LITERATURE CITED

1. A. I. Chekhlov, Kristallografiya, 26, 596 (1981).
2. V. I. Andrianov, Z. Sh. Safina, and B. L. Tarnopol'skii, Instructions for Working with the Rentgen-75 Program [in Russian], Chernogolovka (1975).

TRITERPENE GLYCOSIDES OF Astragalus AND THEIR GENINS.

XXIII. CYCLOCANTHOGENIN FROM Astragalus tragacantha

Yu. M. Fadeev, M. I. Isaev,
Yu. A. Akimov, P. K. Kintya,
M. B. Gorovits, and N. K. Abubakirov

UDC 547.918:547.926

The epigeal part of the plant Astragalus tragantha Habl. (Leguminosae) has yielded (in addition to cyclosieversigenin, cyclocyclosiversioside F, and β-sitosterol β-D-glucopyranoside) a new methylsteroid of the cycloartane series – cyclocanthogenin – the structure of which has been established on the basis of chemical transformations and spectral characteristics, and also of a chemical correlation with the structure of cycloasgenin C, as 24S-cycloartane-3β,6α,16β,24,25-pentaol.

Continuing investigations of the cycloartane triterpenoids of the plants of the genus Astragalus [1], we have begun a study of Astragalus tragacantha Habl. (Leguminosae). In a methanolic extract of the epigeal part of this plant, on TLC in various solvent systems, at least 18 compounds of sterol and triterpene nature were detected, and they have been designated in order of increasing polarity substances (1-18). From the total extractive substances compounds (1, 2, 5, 6, and 9-14) were isolated by column chromatography on silica gel. Glycosides (11) and (12) predominated in the extract. Substances (1, 2, and 11) were identified as cyclosieversigenin [2, 3], β-sitosterol β-D-glucopyranoside [4], and cyclosieversioside F [5, 6], respectively.

The acid hydrolysis of glycoside (12) gave the genin (I) (Scheme 1), which we have called cyclocanthogenin. The present paper is devoted to a proof of the structure of this compound.

The elementary composition of cyclocanthogenin, $C_{30}H_{52}O_5$, the presence in the PMR spectra of the signals of seven methyl groups and also of two one-proton doublets at 0.20 and 0.48 ppm (Table 1) showed that the new genin belonged to the cycloartane series [7]. At the same time, in the PMR spectrum of compound (III), obtained under more severe conditions and having the same elementary composition as genin (I), the signals of eight methyl groups and of one olefinic proton were observed. Consequently, substance (III) was a triterpenoid of the lanost-9(11)-ene series formed by the acid isomerization of cyclocanthogenin.

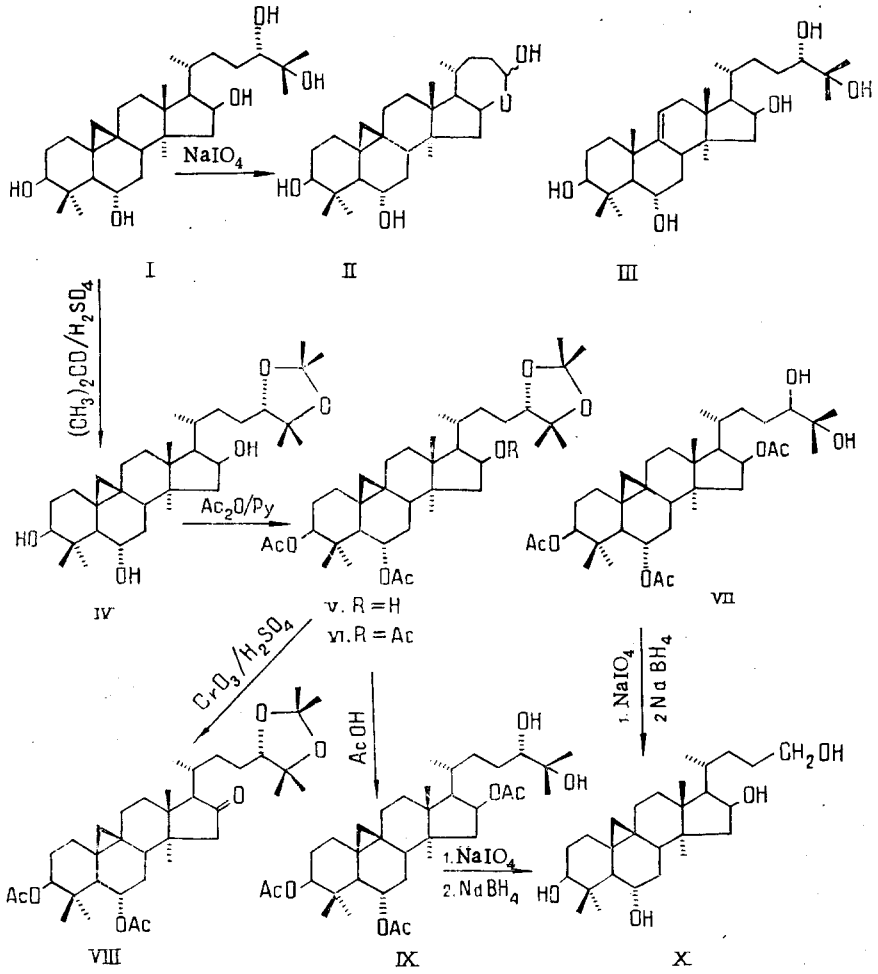
It followed from the elementary composition $C_{30}H_{52}O_5$ of triterpenoids (I) and (III) that all the oxygen atoms are represented by hydroxy groups, which meant that the side chains of these substances were acyclic.

In the PMR spectrum of substance (III) the signals of four protons located geminally to hydroxy functions were clearly traced at 3.40, 3.78, 4.32, and 4.60 ppm. In the sepctrum of genin (I), these protons resonated in the form of multiplets at 3.40-3.90 and 4.58 ppm with integral intensities of three and one proton units, respectively. The fifth hydroxy group was tertiary.

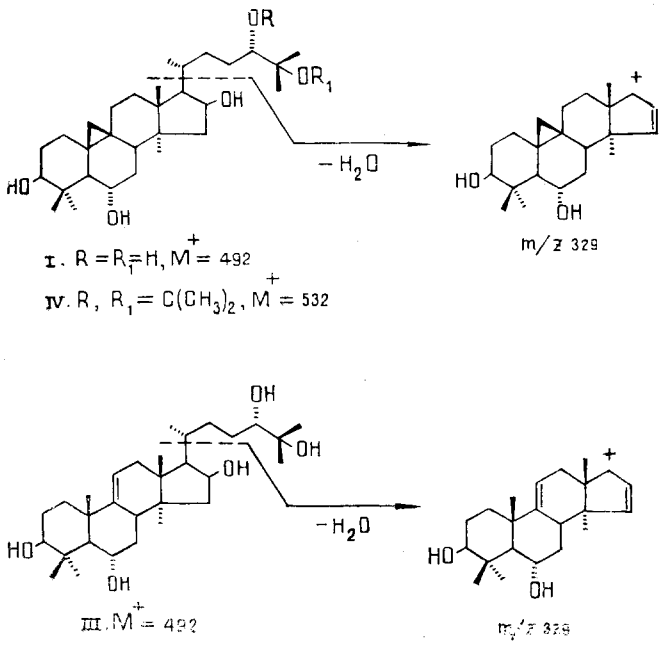
The mass spectra of triterpenoids (I) and (III) each exhibited the peak of an ion with m/z 329 formed by the cleavage of the C-17–C-20 bond and the ejection of one molecule of water from the polycyclic fragment (Scheme 2) [3]. This peak was the maximum peak in the spectrum of compound (III).

Institute of the Chemistry of Plant Substances, Uzbek SSR Academy of Sciences, Tashkent.
Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 817-824, November-December, 1987. Original article submitted April 6, 1987.

 0009-3130/87/2306-0678$12.50



Scheme 1



Scheme 2

TABLE 1. Chemical Shifts of the Protons of Cyclocanthogenin (I) and Its Derivatives (δ, ppm; 0 – HMDS, TMS)

Compound	Positions of the protons			
	H-3	H-6	H-16	2H-19 / H-11
I	[3,40 — 3,90]*	[3,40 — 3,90]*	[4,58 m $W_{1/2}$ = 14 Hz]	[0,20; 0,48 d ^2J = 4 Hz]
II	[3,60 m]*	[3,60 m]*	[4,15 q	[0,18; 0,47 d ^2J = 4 Hz]
III	[3,40 q ^3J = 10; 6 Hz]	[4,32 td ^3J = 10; 10; 4 Hz]	[4,60 m $W_{1/2}$ = 14 Hz]	[5,24 br.d ^3J = 6 Hz]
IV	3,28 q ^3J = 8; 5 Hz	3,52 td. ^3J = 9; 9; 4 Hz	4,40 m $W_{1/2}$ = 15 Hz	0,56; 0,72 d ^2J = 4 Hz
V	4,26 — 4,82*	4,26 — 4,82*	4,26 — 4,82*	0,32; 0,59 d ^2J = 4 Hz
VI	4,44 — 4,80*	4,44 — 4,80*	5,23 m $W_{1/2}$ = 16 Hz	0,36; 0,59 d ^2J = 4 Hz
VIII	4,44 — 4,82*	4,44 — 4,82*	—	0,40; 0,63 d ^2J = 4 Hz
IX	4,40 — 4,80*	4,40 — 4,80*	5,26 m $W_{1/2}$ = 16 Hz	0,36; 0,59 d ^2J = 4 Hz
	[4,38 — 4,93]*	[4,38 — 4,93]*	[5,30 m]	[0,16; 0,43 d ^2J = 5 Hz]
X	[3,40 — 3,86]*	[3,40 — 3,86]*	[4,52 m $W_{1/2}$ = 14 Hz]	[0,20; 0,48 d ^2J = 4 Hz]

Compound	Positions of the protons		
	H-24	CH_3 groups	OAc
I	[3,40 — 3,90]*	[0,91; 0,96 d (^3J = 6 Hz); 1,22; 1,30; 1,32; 1,34; 1,73]	—
II	[4,79 q ^3J = 7; 3 Hz]	[0,84 d (^3J = 6 Hz); 0,90; 1,17; 1,21; 1,73]	—
III	[3,78 q ^3J = 10; 3 Hz]	[0,72; 0,98 d (^3J = 6 Hz); 1,00; 1,08; 1,32; 1,34; 1,38; 1,80]	—
IV	3,82 q ^3J = 9; 4 Hz	0,92; 0,94 d; 0,96; 1,11; 1,15; 1,25 (2 × CH_3); 1,34; 1,40	—
V	3,79 q ^3J = 10; 4 Hz	0,84; 0,92; 0,94 d; 0,98; 1,10; 1,13; 1,25; 1,33; 1,40	1,97; 2,04
VI	3,55 q ^3J = 9; 3 Hz	0,84; 0,93; 0,94 d; 0,98; 1,06; 1,11; 1,20; 1,30; 1,39	1,96; 1,98; 2,04
VIII	3,66 m $W_{1/2}$ = 8 Hz	0,84; 0,97 d (^3J = 6 Hz); 0,99; 1,12 (3 × CH_3); 1,25; 1,32; 1,40	1,97; 2,04
IX	3,26 t ^3J = 6 Hz [3,54 m]	0,84; 0,90 — 0,98 (3 × CH_3); 1,13 (2 × CH_3); 1,18 [0,75; 0,87; 0,90 d; 0,99 (2 × CH_3); 1,36; 1,38]	1,98; 2,00; 2,04 [1,91; 1,92; 2,04]
X	[3,77 t* (2H) ^3J = 7 Hz]	[0,92; 0,94 d (^3J = 6 Hz); 1,22; 1,29; 1,72]	—

The spectra were taken in deuterochloroform (with TMS as internal standard) or in deuteropyridine (with HMDS as internal standard). The indices given in square brackets were obtained with the use of deuteropyridine. The signals marked with asterisks in the horizontal rows were superposed upon one another. The signals of the methyl groups had a singlet nature, with the exception of the CH_3 group at C-20, having doublet splitting; d – doublet; br.d. – broadened doublet; t – triplet; q – quartet; td – triplet of doublets; m – multiplet.

In acetone in the presence of sulfuric acid, cyclocanthogenin formed a monoacetonide (IV), which showed the presence of an α-glycol grouping. The retention of the peak of the ion with m/z 329 in the mass spectrum of the acetonide (IV) showed that the α-diol function was located in the side chain.

Since only one methyl group (CH_3-21) resonated in the form of a doublet, the α-diol grouping, which includes a tertiary hydroxy function, must be present at C-24—C-25.

The acetylation of the acetonide (IV) with acetic anhydride in pyridine gave the triacetate (VI) [$(M - 15)^+$ 643] and a diacetate (V) [$(M - 15)^+$ 601]. The Jones oxidation [8] of the latter led to a monoketo derivative (VIII) [$(M - 15)^+$ 599]. The IR spectrum of the keto compound (VIII) showed an absorption band at 1738 cm^{-1} characteristic of a five-membered cyclic ketone. Consequently, the keto function in compound (VIII) and the corresponding hydroxy group remaining free in the diacetate (V) were present in ring D. The CD spectrum of the ketone (VIII) exhibited a negative Cotton effect at 304 nm ($\Delta\varepsilon = -5.7$), showing the position of the keto function at C-16 [9].

The increment of molecular rotation between the triacetate (VI) and the diacetate (V) {$[M]_{D\text{-}VI} = +526°$, $[M]_{D\text{-}V} = +359°$, $\Delta[M]_D = +167°$} demonstrated the β-orientation of the hydroxy group at C-16 [10].

In the PMR spectra of compounds (I) and (III), taken in deuteropyridine, the resonance of one of the methyl groups gave signals at 1.73 and 1.80 ppm, respectively. This fact permitted the assumption that the triterpenoids (I) and (III) contained a 6α-hydroxy group [2, 3, 7]. In the spectrum of compound (III), the proton geminal to the hydroxy function under consideration resonated at 4.32 ppm in the form of a triplet of doublets with SSCCs $^3J_1 = {}^3J_2 =$ 10 and $^3J_3 = 4$ Hz. The good agreement of the facts given with the corresponding indices of the spectrum of sieversigenin [2] served as an additional confirmation of the conclusion that a 6α-hydroxy group was present.

The signal of the proton located geminally to the unidentified hydroxy function was observed at 3.40 ppm in the spectrum of compound (III) and had quartet multiplicity with SSCCs $^3J_1 = 10$ and $^3J_2 = 4$ Hz. These values are characteristic for 3α-H atoms and showed the presence of a 3β-OH group [2, 3].

Thus, cyclocanthogenin, just like cycloasgenin C [3] contains 3β,6α,16β-hydroxy groups in the polycyclic moiety of the molecule and an α-diol system at C-24—C-25. Consequently, the difference in the structures of the compounds being compared lies in the stereochemistry of the C-24 chiral center. Since cycloasgenin C has the 24R stereochemistry, the 24S configuration must be assigned to cyclocanthogenin.

To confirm the proposed structure, passage was made from cycloasgenin C and cyclocanthogenin to compounds (II) and (X).

The periodate oxidation of cyclocanthogenic gave the nor-compound (II) with a molecular weight of 432. The spectral characteristics of this compound were close to those of the analogous product obtained from cycloasgenin C and determined the substance under consideration as 16β-24ξ-epoxy-25-norcycloartane-3β-6α-24-triol [3].

The indeterminacy of a stereochemistry of C-24 in compound (II) impelled us to carry out a correlation of the structures of cyclocanthogenin and cycloasgenin C by another method. For this purpose, the isopropylidene grouping in the acetonide (VI) was eliminated by treatment with acetic acid, the 3,6,16-triacetate 24,25-diol (IX) (M^+ 618) being obtained. The periodate oxidation of this compound followed by reduction with sodium tetrahydroborate led to the formation of compound (X) (M^+ 434). Its IR, PMR, and mass spectra showed that the substance (X) was 25-norcycloartane-3β,6α,16β,24-tetraol. A product identical with the tetraol (X) was obtained from cycloasgenin C 3,6,16-triacetate (VII) after its treatment under analogous conditions. On the basis of the experimental facts given we are justified in concluding that cyclocanthogenic has the structure of 24S-cycloartane-3β,6α,16β,24,25-pentaol.

EXPERIMENTAL

General Observations. Silufol plates were used for thin layer chromatography (TLC). Column chromatography was performed on silica gel of type KSK or L (Czechoslovakia) with a grain size of 50-100 μ. In TLC, the substances were detected by spraying with a 25% methanolic solution of tungstophosphoric acid followed by heating at 100-110°C for 3-5 min.

The following solvent systems were used: 1) chloroform–methanol (15:1); 2) chloroform–methanol–water (70:12:1); 3) chloroform–methanol–water (70:23:4); 4) chloroform–ethyl acetate (1:3); 5) benzene–chloroform-ethyl acetate (5:1:1); and 6) chloroform–ethyl acetate (3:2).

PMR spectra were taken on XL-200 (Varian) and Tesla BS-567 A spectrometers in deuteropyridine and deuterochloroform (δ, ppm, 0 – HMDS, TMS). Mass spectra were obtained on a MKh-1310 instrument with an ionizing voltage of 50 V and temperatures of 130-170°C. IR spectra were recorded on a UR-20 instrument in KBr, and CD curves on a Jasco J-20 spectropolarimeter.

Isolation of the Cycloartane Triterpenoids of Astragalus tragacantha. The dried and comminuted stems (5 kg) of the plant Astragalus tragacantha in July, 1985 (Alushta region of Crimea Oblast), were exhaustively extracted with methanol. The methanolic extract was evaporated to dryness. Part of the dry extract was chromatographed on a column with elution by chloroform and by systems 1, 2 and 3. By repeated chromatography substances (1, 2, 5, 6, and 9-14) were isolated in the individual form.

Cyclosieversigenin (substance 1), $C_{30}H_{50}O_5$, mp 239-241°C (from methanol); $[\alpha]_D^{24}$ +50 ± 2° (c 1.2; methanol) [2, 3].

β-Sitosterol β-D-glucopyranoside (substance 2), $C_{35}H_{60}O_6$; mp 276-279°C (from methanol), $[\alpha]_D^{24}$ −3.7 ± 2 (c 1.1; pyridine) [4].

Cyclosieversioside F (substance 11), $C_{41}H_{68}O_{14}$; mp 284-286°C (from methanol); $[\alpha]_D^{24}$ + 40 ± 2° (c 0.6; methanol) [5, 6].

Cyclocanthogenin (I). Glycoside (12) (1.9 g) was heated in 200 ml of a 0.5% methanolic solution of sulfuric acid at 60°C for 48 h. The reaction mixture was diluted with water and extracted with chloroform. The chloroform extract was washed with water and evaporated. The products were chromatographed on a column with elution by system 1. This gave 550 mg of cyclocanthogenin (I), $C_{30}H_{52}O_5$; mp 194-195°C (from methanol); $[\alpha]_D^{23}$ +57.5 ± 2° (c 0.87; methanol). ν_{max}^{KBr}, cm^{-1}: 3560-3280 (OH), 3040 (CH_2 of a cyclopropane ring). Mass spectrum, m/z (%): M^+ 492 (4.2), 474 (100), 459 (65.2), 456 (86.9), 441 (84.8), 438 (21.7), 423 (73.9), 415 (47.8), 405 (39.1), 397 (86.9), 379 (43.5), 329 (69.6), 311 (95.7), 293 (30.4).

24S-Lanost-9(11)-ene-3β,6α,16β,24,25-pentaol (III). Glycoside (12) (250 mg) was boiled in 30 ml of a 0.5% methanolic solution of sulfuric acid for 8 h. After the workup by the method described above and the chromatography of the reaction products on a column in system 1, 30 mg of compound (III) was obtained: $C_{30}H_{52}O_5$, mp 258-260°C (from methanol), $[\alpha]_D^{22}$ + 100 ± 2 (c 0.50; methanol); ν_{max}^{KBr}, cm^{-1}: 3500-3285 (OH), 3055 (=CH–). Mass spectrum, m/z (%): M^+ 492 (6.0), 474 (54.8), 459 (27.4), 456 (59.5), 441 (78.6), 438 (10.1), 423 (57.7), 415 (34.5), 405 (19.0), 397 (57.1), 379 (20.8), 329 (100), 311 (85.7), 293 (17.9).

Cyclocanthogenin 24,25-Acetonide (XXIV) from (I). A solution of 500 mg of genin (I) in 20 ml of acetone containing 0.2% of sulfuric acid was left at room temperature for 2 days. After the workup and chromatography of the reaction products on a column in system 4, 460 mg of the acetonide (IV) was obtained: $C_{33}H_{56}O_5$, mp 222-225°C (from ethyl acetate), $[\alpha]_D^{23}$ + 69 ± 2° (c 0.55; methanol). ν_{max}^{KBr}, cm^{-1}: 3560-3450 (OH), 3060 (CH_2) of a cyclopropane ring. Mass spectrum, m/z (%): M^+ 532 (3.3), 517 (100), 514 (58.3), 499 (37.5), 496 (41.6), 481 (10.8), 474 (7.1), 456 (50.0), 441 (37.5), 438 (33.3), 423 (50.0), 405 (41.7), 401 (37.5), 329 (33.3), 311 (58.3), 201 (58.3).

Cyclocanthogenin 3,6-Di-acetate 24,25-Acetonide (V) and 3,6,16-Triacetate 24,25-Acetonide (VI) from (IV). The acetonide (IV) (360 mg) was acetylated with 4 ml of acetic anhydride in 8 ml of absolute pyridine for 12 h. The residue after the solvent had been evaporated was chromatographed on a column with elution by system 5. This gave 285 mg of the amorphous cyclocanthogenin 3,6,16-triacetate 24,25-acetonide (VI): $C_{39}H_{62}O_8$, $[\alpha]_D^{23}$ + 80 ± 2° (c 1.1; methanol). ν_{max}^{KBr}, cm^{-1}: 3040 (CH_2 of a cyclopropane ring); 1740, 1250 (ester groups). Mass spectrum, m/z (%): $(M - 15)^+$ 643 (44.4), 598 (27.7), 583 (7.8), 556 (3.3), 538 (66.7), 523 (23.3), 480 (26.7), 463 (23.3), 421 (24.4), 413 (21.1), 405 (41.1), 353 (25.6), 331 (24.4), 311 (16.7), 293 (66.7), 273 (100), 201 (88.9).

When the elution of the column was continued with the same solvent system, 97 mg of cyclocanthogenin 3,6-diacetate 24,25-acetonide (V) was obtained: $C_{37}H_{60}O_7$, mp 124-126°C (from methanol) $[\alpha]_D^{24}$ +58.3 ± 2° (c 0.72; methanol). ν_{max}^{KBr}, cm^{-1}: 3500 (OH); 3060 (CH_2 of a cyclo-

propane ring); 1740, 1250 (ester groups). Mass spectrum, m/z (%): $(M - 15)^+$ 601 (46.2), 556 (42.3), 541 (19.2), 496 (69.2), 481 (34.6), 438 (23.1), 423 (30.8), 413 (19.2), 405 (30.8), 369 (10.4), 353 (19.2), 311 (16.9), 293 (38.5), 273 (100), 201 (84.6).

3β,6α,24,25-Tetrahydroxy-24S-cycloartan-16-one 3,6-Diacetate 24,25-Acetonide (VIII) from (V). A solution of 60 mg of the diacetate (V) in 15 ml of acetone was treated with 0.15 ml of the Jones reagent [8]. Oxidation was carried out at −5°C with constant stirring for 40 min. The excess of oxidant was decomposed by the addition of 1 ml of methanol. After the usual working up procedure, the product obtained was chromatographed on a column with elution by system 5. This yielded 40 mg of the keto compound (VIII), $C_{37}H_{58}O_7$, mp 155-158°C (from hexane), $[\alpha]_D^{24}$ +26.7 ± 2° (c 0.60 methanol). ν_{max}^{KBr}, cm^{-1}: 3042 (CH_2 of a cyclopropane ring); 1738 (C=O at C-16); 1738, 1250 (ester groups). CD (c 0.11; ethanol) $\Delta\varepsilon = -5.7$ (304 nm). Mass spectrum, m/z (%): $(M - 15)^+$ 599 (42.1), 556 (23.7), 554 (17.1), 541 (52.6), 539 (82.9), 494 (96.1), 485 (94.7), 479 (38.2), 436 (47.4), 425 (36.8), 421 (100), 403 (28.9), 378 (23.7), 365 (42.1), 253 (63.2), 201 (48.7).

16β,24ξ-Epoxy-25-norcycloartane-3β,6α,24-triol (II) from (I). A solution of 200 mg of sodium periodate in 3 ml of water was added to a solution of 100 mg of cyclocanthogenin (I) in 15 ml of methanol, and the mixture was stirred at room temperature for 6 h. A few drops of ethylene glycol were added to the reaction mixture to decompose the excess of oxidant. After working up and the chromatography of the product obtained on a column in system 1, 53 mg of the nor-compound (II) was isolated: $C_{27}H_{44}O_4$, mp 149-150°C (from acetone) or 202-203°C (from ethyl acetate); $[\alpha]_D^{22}$ +30 ± 2° (c 0.8; methanol) shown to be identical with 16β,24ξ-epoxy-25-norcycloartane-3β,6α,24-triol [3] with respect to the constants given and to spectral characteristics.

Cyclocanthogenin 3,6,16-triacetate (IX) from (VI). Cyclocanthogenin 3,6,16-triacetate 24,25-acetonide (VI) (250 mg) was heated in 15 ml of acetic acid at 40°C for 8 h. Then the mixture was worked up and the products were chromatographed on a column with elution by system 6. This yielded 190 mg of the amorphous cyclocanthogenin 3,6,16-triacetate (IX), $C_{36}H_{58}O_8$, $[\alpha]_D^{23}$ +92.7 ± 2°(c 1.1; methanol). ν_{max}^{KBr}, cm^{-1}: 3560-3420 (OH); 3050 (CH_2 of a cyclopropane ring); 1740, 1250 (ester groups). Mass spectrum, m/z (%): M^+ 618 (0.2), 603 (0.2), 600 (0.3), 558 (44.4), 540 (13.9), 515 (3.5), 514 (3.6), 506 (4.2), 498 (100), 483 (50.0), 480 (33.3), 465 (19.4), 438 (38.9), 423 (55.6), 413 (38.9), 405 (33.3), 379 (27.8), 353 (33.3), 301 (22.2), 293 (72.2).

25-Norcycloartane-3β,6α,16β,24-tetraol (X) from (IX). The triacetate (IX) (100 mg) in 15 ml of methanol was treated with 200 mg of sodium periodate in 2 ml of water. The reaction mixture was stirred for 3 h. A few drops of ethylene glycol were added to the solution to decompose the excess of oxidant. Then the reaction mixture was diluted with water and extracted with chloroform. The chloroform extract was washed with water, dried with anhydrous sodium sulfate, and evaporated. The residue was dissolved in 15 ml of methanol, 200 mg of sodium tetrahydroborate was added in small portions, the mixture was left at room temperature for 1 h, and after this a twofold volume of water was added and the reaction products were extracted with chloroform. The chloroform extract was washed with water and evaporated. The residue was chromatographed on a column with elution by system 1. This gave 46 mg of the tetraol (X), $C_{27}H_{46}O_4$, mp 192-194°C (from ethanol); $[\alpha]_D^{23}$ +43.5 ± 2° (c 0.46; methanol). ν_{max}^{KBr}, cm^{-1}: 3500-3320 (OH); 3040 (CH_2 of a cyclopropane ring). Mass spectrum, m/z (%): M^+ 434 (4.3), 416 (69.2), 401(76.9), 398 (69.2), 383 (46.2), 365 (30.8), 357 (38.5), 329 (15.4), 311 (30.8), 233 (50.0), 201 (53.8), 161 (84.6), 151 (100).

25,Norcycloartane-3β,6α,16β,24-tetraol (X) from (VII). Cycloasgenin C 3,6,16-triacetate ((VII), for its preparation, see [3]) (70 mg) was subjected to oxidation with sodium periodate followed by reduction with sodium tetrahydroborate in the manner described in the preceding experiment. This gave 33 mg of product (X), $C_{27}H_{46}O_4$, mp 191-193°C (from ethanol) $[\alpha]_D^{24}$ + 44 ± 2°(c 0.6; methanol), which was also shown to be identical with 25-norcycloartane-3β,6α, 16β,24-tetraol by its spectral characteristics.

SUMMARY

In addition to cyclosieversigenin and cyclosieversioside F, a new methyl steroid of the cycloartane series – cycloanthogenin – has been isolated from the epigeal part of the plant Astragalus tragacantha, and its structure has been established as 24S-cycloartane-3β,6α,16β,24,25-pentaol.

LITERATURE CITED

1. M. A. Agzamova, M. I. Isaev, M. B. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 719 (1986).
2. A. N. Svechnikova, R. U. Umarova, M. B. Gorovits, K. L. Seitanidi, Ya. V. Rashkes, M. R. Yagudaev, and N. K. Abubakirov, Khim. Prir. Soedin., 67 (1981).
3. M. I. Isaev, M. B. Gorovits, N. D. Abdullaev, and N. K. Abubakirov, Khim. Prir. Soedin., 458 (1982).
4. L. J. Swift, J. Am. Chem. Soc., 74, 1099 (1952).
5. A. N. Svechnikova, R. U. Umarova, M. B. Gorovits, N. D. Abdullaev, and N. K. Abubakirov, Khim. Prir. Soedin., 208 (1982).
6. M. A. Agzamova, M. I. Isaev, M. B. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 117 (1986).
7. M. I. Isaev, M. B. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 431 (1985).
8. C. Djerassi, R. R. Engle, and A. Bowers, J. Org. Chem., 21, 1574 (1956).
9. P. Carbbé, ORD and CD in Chemistry and Biochemistry, Academic Press, New York (1972), p. 35.
10. L. Fieser and M. Fieser, Steroids, Reinhold, New York (1959) [Russian translation], Moscow (1964), p. 189.

TRITERPENOIDS FROM Abies SPECIES.

IV. NEW TRITERPENE ACIDS FROM THE NEEDLES OF Abies sibirica

V. A. Raldugin, S. A. Shevtsov,
N. I. Yaroshenko, Yu. V. Gatilov,
I. Yu. Bagryanskaya, L. I. Demenkova,
and V. A. Pentegova

UDC 547.914.2+539.26

Four new triterpene acids of the mariesiic acid series have been isolated from an extract of the needles of the Siberian fir in the form of their methyl esters, and their structures have been established on the basis of chemical transformations, spectral characteristics, and x-ray structural analysis.

Continuing an investigation of the triterpenoids of Abies sibirica Ledeb. (Siberian fir) [1-4], we found that an ethereal extract of it (yield 9%) contained 51% of acids the bulk of which were triterpene acids. The acids were separated by a known method [5] into "strong" (21% of the total amount of acids) and "weak." The 24-methylene-3,4-secocycloart-4(28)-en-3-oic acid described previously [3] and also all the resin and fatty acids, which were present in a ratio of 91:9 (GLC), passed into the weak-acid fraction. According to the GLC of their methyl esters, the diterpene (resin) acids consisted of dehydroabietic (38.3%), abietic (24.4%), palustric (20.2%), neoabietic (14.2%), and sandaracopimaric (2.8%) acids.

We have previously [4] described two new triterpene acids present in the strong-acid fraction for which structures (I) and (II) were suggested on the basis of spectral characteristics. In a further analysis of its composition, we isolated in the form of methyl esters four other new acids with the carbon skeleton of mariesiic acid A (III) – a component of an extract of the weeds of the fir Abies mariesii Mast. [6]. (See following page.)

Chromatography of the strong acids on silica gel gave a number of fractions which were methylated with diazomethane and chromatographed on the same sorbent. In this way, four methyl esters corresponding to the main components of the initial mixture were isolated (see the Experimental part). Two of them – the esters (IV) and (V) – had been described previoulsy [4], while the other two were new compounds having the structures expressed by formulas (VI) and (VII). The latter was isolated in the form of the acetate (VIII), crystalliz-

Novosibirsk Institute of Organic Chemistry, Siberian Branch, USSR Academy of Sciences.
Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 824-831, November-December, 1987. Original article submitted April 17, 1987.

 0009-3130/87/2306-0684$12.50