 539 (62.5), 494 (50.0), 485 (45.8), 437 (37.5), 421 (100), 403 (25.0), 393 (16.7), 378 (29.2), 363 (29.2), 309 (29.2).

Cycloasgenin C 3,6,16-Triacetate (IX) from (VII). A mixture of 60 mg of cycloasgenin C 3,6,16-triacetate 24,25-acetonide (VII) and 10 ml of glacial acetic acid was heated in the boiling water bath for 8 h. After the addition of 30 ml of water, the reaction mixture was extracted with chloroform. The residue obtained after the evaporation of the chloroform was chromatographed on a column of silica gel with elution by system 5. This gave 40 mg of compound (IX), $C_{36}H_{58}O_8$, mp 179-180°C (from methanol), $[\alpha]_D^{25}$ +86.6 ± 2° (c 0.3; methanol); ν_{max}^{KBr} (cm^{-1}): 3480-3400 (OH), 1730-1720, 1265-1240 (ester group). Mass spectrum, m/z (%): M^+ 618 (0.5), 600 (1.8), 558 (58.1), 540 (16.1), 498 (100), 483 (58.1), 480 (22.6), 465 (14.5), 439 (48.4), 429 (22.6), 423 (51.6), 413 (41.9), 405 (22.6), 379 (32.3), 365 (19.4), 353 (25.8), 311 (22.6), 293 (54.8), 291 (48.4), 273 (32.3), 201 (61.3), 185 (64.5), 145 (58.1).

To measure the CD curve, we took aliquot volumes of 0.0002 M solutions of $Eu(fod)_3$ and of substance (IX) in absolute CCl_4 [11, 12]; $\Delta\varepsilon$ = −6.05 (320 nm).

Methanolysis of the Combined Glycosides E and F. A solution of 15 g of the combined glycosides E and F [1] in 1.5 liter of methanol containing 0.5% of sulfuric acid was boiled on the water bath for 2 h. The methanol was evaporated to half its initial volume, the residue was diluted with water to 1.5 liter, and the remaining methanol was distilled off. The precipitate that deposited was filtered off. The combined genins so obtained were separated on a column of silica gel with elution by system 2. This yielded 2.75 g of cyclosieversigenin with mp 239-241°C (from methanol), $[\alpha]_D^{29}$ + 51.0 ± 2° (c 1.5; methanol) [2]. Continuing the elution of the column with system 6 yielded 0.75 g of a compound which was identified by its spectral characteristics and physicochemical constants as cycloasgenin C (I), mp 244-246°C (from acetone), $[\alpha]_D^{25}$ +34.1 ± 2° (c 1.3; methanol). .

SUMMARY

The roots of the plant *Astragalus taschkendicus* Bge. have yielded a new isoprenoid — cycloasgenin C, which has the structure of 24(R)-cycloartane-3β,6α,16β,24,25-pentaol.

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GLYCOSIDES OF MARINE INVERTEBRATES.

XV. A NEW TRITERPENE GLYCOSIDE — HOLOTHURIN A_1 — FROM CARIBBEAN HOLOTHURIANS OF THE FAMILY HOLOTHURIIDAE*

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A glycoside, holothurin A_1 has been isolated from the polar glyosidic fractions of the holothurians *H. floridana* and *H. grisea*. The complete structure of the glycoside has been established; it is: 3β-[O-(3-O-methyl-β-D-glucopyranosyl)-(1 → 3)-O-β-D-glucopyranosyl-(1 → 4)-O-β-D-quinovopyranosyl-(1 → 2)-(4-sulfato-β-D-xylopyranosyl)oxy]holosta-9(11)-ene-12α,17α,22ξ-triol. Details of the IR and ^1H and ^{13}C NMR spectra of the compounds obtained are given.

It has been established that holothurians of the family of Holothuriidae synthesize, in addition to triterpene biosides (holothurins B), a series of polar glycosides — tetraosides (holothurins A) [1, 2] and hexaosides (bivittosides [3]). The results of a study of the products of acid hydrolysis of these metabolites has permitted the conclusion to be drawn that they are not individual compounds but difficulty separable mixtures of substances close in structure. The sets of components in these mixtures are different for different species of holothurians [1]. Recently, in connection with the study of the mechanism of the physiological action of the holothurian triterpene glycosides and the biosynthesis of these compounds, great value has been placed upon work on the isolation of individual substances from the glycosidic fractions and the determination of their complete chemical structures. For glycosides of the holothurin A type, the chemical structures of only a few oligosides having the aglycones (I) and (II) have been established [4, 5].

We have shown that in the polar glycosidic fractions of holothurians of the sublittoral of the island of Cuba, *Holothuria floridana* and *Holothuria grisea* (the species of holothurian were determined by V. V. Kiselev), include a new triterpene glycoside — holothurin A_1.

The compositions of the holothurin A fractions of the holothurians studied were different. Thus, the glycosidic fraction of the holothurian *H. floridana* contained, in addition to holothurin A_1 (65%), a glycoside with the aglycone (I), and the same fraction of *H. grisea* also contained oligosides with the genins (I), (II), and (IIa). To separate compounds so close in structure we used reversed-phase chromatography on Polykhrom-1 and isolated the individual holothurin A_1 (IV) from the glycosidic fraction of *H. floridana*. The IR spectrum of (IV)

*For Communication XIV, see. p. 449.

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