TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS.

III. CYCLOASGENIN A FROM *Astragalus taschkendicus*

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The new isoprenoid cycloasgenin A has been isolated from the roots of the plant *Astragalus taschkendicus* C. Bge., and its structure has been established on the basis of chemical transformations and spectral characteristics as 6α,11α,16β, 25-tetrahydroxy-20(S),24(R)-epoxycycloartan-3-one.

Continuing a study of the isoprenoids of plants of the genus *Astragalus* [1], from a methanolic extract of the roots of *Astragalus taschkendicus* C. Bge. we have isolated six compounds denoted in order of increasing polarity A, B, C, D, E, and F. Substances A and B are genins and the others proved to be glycosides. In the present paper we give a proof of the structure of compound A, which we have called cycloasgenin A (I, Scheme 1)

The molecular formula of the genin, $C_{30}H_{48}O_6$, and the presence in the PMR spectrum of signals from seven CH_3 groups (Table 1) and also of two one-proton doublets at 0.45 and 1.63 ppm interacting in the manner of a AB system has permitted compound (I) to be assigned to the methylsteroids of the cycloartane series [2]. A confirmation of this is the presence in the IR spectrum of cycloasgenin A of an absorption band at 3060 cm^{-1} due to a cyclopropane ring [3]. The mass-spectrometric fragmentation, leading to the splitting out of ring A and to the formation of an ion with m/z 365 (Scheme 2) is also characteristic for the cycloartanes [4].

The IR spectrum of cycloasgenin A has, in addition to that mentioned, another two absorption bands, at 3450-3300 cm^{-1} (OH) and 1695 cm^{-1} (C=O). The absence of a resonance signal of an aldehyde proton in the PMR spectrum and the presence in the ^{13}C NMR spectrum of compound (I) of a signal at 216.9 ppm show that the carbonyl absorption is due to a keto group.

It is known [5] that in the ^{13}C NMR spectrum of cycloartanol signals characteristic for the C-3 and C-4 carbon atoms appear at 78.5 and 40.3 ppm, respectively. In the case of its 3-keto derivative, these signals are located at 215.1 and 50.0 ppm, i.e., under the action of a 3-keto group the C-4 chemical shift undergoes a change of +9.7 ppm. In the ^{13}C NMR spectrum of cycloasgenin A the signal characteristic of a C-3 carbon atom to which a hydroxyl is attached is absent. The carbon atom of the ketone group resonates at 216.9 ppm, and the signal of the quaternary C-4 atom appears at 50.6 ppm. Consequently, in the genin (I) the ketone group is present at C-3.

The acetylation of cycloasgenin A with acetic anhydride in pyridine led to the diacetate (IV) and the triacetate (V). A comparison of the PMR spectral characteristics (Table 1) of the genin(I) and its acetates (IV) and (V) permitted the one-proton multiplets in the PMR spectrum of the triacetate (V) at 4.85, 5.11, and 5.44 ppm to be assigned to protons geminal to three secondary hydroxy groups.

The presence of the 100% peak of an ion with m/z 143 (Scheme 2) in the mass spectrum of each of compounds (I), (IV), and (V) and also of one-proton H-24 signals at 3.74, 3.69, and 3.77 ppm, respectively, in the PMR spectra of the genin (I) and the acetates (IV) and (V) show that the side chain of each of the compounds under discussion has a structure similar to that of the side chain of cyclosieversigenin (III) [1].

It is not a matter of doubt that in the molecule of cycloasgenin A (I) the three secondary hydroxy groups are present in the pentacyclic nucleus and the one tertiary hydroxy group in the side chain.

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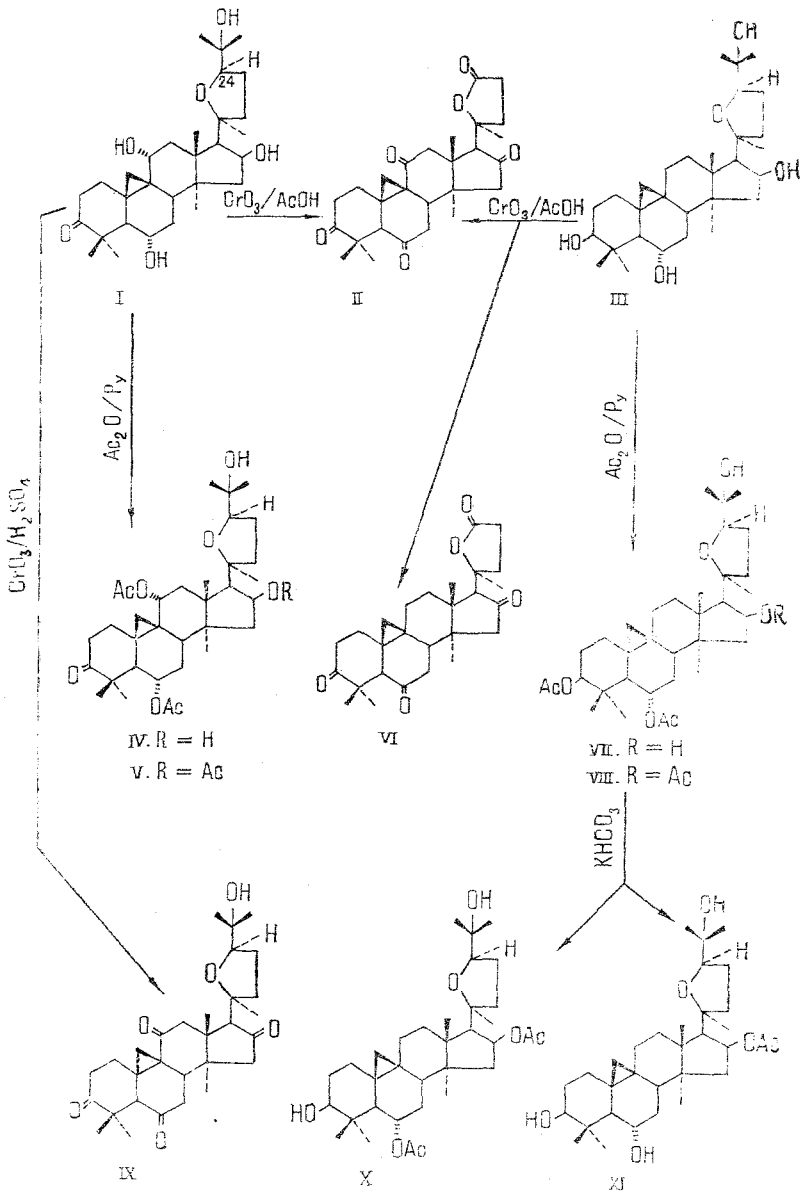


Scheme 1

The peak of the ion with m/z 365 ($C_{21}H_{33}O_5$) in the mass spectrum of the genin (I) and the fragments with m/z 450 and 492 corresponding to it in the mass spectra of the diacetate (IV) and the triacetate (V) permit the assumption that the secondary hydroxy groups are located in rings B, C, and D. This nature of the fragmentation is a new confirmation of the conclusion that the ketonic carbonyl is present in ring A.

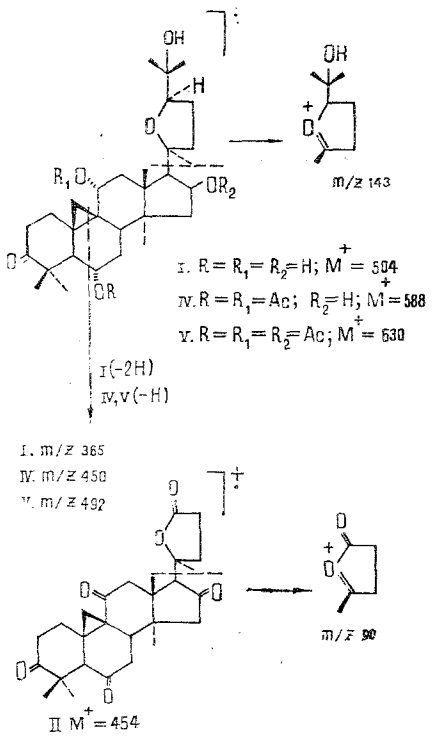
The negative periodate oxidation reaction of cycloasgenin A, showing the absence of an α-diol grouping, excludes the possibility of the presence of two hydroxy groups in the same ring.

The Jones [6] oxidation of cycloasgenin A (I) led to the tetraketone (IX). The IR spectrum of this compound has, in the region of absorption of carbonyl groups, maxima characteristic for five-membered (1740 cm^{-1}) and six-membered (1708 cm^{-1}) cyclic ketones, and also a band at 1675 cm^{-1}. The lowered frequency of the last-mentioned band is obviously due to the conjugation of the keto group in ring C with the 9,19-cyclopropane ring [7]. Thus, in compound (IX) the keto group, and therefore also the hydroxy function of cycloasgenin A, is located in ring C at the 11th carbon atom.

TABLE 1. Chemical Shifts of the Protons of Cycloasgenin A (1) and Cyclosieversigenin (III) and Their Derivatives (δ, ppm, O — HMDS)

Compound	Positions of the protons						
	H-3	H-6	H-11	H-16	2H-19	H-24	CH_3 groups
I	—	3,71 m	4,19 q (^3J=9,9; 2,5 Hz)	4,90 q (^3J=7,3; 7,3; 7,3 Hz)	0,45; 1,63 d (^2J=4,0 Hz)	3,74 q (^3J=8,8; 5,6 Hz)	0,85; 1,17; 1,21; 1,42; 1,43; 1,46; 1,70
II	—	—	—	—		—	1,03; 1,19; 1,25; 1,31; 1,43
III	~3,57m	~3,57 m		4,90 q (^3J = 7,0 Hz)	0,23; 0,51 d (^2J=4,0 Hz)	3,78 q	0,90; 1,18; 1,20; 1,25; 1,33; 1,45; 1,78
IV	—	4,85 m	5,13 q (^3J=6,8; 2,0 Hz)	4,78m	0,63; 0,81 d (^2J=5,8 Hz)	3,69 q (^3J=8,2; 5,4 Hz)	0,84; 1,04; 1,06; 1,08; 1,14; 1,34; 1,41 (1,90; 1,93 —OAc)
V	—	4,85 m	5,11 q	5,44m	0,63; 0,89 d (^2J=5,8 Hz)	3,77 t (Σ J =14 Hz	0,78; 1,05; 1,07; 1,19; 1,24; 1,24; 1,30 (1,88; 1,91; 1,98—OAc)
VI	—	—		—		—	0,93; 1,01; 1,16; 1,32; 1,45
IX	—	—	—	—		3,71 t (ΣJ=14 Hz)	1,04; 1,10; 1,16; 1,19; 1,19; 1,29; 1,42
X	3,41 q (^3J=10,6; 5,0 Hz)	4,87 d,t (^3J=10,0; 10,0; 3,7 Hz)		5,41 m	0,19; 0,47 d (^2J—4,5 Hz)	3,79 t (Σ J=15 Hz)	0,79; 1,11; 1,17; 1,24; 1,24; 1,26; 1,27 (1,95; 2,03—OAc)
XI	~3,54m	~3,54m		5,45m	0,21; 0,52 d (^2J=4,5 Hz)	3,80 t (Σ J= 15 Hz)	0,85; 1,22; 1,23; 1,24; 1,24; 1,24; 1,74 (1,98 —OAc)

Note. The spectra of the compounds mentioned were taken in deuterochloroform. Abbreviations: s) singlet; d) doublet; t) triplet; dt) doublet of triplets; q) quartet; m) multiplet. All the signals from methyl groups were of singlet nature.



Scheme 2

It was mentioned above that the resonance signals of the cyclopropane protons of the genin (I) appear at 0.45 and 1.63 ppm. The corresponding protons of cyclosieversigenin (III) resonate at 0.23 and 0.51 ppm. From a comparison of the first chemical shifts in each of the pairs mentioned it can be seen that one of the cyclopropane protons of compound (I) is descreened by 0.22 ppm. The difference in the values of the chemical shifts becomes understandable if the known descreening influence of a hydroxy group at C-11 [8] and of a carbonyl at C-3 [9, 10] is taken into account. The considerable difference in the chemical shifts of the other proton at C-19 in compounds (I) and (III) ($\Delta\delta$ = 1.12 ppm) can be explained by the spatial propinquity of this proton to the hydroxy group at C-11. In this case, the influence of the above-mentioned factors is summed with the specific descreening action of the solvent — pyridine [11]. The correctness of this explanation is confirmed by the small difference in the chemical shifts of the C-19 methylene protons in the acetates (IV) and (V) (0.18-0.26 ppm), since the acetylation of the 11-hydroxy group in compound (I) eliminates the action of the pyridine.

In the PMR spectrum of compound (I) at 4.19 ppm there is a one-proton quartet signal of the proton geminal to the hydroxy group at C-11. This proton couples vicinally with the two methylene protons at C-12, with ^3J = 9.9 and 2.5 Hz. The values of the spin—spin coupling constants of the proton under consideration show its β-axial orientation and, consequently the α-orientation of the hydroxy group at C-11.

The positions and configurations of the hydroxy groups in rings B and D were ascertained in the following way.

The acetylation of cyclosieversigenin (III) gave the diacetate (VII) and the triacetate (VIII), which have been described previously [1]. Selective saponification of the triacetate (VIII) led to the diacetate (X) and the monoacetate (XI). A comparison of the PMR spectra of cyclosieversigenin (III), the triacetate (VIII), and the diacetate (X) permitted the signals at 3.41, 4.87, and 5.41 ppm in the spectrum of compound (X) to be assigned to the H-3, H-6, and H-16 protons, respectively. It follows from this that substance (X) is the 6,16-diacetate of cyclosieversigenin. The appearance in the PMR spectrum of the acetate (XI) of a

signal at 5.45 ppm corresponding to H-16 permitted this compound to be determined as the 16-monoacetate of cyclosieversigenin.

The signal of the H-6 proton at 4.87 ppm in the PMR spectrum of the diacetate (X) consists of a sextet with the coupling constants $^3J_1 = {}^3J_2 = 10.0$ Hz and $^3J_3 = 3.7$ Hz. The analogous signal observed in the PMR spectrum of the triacetate of cycloasgenin A (V) shows that the hydroxy group in ring B is located at C-6 and has the α configuration.

The signal of the proton geminal to the remaining, unidentified, hydroxy group in the PMR spectrum of the genin (I) appears at 4.90 ppm in the form of a quartet with an intensity distribution of its lines as 1 : 3 : 3 : 1, and with $^3J_1 \simeq {}^3J_2 = {}^3J_3 = 7.3$ Hz. The proton under consideration interacts with three hydrogen atoms located vicinally to it with extremely close values of the SSCCs, as was established by using the method of multifrequency resonance. The agreement of the values of the chemical shift and the nature of the multiplicity if this signal with the analogous indices of the spectrum of cyclosieversigenin (III) shows that the molecule of cycloasgenin A has a 16β-hydroxy group.

As was to be expected, in the PMR spectrum of triacetate (V) the signals of the protons geminal to the C-6, C-11, and C-16 hydroxy groups are shifted downfield in relation to those of compound (I) and are formed at 4.85, 5.11, and 5.44 ppm, respectively. At the same time, as can be seen from Table 1, in the acetate (IV) a free hydroxy group remained at C-16 (H-16 chemical shift = 4.87 ppm). Consequently, there is no doubt that this derivative is the 6,11-diacetate of cycloasgenin A.

The increment in molecular rotation between the triacetate (V) and the diacetate (IV) ($[M]_{D-V} = +745°$; $[M]_{D-IV} = +536°$, $\Delta[M]_D = +209°$) confirms the β orientation of the hydroxy group at C-16 [12].

The positions of the hydroxy groups in the pentacyclic nucleus of cycloasgenin A were also confirmed by the passage from the genin (I) and cyclosieversigenin in (III) to one and the same compound (II).

The oxidation of cycloasgenin A with CrO_3 in glacial acetic acid led to the tetraketolactone (II) with a molecular weight of 454. The mass spectrum of this product lacked an ion with m/z 143 but showed the presence of a fragment with m/z 99 formed as the result of the cleavage of the C-17—C-20 bond (Scheme 2). As was to be expected, the IR spectrum of the oxidized derivative (II) showed absorption bands at 1672, 1705, and 1737 cm^{-1} corresponding to the keto groups of the cyclic moiety, and an additional band at 1760 cm^{-1} relating to the C=O vibrations of a γ-lactone [13].

On the basis of the fact that the treatment of the 3-acetate of cycloartanol with chromium trioxide leads to 11-oxocycloartanone, in order to introduce a keto group into position 11, we oxidized cyclosieversigenin (III) with CrO_3 in glacial acetic acid. This gave compounds (II) and (VI). Substance (VI), isolated with a yield of 25%, had bands in the IR spectrum at 1710, 1715, and 1734 cm^{-1} (carbonyl C=O groups) and at 1770 cm^{-1} (γ-lactone C=O). These characteristics, and also the molecular weight of 440 and the presence in the mass spectrum of a fragment with m/z 99 show that this compound is the 3,6,16-trioxolactone (VI).

The other oxidation product, isolated in low yield, was identified from its melting point, R_f value on TLC, and the indices of its mass and IR spectra as the 3,6,11,16-tetraketolactone (II).

The formation of the tetraketolactone (II) from cyclosieversigenin (III) unambiguously determines the position of the oxygen functions in the pentacyclic nucleus of cycloasgenin A at C-3, C-6, C-11, and C-16 and, in addition, the S configuration of C-20 in the side chain. The agreement of the H-24 chemical shifts in the PMR spectra of the genin (I) and the acetates (IV) and (V) with the corresponding figures for cyclosieversigenin (III) and its acetates (VIII), (X), and (XI) shows the R orientation of the C-24 chiral center in the molecule of (I).

Thus, cycloasgenin A is 6α,11α,16β,25-tetrahydroxy-20(S),24(R)-epoxycycloartan-3-one.

EXPERIMENTAL

General Observations. Thin-layer chromatography (TLC) was performed on plates prepared from type L silica gel (< 50 μ) containing 7% of gypsum and on Silufol plates. In TLC the compounds were revealed by spraying with 25% methanolic tungstophosphoric acid followed by

heating at 100-110°C for 2-5 min. For column chromatography we used the same type of silica gel with a grain size of 50-100 μ. The following solvent systems were used: 1) chloroform—methanol (15 : 1); 2) chloroform—methanol—water (70 : 23 : 4); 3) benzene—ethyl acetate (2 : 1); 4) benzene—ethyl acetate (1 : 1); and 5) chloroform—hexane—ethyl acetate (1 : 1 : 1).

The mass spectra and the elementary compositions of the ions were measured in an MKh-1310 instrument at an ionization voltage of 50 V and a temperature of 130-170°C. IR spectra were recorded on a UR-20 spectrophotometer in KBr, PMR spectra on a JNM-4H-100 spectrometer in C_5D_5N (δ, 0 — HDMS), and ^{13}C NMR spectra on a Varian CFT-20 instrument in C_5D_5N (δ, 0 — TMS).

Circular dichroism curves were measured on a Jasco J-20 spectropolarimeter.

Isolation of the Isoprenoids. The dried and comminuted roots (1.8 kg) of the plant *Astragalus taschkendicus* gathered in May, 1979 (TadzhSSR, gorge of the Shar-Shar river, Baba-Dag range) were exhaustively extracted with methanol (40 liters) at room temperature. The methanolic extracts were evaporated to a volume of 1 liter. The precipitate that had deposited (22.4 g, precipitate A), consisting of glycosides E and F (TLC, system 2), was filtered off. The mother liquor was evaporated and the dry extract (206 g) was dissolved in 1 liter of methanol, and then 3 liters of chloroform was added with constant stirring. After an hour, the supernatant liquid was poured off. The resinous residue did not, according to TLC, contain the desired compounds. After the decanted solution had been evaporated, the process was repeated once more, and after the solvent had been driven off 108 g of purified total isoprenoids was obtained and this material was separated by column chromatography. On elution with system 1, 650 mg (0.036%; yields here and below calculated on the air-dry raw material) of cycloasgenin A (I) and 200 mg (0.011 %) of compound B were obtained. Elution of the column in system 2 led to the following substances: C — 150 mg (0.008%); D — 500 mg (0.03%); E — 15.0 g; and F — 5.0 g. The total yield of the isoprenoids E and F, taking precipitate A into account, was 2.35%.

Cycloasgenin A (I). $C_{30}H_{48}O_6$, mp 235-236°C (from methanol), $[\alpha]_D^{23}$ + 130 ± 2° (c 0.77; methanol); ν_{max}^{KBr} (cm^{-1}); 3450-3350 (OH), 3060 (CH_2 of a cyclopropane ring), 1695-1706 (C=O); CD (c 0.1; methanol) Δε = −0.1 (320 nm); Δε = +1.44 (287 nm). (The CD indices, uncharacteristic for 3-keto derivatives of cycloartane, are apparently explained by the influence of the 6α-hydroxy group. This effect will be discussed in more detail subsequently. Mass spectrum m/z (%): M^+ 504 (0.82), 486 (8.0), 468 (5.6), 450 (3.7), 442 (3.7), 435 (3.0), 427 (4.9), 409 (8.0), 391 (4.9), 365 (34), 349 (7.4), 347 (3.0), 143 (100), 125 (33.3).

The 6,11,16-Triacetate (V) and the 6,11-Diacetate (IV) of Cycloasgenin A. The acetylation of 150 mg of cycloasgenin A was carried out with 2 ml of acetic anhydride in 4 ml of pyridine at room temperature for 12 h. The reaction mixture was poured into cold water and the resulting precipitate was filtered off. The reaction products were separated in a column with elution by system 3. This gave 30 mg of the amorphous 6,11,16-triacetate of cycloasgenin A (V), $C_{36}H_{54}O_9$, $[\alpha]_D^{32}$ + 118.4 ± 2° (c 0.76; methanol); ν_{max}^{KBr} (cm^{-1}): 3560-3540 (OH), 3060 (CH_2 of a cyclopropane ring), 1718 (C=O), 1745, 1255-1245 (ester group). Mass spectrum, m/z (%): M^+ 630 (5, 3); 615 (0.95), 570 (2.9), 555 (2.1), 542 (2.3), 528 (5.7), 510 (18.0), 495 (4.9), 492 (4.8), 468 (3.8), 450 (18), 435 (4.8), 432 (6.2), 391 (9.0), 307 (6.7), 306 (4.8), 305 (6.7), 279 (7.6), 266 (28.5), 256 (15.7), 143 (100), 125 (28.6).

When elution of the column was continued in the same system, 65 mg of the amorphous 6,11-diacetate of cycloasgenin A (IV) was obtained, $C_{34}H_{52}O_8$, $[\alpha]_D^{31}$ + 91.2 ± 2°, (c 1.25; methanol); ν_{max}^{KBr} (cm^{-1}): 3430-3340 (OH), 3060 (CH_2 of a cyclic propane ring), 1718 (C=O), 1745-1735, 1250 (ester group). Mass spectrum m/z (%): M^+ 588 (1.0), 573 (0.6), 528 (1.5), 510 (2.2). 468 (9.2), 450 (7.7), 435 (4.0), 432 (3.3), 392 (5.9), 391 (8.8), 373 (2.9), 307 (6.3), 305 (5.1), 143 (100), 125 (29.4).

25-Hydroxy-20(S),24(R)-epoxycycloartane-3,6,11,16-tetraone (IX) from (I). A solution of 70 mg of cycloasgenin A (I) in 70 ml of acetone was treated at 0°C with 0.3 ml of the Jones reagent and the mixture was stirred for 25 min. Then it was poured into 200 ml of water containing 1.5 g of Na_2SO_3, and the reaction products were extracted with chloroform. The chloroform extract was washed with dilute sulfuric acid and with water, and the solvent was evaporated off. The oxidation products were separated on a column with elution by system 4. This gave 50 mg of 25-hydroxy-20(S),24(R)-epoxyartane-3,6,11,16-tetraone (IX), $C_{30}H_{42}O_6$, mp 245-246°C (from methanol), $[\alpha]_D^{23}$ 0 ± 3° (c 0.3; chloroform); ν_{max}^{KBr} (cm^{-1}): 3475, 3440 (OH), 3040 (CH_2 of a cyclopropane ring); 1740 (C=O at C-16), 1708 (C=O groups at C-3 and C-6), 1675

(C=O at C-11). Mass spectra, m/z (%): M^+ 498 (7.8), 483 (8.4), 480 (10.9), 465 (12.5), 440 (50), 439 (37.5), 397 (43.8), 396 (28.1), 379 (12.5), 149 (34.4), 143 (37.5), 125 (100).

The 3,6,11,16-Tetraketolactone (II) from (I). A solution of 130 mg of CrO_3 in 14 ml of glacial acetic acid was added to a solution of 80 mg of cycloasgenin A (I) in 5 ml of the same solvent, and the mixture was left at room temperature for 12 h. Then it was poured into 40 ml of water. The excess of oxidizing agent was decomposed by the addition of 10 ml of isopropanol. The reaction products were extracted with chloroform. After the usual working up and evaporation of the solvent, 61 mg was obtained of a crude product which was purified by chromatography in a column using system 4. In this way, 37 mg of the 3,6,11,16-tetraketolactone (II) was isolated; $C_{27}H_{34}O_6$, mp 200-201°C (from methanol), $[\alpha]_D^{22}$ 0 ± 3° (c 0.73; chloroform); ν_{max}^{KBr} (cm^{-1}): 1760 (C=O of a γ-lactone ring), 1737 (C=O at C-16), 1705 (C=O at C-3 and C-6), 1672 (C=O at C-11). Mass spectrum, m/z (%): M^+ 454 (100), 436 (8.57), 426 (18.3), 421 (12); 411 (12.6), 408 (5.7), 397 (10.3), 393 (21), 383 (9.7), 341 (9.7), 317 (13), 149 (24).

The 3,6-Diacetate (VII) and the 3,6,16-Triacetate (VIII) of Cyclosieversigenin. The acetylation of 1.111 g of cyclosieversigenin (III) with 11 ml of acetic anhydride in 22 ml of pyridine at room temperature for a day gave a mixture of acetates which was separated in a column (system 3). In this way, 857 mg of the 3,6,16-triacetate of cyclosieversigenin (VIII) with mp 211-212°C (from methanol) and 69 mg of the 3,6-diacetate of cyclosieversigenin (VIII) with mp 228-229°C (from methanol) [1] were isolated.

The 6,16-Diacetate (X) and the 16-Monoacetate (XI) of Cyclosieversigenin. A solution of 140 mg of $KHCO_3$ in 15 ml of methanol was added to a solution of 743 mg of the 3,6,16-triacetate of cyclosieversigenin in 25 ml of the same solvent, and the mixture was left at 60°C for 72 h. After this, the reaction mixture was poured into 100 ml of water and the reaction products were extracted with chloroform. The residue obtained after the usual working up of the chloroform extract and elimination of the solvent was chromatographed in a column with elution by system 3. This gave 85 mg of the initial cyclosieversigenin 3,6,16-triacetate (VIII) and 480 mg of the noncrystalline cyclosieversigenin 6,16-diacetate (X); $C_{34}C_{53}O_7$, $[\alpha]_D^{23}$ + 120.6 ± 2° (c 0.58; methanol); ν_{max}^{KBr} (cm^{-1}): 3555-3450 (OH), 3045 (CH_2 of a cyclopropane ring), 1740, 1260 (ester group). Mass spectrum, m/z (%): M^+ 574 (0.1), 559 (3.2), 556 (2.3), 515 (9.7), 514 (13.4), 497 (14.4); 496 (25), 481 (2.3), 454 (8.3), 439 (10.6), 437 (9.3), 421 (6.5), 403 (2.3), 396 (10.2), 395 (218), 378 (7.8), 377 (16.2), 271 (7.4), 253 (8.3), 143 (100), 125 (58.3).

The continuation of the elution of the column with the same system led to the isolation of 17 mg of cyclosieversigenin 16-monoacetate (XI), $C_{32}H_{52}O_6$, mp 205-206°C (from methanol), $[\alpha]_D^{23}$ + 85.7 ± 2° (c 0.28; methanol); ν_{max}^{KBr} (cm^{-1}): 3535, 3485 (OH), 3038 (CH_2 of a cyclopropane ring), 1725, 1265 (ester group). Mass spectrum, m/z (%): M^+ 532 (7.5), 514 (37.7), 496 (13.2); 473 (13.2, 473 (13.2), 455 (11.3), 439 (9.4), 421 (4.7), 413 (7.5), 395 (17.0), 377 (9.4), 271 (11.3), 143 (100), 125 (52.8).

The 3,6,16-Triketolactone (VI) and the 3,6,11,16-Tetraketolactone (II) from Cyclosieversigenin. A solution of 1.1 g of CrO_3 in 90 ml of glacial acetic acid was added to a solution of 550 mg of cyclosieversigenin in 50 ml of the same solvent and the mixture was left at room temperature for seven days, Then it was poured into 500 ml of water and 200 ml of isopropanol was added. The mixture was extracted with chloroform. The chloroform extract was washed with dilute sulfuric acid and with water. Then it was dried with anhydrous Na_2SO_4 and the solvent was evaporated off. By chromatography and repeated rechromatography in system 5, the reaction products yielded 138 mg of the 3,6,16-triketolactone (VI). $C_{27}H_{36}O_5$, mp 207-208°C (from methanol) $[\alpha]_D^{20}$ 0 ± 3° (c 0.12; chloroform), ν_{max}^{KBr} (cm^{-1}): 3060 (CH_2 of a cyclopropane ring), 1770 (C=O of a γ-lactone ring), 1733 (C=O at C_{16}), 1718, 1710 (C=O at C-3 and C-6). Mass spectrum, m/z (%): M^+ 440 (52.5), 425 (12.5), 422 (3.5), 412 (25), 407 (6.0), 398 (20.0), 383 (42.5), 379 (5.7), 369 (3.5), 356 (8.7), 342 (8.2), 341 (7.8), 327 (9.7), 301 (2.8), 285 (20.0), 99 (100).

In addition to compound (VI), 5 mg of a substance $C_{27}H_{34}O_6$ with mp 199-200°C (from methanol) was isolated from the reaction mixture; ν_{max}^{KBr} (cm^{-1}): 1760 (C=O of a γ-lactone ring), 1737 (C=O at C-16), 1705 (C=O at C-3 and C-6), 1672 (C=O at C-11). This substance was identical with the 3,6,11,16-tetraketolactone (II) obtained from cycloasgenin A likewise from its R_f values in TLC (systems 4 and 5) and by the indices in its mass spectrum.

SUMMARY

The new isoprenoid cycloasgenin A has been isolated from the roots of the plant *Astragalus taschkendicus* C. Bge.; it has the structure of 6α,11α,16β,25-tetrahydroxy-20(S),24(R)-epoxycycloartan-3-one.

LITERATURE CITED

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STEROID ALCOHOLS FROM THE ASCIDIAN *Halocynthia aurantium*

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The total sterols have been isolated from *Halocynthia aurantium* by column chromatography on silica gel. The following steroid alcohols have been identified in it with the aid of GLC, GLC-MS, and ^{1}H NMR: 5α-cholestan-3β-ol, 24ξ-methylcholestan-3β-ol, 24ξ-ethylcholestan-3β-ol, 4ξ-methyl-24ξ-ethyl-5α-cholestan-3β-ol, cholest-5-en-3β-ol, 24ξ-methylcholest-5-en-3β-ol, 24ξ-ethylcholes-5-en-3β-ol, 5α-cholest-22-en-3β-ol, 24-nor-5α-cholest-22-en-3β-ol, cholesta-5,22-dien-3β-ol, 24ξ-methylcholesta-5,22-dien-3β-ol, 24-norcholesta-5,22-dien-3β-ol, 24-ethylcholesta-5,24(28)-dien-3β-ol, and 24-methylcholesta-5,24(28)-dien-3β-ol.

Continuing a study of the steroid alcohols of ascidians (subtype *Tunicata*, class Ascidiae [1], we have investigated the sterols isolated from the Far Eastern species *Halocynthia aurantium*.

The combined sterols were obtained from a chloroform—methanol extract of the animals after column chromatography on silica gel.

To facilitate their subsequent analysis, the sterols were acetylated with acetic anhydride in pyridine (1 : 1), and were then first separated into groups according to degree of unsaturation by chromatography on a column containing silica gel impregnated with silver nitrate [2]. The separation was monitored by gas—liquid chromatography and thin-layer chromatography (plates coated with silica gel impregnated with silver nitrate) [3]. Each of the acetate fractions obtained was studied by the GLC, GLC-MS, and ^{1}H NMR methods. After the

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