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TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS.

II. THE STRUCTURE OF CYCLOSIEVERSIGENIN

UDC 547.587+581.192

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The bitter plant *Astragalus sieversianus* has yielded a new isoprenoid cyclosieversigenin the structure of which has been established on the basis of spectral characteristics and chemical transformations as 20(S),24(R)-epoxycycloartane-3β,6α,16β,25-tetraol.

The wide genus *Astragalus* (family Leguminosae), which is represented in the flora of the USSR by almost 850 species, has been studied little in the chemical respect. Of its low-molecular weight compounds, there is only a certain amount of information on the flavonoids [1]. We have now investigated the isoprenoids of the Central Asian plant *Astragalus sieversianus* Pall.

The sum of the extractive compounds obtained from the roots by extraction with methanol was subjected to hydrolysis with 8% sulfuric acid. From the reaction products we isolated substances (I) and (IV) with close R_f values — 0.35 and 0.42 respectively.

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Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 67-76, January-February, 1981. Original article submitted July 8, 1980.

0009-3130/81/1701-0060$07.50

The IR spectrum of compound (I), which we have called cyclosieversigenin, showed the presence of hydroxyl absorption (3300-3450 cm^{-1}). There were no frequencies characteristic for a double bond of a carbonyl group in the IR and UV spectra of this substance. In agreement with this, the PMR spectrum of the genin had no signal of an olefinic proton.

In the high-field region of the PMR spectrum of cyclosieversigenin (taken in $CDCl_3$), the signals of the protons of seven methyl groups were observed (Table 1), and also one-proton doublets of the AB type at 0.30 and 0.46 ppm (J = 4.0 Hz), which are characteristic for a methylene group in a cyclopropane ring [2]. The presence of a three-membered ring was confirmed by an adsorption band at 3050 cm^{-1} in the IR spectrum of the genin (I) [3].

These facts, and also the molecular formula of the compound under consideration — $C_{30}H_{50}O_5$ — permitted the assumption that compound (I) was a methylsteroid of the cycloartane group.

In the mass spectra of cyclosieversigenin there is an intense band of an ion with m/e 143 (100%) ($C_8H_{15}O_2$). Fragments of this type (ion a) arise in the mass spectrometric fragmentation of isoprenoids with side chains of the ocotillone type [4-6]. The presence of such a side chain is also shown by a triplet at 3.66 ppm in the PMR spectrum ($CDCl_3$) of the genin (I). This signal must belong to H-24, since it is observed in the spectra of ocotillone-II and its derivatives [5-9].

The acetylation of the genin (I) with acetic anhydride in pyridine at room temperature led to the formation of the diacetate (II) and the triacetate (III). The IR spectra of both compounds contains the absorption of hydroxy groups, and the mass spectrum retained an intense peak of an ion with m/e 143.

A comparison of the features of the PMR spectra of the acetates (I) and (III) with those of compound (I) permitted the one-proton signal in the PMR spectrum ($CDCl_3$) of cyclosieversigenin at 3.18, 3.46, and 4.58 ppm to be assigned to protons geminal to hydroxy groups.

The facts given above indicate that of the five oxygen atoms of the cyclosieversigenin molecule one is present in a tetrahydrofuran ring and the other four belong to hydroxy functions, three being in secondary hydroxy groups located in a polycyclic nucleus and one in a tertiary hydroxy group in the side chain.

Cyclosieversigenin was not oxidized by periodic acid and, consequently, contains no α-glycol grouping. When the genin (I) was heated in a 3.5% aqueous methanolic solution of sulfuric acid, a compound was obtained which was identical in its physicochemical constants and spectral characteristics with compound (IV) isolated directly in the hydrolysis of the total extractive substances. We have previously called this compound sieversigenin [10].

The terpenoid (IV) likewise has the elementary composition $C_{30}H_{50}O_5$, but, in contrast to the genin (I), its UV spectrum shows absorption at 206 nm (ε 3225) to a trisubstituted double bond [11]. Correspondingly, the PMR spectrum of compound (IV) (in $CDCl_3$) contains a one-proton signal of an olefinic proton at 5.02 ppm. We may also note that in the strong-field region there are the singlets of eight methyl groups. As was to be expected, the signals of the cyclopropane ring are absent.

It is known [12] that under the influence of acids a 9,19-cyclopropane ring is opened with the formation of a 9(11) double bond. The circular dichromism curve of compound (IV) with a positive Cotton effect at 201 nm ($\Delta\varepsilon$ = + 20.6) confirms this arrangement of the double bond [13, 14].

On passing from (I) to (IV), the side chain did not change, as was confirmed by a fragment with m/e 143 (100%) in the mass spectrum and a triplet at 3.66 ppm relating to H-24 in the PMR spectrum of the olefin (IV).

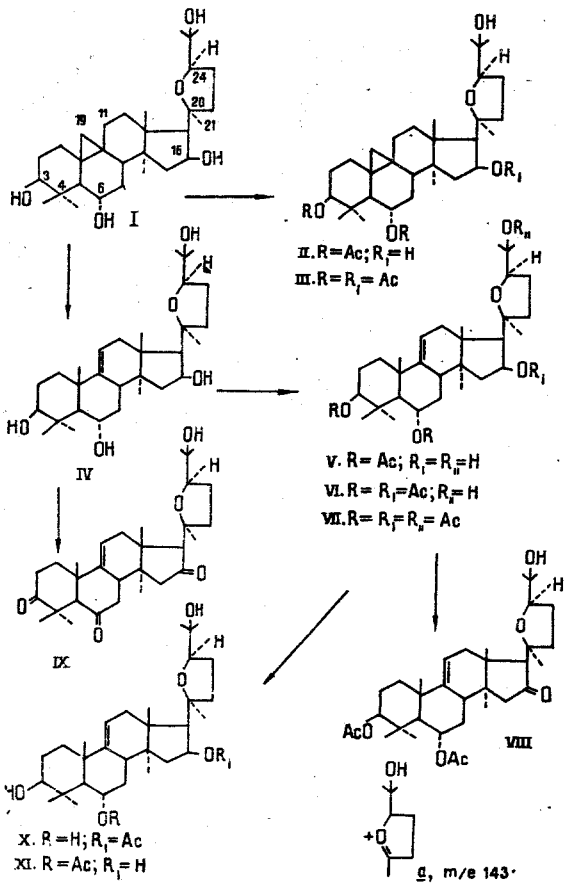
The acetylation of compound (IV) by heating it with acetic anhydride in pyridine led to products (V), (VI), and (VII), which, according to PMR and mass spectroscopy, were, respectively, di-, tri-, and tetraacetates.

The oxidation of the olefin (IV) with the Jones reagent [15] in acetone gave a triketo derivative (IX) with the composition $C_{30}H_{44}O_5$, the IR spectrum of which retained the absorption band of a tertiary hydroxy group. The absence from the UV spectrum of compound (IX) of the absorption characteristic for an α,β-unsaturated keto grouping in a 1,3-diketone [16], in combination with the negative reaction to periodate oxidation of the tetraol (IV) excludes

TABLE 1. Chemical Shifts of the Protons of Cyclosieversigenin and its Derivatives (δ, ppm, HMDS)

Compound	Positions of the protons						
	H-3	H-6	H-11	H-16	2H-19	H-24	CH_3 group
I	3,18 $W_{1/2}$= =17 Hz, 3,69*m]	3,46, sx (10,0; 5,0 Hz) [3,69*, m]		4,58, q (J 7,0 7,0 Hz each) [4,90, q (7,0 7,0 Hz each)	0,30; 0,46 d (J=4,0 Hz) 0,31; 0,51, d (J=4,0 Hz)	3,66, t 6,5 Hz) [3,78*, m]	1,20; 1,18 (2×CH_3); 1,13 (2I=CH_3); 1,06; 0,90 (2×CH_3) [1,78; 1,47; 1,33 1,28; 1,20; 1,18; 0,96)]
II	4,61*, m	4,61*, m		4,61*, m	0,50; 0,57, d (J=4,5Hz)	3,68, t (7,0 Hz)	1,22; 1,15 (2×CH_3); 1,05; 0,91; 0,88; 0,79
III	4,58*, m	4,58*, m		5,38, m	0,30; 0,58; d (J=4,5 Hz)	3,64, t (7,(Hz)	1,22 (2×CH_3); 1,13; 1,03; 0,92 (2×CH_3); 0,81
IV	3,16, m $W_{1/2}$=17 Hz) [3,40, t (7,5 Hz)]	4,12, sx (10,5; 4,0 Hz) [4,34, sx (10,5; 4,0 Hz)]	5,20 [5,25]	4,58, q (7,0 7,0 Hz each) [4,88, m (J F.O Hz each)		3,66, t (7,5 Hz) [3,73, t (8,0; 6,0 Hz)]	1,24 (2×CH_3); 1,14 (2I=CH_3); 1,06; 1,00 (2×CH_3); 0,83; 0,70 [1,81; 1,44; 1,40; 1,20; 1,18; 1,08; 0,97; 0,70)
V	[4,65, m $W_{1/2}$≈17Hz.)	[5,48, sx (10,5; 4,0 Hz)	[5,15]	[4,80, q (7,0 7,0 Hz each)]		[3,72, q (8,0; 5,5 Hz)]	[1,42; 1,17; 1,15; 1,06; 0.96; 0,94; 0,89; 0,64]
VI	[4,58, m $W_{1/2}$≈17 Hz)]	[5,41*, m]	[5,12]	[5,41* m]		[3.80, t (7,5 Hz)]	[1,28; 1,25 (2×CH_3); 1,10; 1,03; 0,99: 0,78; 0,60]
VII	[4,50, $W_{1/2}$≈17 Hz)]	[5,30*, m]	[5,30*, m]	[5,30*, m]		[4,00, t (6,0 Hz)]	[1,45 (2×CH_3); 1,21; 1,08; 1,00; 0,95: 0,82; 0,59]
VIII	[4,57 m $W_{1/2}$=16Hz)]	[5,47, sx 10,5; 4,0 Hz)]	[5,19]			[3,73, t (6,5 Hz)]	[1,36; 1,13; 1,11; 1,09; 0,99; 0,97; 0,69 (2×CH_3)]
IX			[5,36]			[3,76, t (6,5 Hz)]	[1,89; 1,52; 1,37; 1,20; 1,18 (2×CH_3); 1,16; 0,77]
X	[3,34 t (7,5 Hz)]	[4,32, sx (10,5; 4,0 Hz)]	[5,20]	[5,50, m]		[3,75 t, (6,0 Hz)]	[1,70; 1,30; 1,25 (2×CH_3); 1,20; 1,09; 0,85; 0,62]
XI	[3,30 t (7, 5 Hz)]	[5,52, sx (10,5; 4,0Hz)]	[5,22]	[4,77, m $W_{1/2}$=17Hz]		[3.72, t (6,5Hz)]	[1,40 (2×CH_3); 1,17 (2×CH_3); 1,02; (2×CH)$_3$; 0,89; 0,68]

Note: The spectra were taken in $CDCl_3$ or in C_5D_5N. The indices given in square brackets were obtained by the use of C_5D_5N. The signals marked with asterisks in the horizontal lines are interchangeable. The signals of methyl groups have a singlet nature. The H-11 protons appears in the form of broadened singlet. Abbreviations: s — singlet, d — doublet, q — quartet, sx — septet, m — multiplet.



the simultaneous presence of two hydroxy functions in one ring and at the same time indicates an arrangement of hydroxy groups in rings A, B, and D.

In harmony with this conclusion is the IR spectrum of the triketone (IX), having carbonyl absorption at 1710 and 1728 cm^{-1}.

Further information on the positions and configurations of the hydroxy groups was obtained in the following way. In the PMR spectrum (in C_5D_5N) of the olefin (IV) one-proton signals — triplet at 3.40, sextet at 4.34, and quartet at 4.88 ppm — relate to protons arranged geminally to three secondary hydroxy groups. This assignment is based on the fact that in the PMR spectrum of the triacetate (VI) and of the tetraacetate (VII) these signals are shifted downfield by 0.8-1.2 ppm.

The triplet at 3.40 ppm, appearing at 3.16 ppm when the spectrum was taken in $CDCl_3$, with a half-width splitting ($W_{1/2}$) of 17 Hz, must be assigned to 3α-H [8, 9, 17], which, in its turn, shows the β orientation of the hydroxy group at C-3. The nature of the H-3 signal ($W_{1/2}$ = 17 Hz) in the acetates (V-VII) confirms this assignment.

As follows from a comparison of the PMR spectra of compounds (IV) and (V), the proton signal at 4.80 ppm in the spectrum of the diacetate (V) shows that the hydroxy group geminal to this proton has remained free.

It was established for compound (IV) by the methods of double resonance and INDOR that this proton interacts with another proton giving a doublet (J = 7Hz) at 2.40 ppm (C_5D_5N). On double irradiation with ν_2 = 488 Hz, the doublet under consideration was converted into a singlet. This fact permits the assumption that the doublet at 2.40 ppm corresponds to the H-17 signal and the quartet at 4.88 ppm to the H-16 signal.

In actual fact, oxidation of the diacetate (V) gave compound (VIII) the IR spectrum of which exhibited a band at 1728 cm^{-1} showing the presence of a ketone group in ring D. At the same time, the circular dichroism curve, revealing a negative Cotton effect at 305 nm ($\Delta\varepsilon$ = −4.9), shows the position of the ketone at C-16 [18].

Consequently, in the olefin (IV) there is a hydroxy group at C-16. As was to be expected, in the triacetate (VI) the H-16 signal had shifted downfield and appeared at 5.41 ppm. According to the increment in molecular rotations between the triacetate (VI) and the driacetate (V) ($[M]_{D-VI}$ = 564°; $[M]_{D-V}$ = 359°; $[M]_D$ = + 205°) the hydroxy group at C-16 must have the β orientation [19].

The remaining unidentified secondary hydroxy group is present in ring B on the seventh — or the sixth — carbon atom. This hydroxy group must occupy an equatorial position, since the signals of the corresponding proton at 4.34 ppm in the PMR spectrum of (IV) (C_5D_5N) has the form of a sextet with two large (10.5 Hz) and one small (4.0 Hz) splitting values. To determine the position of this hydroxy group we studied the monoacetates (X) and (XI) obtained by saponifying the triacetate (VI).

The detection of the H-16 signal in the PMR spectrum of compound (X) in the weak field showed that this substance was the 16-monoacetate.

Particular interest is presented by the features of the PMR spectra of the acetate (XI) and of the olefin (IV). As can be seen from Table 1, in the spectrum of compound (XI) the signals of the proton of interest to us (H-6 or H-7) have undergone a paramagnetic shift (δ_{IV} = 4.34 ppm, δ_{XI} = 5.52 ppm, $\Delta\delta$ = 1.8 ppm). Attention is attracted in the PMR spectrum of the olefin (IV) of the singlet of a methyl group resonating at 1.81 ppm. It is characteristic that the signal of this group appears in a relatively weaker field than the signals of the other methyls. This is due to the specific influence of pyridine as solvent, which leads to the interaction of the methyl group with the spatially close hydroxy group [20].

The diamagnetic shift of the same methyl group in the PMR spectrum of (XI) is, naturally, the result of the acetylation of the hydroxy group under consideration. If it is borne in mind that this hydroxy group is oriented equatorially, then of the two alternative positions, C-7, and C-6, the latter must be chosen. Only in this case does the sterically favorable possibility of influence on the adjacent 4α-CH_3 group arise [21].

Thus, the experimental results given show that the tetracyclic nucleus of olefin (IV) and, therefore, also of cyclosieversigenin (I), contains 3β-, 6α-, and 16β-hydroxy groups.

In the IR spectrum of the triketo compound (IX) the absorption band of a hydroxy group at 3460-3470 cm^{-1} with a frequency independent of the dilution shows the presence of an intramolecular hydrogen bond between the C-25 hydroxy group and the carbonyl oxygen at C-16. A consideration of molecular models showed that a hydrogen bond can arise in the case of the 20(S), 24(R) or the 20(R), 24(S) isomers.

In isoprenoids with a side chain of the ocotillone type having the 20(S), 24(R) type of configuration, the C-21 methyl group gives a signal at 1.21 ppm, and H-24 resonates in the form of a triplet at 3.7 ppm (6 Hz) [5-9]. The good agreement of these parameters with the values presented in Table 1 for the tetraols (I) and (IV) (CDCl) gives grounds for the assumption that the C-20 and C-24 chiral centers have analogous stereochemistries.

Thus, the olefin (IV) has the structure of 20(S), 24(R)-epoxylanost-9(11)-en-3β,6α, 16β, 25-tetraol, and cyclosieversigenin (I) that of 20(S), 24(R)-epoxycycloartane-3β,6α, 16β, 25-tetraol.

To answer the question of whether substances (I) and (IV) are native, we performed a Smith degradation [22] of the combined glycosides obtained from the roots of *A. sieversianus*. This gave only the genin (I). With a high probability, this fact permits cyclosieversigenin to be considered as a native compound and the olefin (IV), which has been called sieversigenin [10], to be the product of its acid transformation.

EXPERIMENTAL

General Observations. For thin-layer chromatography (TLC) we used KSK siliga gel (<65 mμ) containing 10% of gypsum. Column chromatography was carried out on silica gel (65-100 mμ) of the same type. Isoprenoids were detected by spraying the plates with a 25% solution of tungstophosphoric acid or concentrated H_2SO_4 followed by heating at 120°C for 5-10 min.

The mass spectra and elementary compositions of the ions were measured on a MKh-1310 instrument at an ionizing voltage of 50 V and a temperature of 130-170 C. IR spectra were taken on a UR-20 spectrometer in KBr, PMR spectra in C_5D_5N on JNM-4H-100/100 MHz and JNH-C60-H instruments, and in $CDCl_3$ on a Varian XL-100-15 instrument with HMDS as internal standard, δ scale.

The circular dichroism curves were measured on a Jasco-20 spectropolarimeter.

Isolation of Cyclosieversigenin (I) and of 20(S), 24(R)-Epoxylanost-9(11)-ene-3β, 6α, 16β, 25-tetraol (IV). Air-dry comminuted roots of *Astragalus sieversianus* Pall. (5 kg) collected in September, 1977, at the foot of Mt. Chimgan (Chatkal range, western Tien-Shan) were extracted with methanol. The mass remaining after the solvent had been distilled off was treated with two volumes of water, and the syrupy extract was shaken with butanol. The butanolic extract was evaporated to dryness. The residue was dissolved in 300 ml of methanol and the solution was poured into 3 liters of acetone. The resulting precipitate (217 g) was filtered off. Part (10 g) of the combined extractive substances so obtained was hydrolyzed by boiling in aqueous methanol (1:1) containing 8% of H_2SO_4 for 10 h. The hydrolysate was diluted with 2 volumes of water and the resulting precipitate (3.3 g) was separated off and was chromatographed on a column of silica gel with elution by chloroform–methanol (50:1).

The product partially saponified in this way (3 g) was rechromatographed on silica gel, the column being washed with ethyl acetate. This gave 1 g of compound (IV), $C_{30}H_{50}O_5$, mp 229-231°C (ethyl acetate), α_D^{20} + 67.1 ± 2° (c 1.92, methanol), $\lambda_{max}^{C_2H_5OH}$ 206 nm (ε 3225). ν_{max}^{KBr} (cm^{-1}): 3450-3250 (OH), 3045 (>C=CH). CD (c 0.01, methanol): Δε = + 20.6 (201 nm). Mass spectrum, m/e (%): M^+ 490 (0.7), 475 (1.2), 472 (3.3), 457 (3.1), 454 (2.4), 439 (2.3), 431 (2.2), 413 (7.3), 395 (5.5), 377 (5.3), 345 (6.1), 327 (25), 309 (7.4), 289 (5.1), 288 (7.0), 287 (8.0), 271 (5.1), 143 (100).

Continued elution of the column with ethyl acetate yielded 500 mg of cyclosieversigenin (I), $C_{30}H_{50}O_5$, mp 239-241°C (methanol), $[\alpha]_D^{20}$ + 44.0 ± 2° (c 1.58, methanol). ν_{max}^{KBr} (cm^{-1}): 3450-3300 (OH), 3050 (>CH_2 of a cyclopropane ring). Mass spectrum, m/e (%): M^+ 490 (0.6), 472 (6.2), 454 (5.3), 439 (3.0), 431 (1.3), 413 (5.4), 395 (6.0), 289 (3.2), 271 (7.3), 143 (100).

3,6-Diacetate (II) and 3,6,16-Triacetate (III) of Cyclosieversigenin. Cyclosieversigen (I) (200 mg) was acetylated with 3 ml of acetic anhydride in 6 ml of pyridine at room temperature for 96 h. The reaction products were poured into ice water and the resulting precipitate was filtered off. The mixture of acetates so obtained was separated on a column with elution by the ethyl acetate–toluene(3:5) system. Eluted first was 84 mg of the triacetate (III), $C_{36}H_{56}O_8$, with mp 210-212°C (methanol), $[\alpha]_D^{20}$ + 76.0 ± 2° (c 1.09, methanol). ν_{max}^{KBr} (cm^{-1}): 3580-3560 (OH), 1745, 1250 (ester group), 3050 (>CH_2 of a cyclopropane ring). Mass spectrum, m/e, %: 601 (M–15)+ (1), 598 (0.2), 556 (4.0), 541 (0.5), 538 (0.6), 496 (11), 481 (3.0), 478 (0.7), 437 (7), 421 (3.0), 395 (2.1), 377 (9.4), 335 (1.2), 289 (1.8), 271 (1.9), 185 (15), 143 (100), 125 (36).

Further washing of the column with the same mixture of solvents yielded 70 mg of the diacetate (II), $C_{34}H_{54}O_7$, with mp 228-229°C (methanol), $[\alpha]_D^{20}$+ 77.5 ± 2° (c 1.88, methanol). ν_{max}^{KBr} (cm^{-1}): 3480-3380 (OH), 3050 (>CH_2 of a cyclopropane ring), 1748, 1720, 1270-1250 (ester group). Mass spectrum, m/e (%): M+ 574 (0.2), 559 (1.8), 556 (0.8), 541 (0.5), 530 (0.7), 514 (12), 499 (2.3), 496 (4.1), 481 (3.0), 454 (22), 436 (5.4), 421 (4.0), 411 (1.8) 395 (20), 377 (6.7), 289 (6.0), 271 (6.0), 185 (12), 143 (100), 125 (12).

20(S),24(R)-Epoxylanost-9(11)-en-3β, 6α, 16β,25-tetraol (IV) from (I). A solution of 100 mg of compound (I) in 25 ml of methanol was treated with 25 ml of 7% H_2SO_4. The reaction mixture was boiled at 100°C for 5 h. The reaction products were extracted with chloroform. After the solvent had been distilled off, the residue was separated on a column with elution by ethyl acetate. This gave 20 mg of a compound $C_{30}H_{50}O_5$ with mp 228-230°C (ethyl acetate). $[\alpha]_D^{22}$ + 71.4 ± 2° (c 0.65, methanol). The IR, mass, and NMR spectra of the product obtained and also its R_f values on TLC coincided with the corresponding indices of compound (IV) isolated in the hydrolysis of the combined glycosides.

The 3,6-Diacetate (V), 3,6,16-Triacetate (VI), and 3,6,16,25-Tetraacetate (VII) of the Tetraol (IV). Compound (IV) (450 mg) in 13 ml of pyridine was acetylated with 8.5 ml of

acetate anhydride at 60°C for 2 h. The usual working up yielded 540 g of a mixture of acetates, which was chromatographed on a column of silica gel. By elution with the toluene–ethyl acetate (5:1) system, 47 mg of the 3β, 6α, 16β, 25-tetraacetate of (VII), $C_{38}H_{58}O_9$, was isolated with mp 130-133°C (methanol), $[\alpha]_D^{20}$ + 140.4 ± 2° (c 0.40, methanol). ν_{max}^{KBr} (cm^{-1}): 1740, 1730, 1260-1240 (ester group). Mass spectrum, m/e (%): M+ 658 (0.2), 643 (1.4), 598 (11), 583 (2.0), 557 (7.2), 538 (53), 523 (9.3), 497 (3.0), 478 (49), 463 (28), 437 (9.5), 403 (40), 377 (18), 351 (10), 309 (11), 291 (26), 185 (33), 143 (36), 125 (100). Further washing of the column with a mixture of the same two solvents in a ratio of 5:2 gave 120 mg of the 3β, 6α, 16β-triacetate (VI), $C_{36}H_{56}O_8$, with mp 223-227°C (methanol), $[\alpha]_D^{20}$ + 91.7 ± 2° (c 0.96, methanol). ν_{max}^{KBr} (cm^{-1}): 3540 (OH), 1730, 1710, 1250 (ester group). Mass spectrum, m/e (%): M^+ 616 (0.2), 601 (0.8), 598 (0.1), 557 (2.2), 556 (2.0), 541 (0.8), 538 (1.2), 497 (2.7), 496 (5.0), 481 (2.7), 478 (1.0), 463 (2.0), 437 (3.6), 421 (3.8), 411 (0.80), 395 (2.7), 377 (7.7), 363 (1.9), 351 (2.5), 291 (4.9), 185 (7.1), 142 (100), 125 (16).

Elution of the column with toluene–ethyl acetate (5:3) led to the isolation of 304 mg of the 3β, 6α-diacetate (V), $C_{34}H_{54}O_7$, with mp 249-243°C (methanol), $[\alpha]_D^{20}$ + 62.6 ± 2° (c 0.96; methanol); ν_{max}^{KBr} (cm^{-1}): 3480-3400 (OH), 1735, 1718, 1265, 1245 (ester group), 3060 (>C=CH). Mass spectrum, m/e (%): M^+ 574 (6.2), 559 (2.0), 556 (4.3), 541 (2.0), 538 (3.0), 514 (5.0), 496 (7.6), 478 (4.4), 470 (5.0), 454 (7.6), 436 (7.0), 429 (3.8), 421 (6.0), 413 (6.7), 395 (8.7), 377 (15.2), 335 (10), 309 (16), 281 (8.3), 185 (15), 143 (100), 125 (39).

3β, 6α-Diacetoxy-25-hydroxy-20(S), 24(R)-epoxylanost-9(11)-en-16-one (VIII) from (V). A solution of 500 mg of diacetate (V) in 50 ml of acetone cooled to −3°C was treated with 0.4 ml of the Jones reagent [15]. After 5 min, the reaction mixture was poured into 200 ml of water containing 300 mg of sodium sulfite. The reaction products were extracted with chloroform. The chloroform extract was washed with a dilute solution of sulfuric acid and with water and was evaporated to dryness. The residue was purified by chromatography on a column of silica gel. Elution by benzene–ethyl acetate (1:1) yielded 390 mg of the ketone (VIII), $C_{34}H_{52}O_7$, with mp 239-241°C, $[\alpha]_D^{20}$ + 7.9 ± 2° (c 0.75, methanol–chloroform (5:1)), ν_{max}^{KBr} (cm^{-1}): 3440 (OH), 3050 (>C=CH), 1740, 1245 (ester group), 1728 (C=O of a cyclopentanone). CD (c 0.01, methanol), $\Delta\varepsilon$ = −4.9 (305 nm). Mass spectrum, m/e (%): M^+ 572 (0.8), 557 (10), 554 (56), 539 (21), 523 (4.4), 513 (100), 499 (19), 495 (6.3), 483 (5), 471 (25), 411 (23), 393 (19), 375 (7.3), 369 (6.9), 351 (30), 325 (11), 313 (46), 253 (75), 185 (47), 143 (84), 125 (87).

25-Hydroxy-20(S),24(R)-epoxylanost-9(11)-ene-3,6,16-trione (IX) from (IV). A solution of 150 mg of the tetraol (IV) in 150 ml of acetone cooled to 0°C was treated with 0.45 ml of the Jones reagent [15]. After 25 min, the reaction mixture was poured into 300 ml of water containing 500 mg of Na_2SO_3 and was extracted with ether. The usual working up and distillation of the solvent gave 87 mg of the triketone (IX), $C_{30}H_{44}O_5$, with mp 217-220°C (methanol), $[\alpha]_D^{20}$ 58.4 ± 2° (c 1.36, methanol). ν_{max}^{KBr} (cm^{-1}): 3470, 3430 (OH), 1728 (C=O of a cyclopentanone), 1705 (C=O of a cyclohexane), 3050 (>C=CH). $\nu_{max}^{CCl_4-CHCl_3}$ (cm^{-1}): 3470-3460 (OH), the frequency being independent of the dilution, 1732 (C=O of a cyclopentane), 1712 (C=O of a cyclohexanone). Mass spectrum, m/e (%): M^+ 484 (11), 469 (19), 466 (43), 451 (37), 433 (7.7), 425 (100), 418 (35), 411 (15), 407 (11), 395 (24), 383 (29), 367 (20), 341 (3.9), 327 (5), 297 (12), 255 (12), 283 (7.7), 143 (22), 125 (40).

The 16-Acetate (X) and the 6-Acetate (XI) of the Tetraol (IV). The triacetate (VI) (240 mg) was saponified in 100 ml of a 0.4% methanolic solution of KOH at room temperature for 48 h. Then the reaction mixture was poured into water and extracted with chloroform. The residue obtained after the usual working up was separated by column chromatography. Elution with the ethyl acetate–benzene (1:1) system yielded 66 mg of the acetate (X), $C_{32}H_{52}O_6$, with mp 219-220°C (ethyl acetate), $[\alpha]^{20}$ + 72.4 ± 2° (c 0.96, methanol), ν_{max}^{KBr} (cm^{-1}): 3566-3480 (OH), 3050 (>C=CH), 1740, 1260 (ester group). Mass spectrum, m/e (%): M^+ 532 (0.9) 517 (2.8), 472 (12), 457 (5.1), 454 (5.6), 439 (5.6), 421 (11), 413 (8), 403 (4.3), 395 (11), 377 (7.7), 363 (2.8), 353 (5.1), 335 (4.0), 327 (7.0), 309 (12), 291 (4.8), 289 (6.0), 288 (12), 185 (12), 143 (100), 125 (34).

Continued elution of the column with the same mixture of solvents yielded 20 mg of the 6-acetate (XI), $C_{32}H_{52}O_6$, mp 245-247°C (ethyl acetate), $[\alpha]_D^{20}$ + 88.6 ± 2° (c 0.58, methanol), ν_{max}^{KBr} (cm^{-1}): 3530, 3490-3460 (OH), 3055 (>C=CH), 1720, 1260 (ester group). Mass spectrum, m/e (%): M^+ 532 (2.2), 517 (3.1), 514 (2.0), 499 (2.0), 496 (2.3), 472 (7.3), 454 (7.1),

439 (7.7), 428 (9.0), 421 (6.0), 413 (12), 395 (20), 377 (12), 327 (10), 309 (21), 271 (14), 270 (13), 269 (11), 185 (18), 143 (100), 125 (30).

Smith Degradation of the Combined Glycosides. The combined glycosides isolated from *A. sieversianus* as described above (2.0 g) were dissolved in 300 ml of aqueous ethanol (1:1), 3 g of sodium periodate was added, and the mixture was stirred for 8 h. The unchanged oxidizing agent was decomposed with ethylene glycol. The methanol was evaporated off and the residue was treated with 100 ml of water and extracted with butanol. The butanolic extracts were washed with water and concentrated to a volume of 40 ml, after which 40 ml of methanol and 4.5 g of sodium tetrahydroborate were added. The reaction mixture was heated at 80°C for 7 h, after which it was acidified to pH 2.0 and was left at room temperature for 17 h. The hydrolyzed products were extracted with chloroform, the solvent was distilled off, and the residue was chromatographed on a column of silica gel with elution by ethyl acetate. This gave 100 mg of a compound $C_{30}H_{50}O_5$ with mp 239-242°C (ethyl acetate). $[\alpha]^{20}$ + 39.0 ± 2° (c 1.63; methanol), identical in its spectral characteristics and R_f value on TLC (ethyl acetate) with cyclosieversigenin (I).

SUMMARY

The hydrolysis of the combined glycosides of *Astragalus sieversianus* Pall, has given a new isoprenoid cyclosieversigenin, which has the structure of 20(S), 24(R)-epoxycycloartane-3β, 6α, 16β, 25-tetraol.

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