TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS.

XXII. CYCLOORBICOSIDE A FROM *Astragalus orbiculatus*

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The quantitatively main glycoside — cycloorbicoside A — has been isolated from the epigeal parts of the plant *Astragalus orbiculatus*, and on the basis of chemical transformations and spectral characteristics its structure has been established as (23R,24S)-16β,23:16α,24-diepoxycycloartane-3β,7β,25-triol 3-O-β-D-xylopyranoside.

In the present paper we consider a proof of the structure of cycloorbicoside A (I) — a new glycoside isolated from the plant *Astragalus orbiculatus* Ledeb. (*Leguminosae*). The genin of cyclorbicoside A is a methyl steroid of the cycloartane series, cycloorbigenin (II), the structure of which was described in a preceding communication [1].

The genin (II) was obtained by the acid hydrolysis of cycloorbicoside A and by the Smith decomposition [2] of glycoside (I). A qualitative and quantitative analysis of the products of the hydrolysis of cycloorbicoside A with the aid of TLC and GLC [3, 4] showed that glycoside (I) contained one D-xylose residue.

The acetylation of glycoside (I) with acetic anhydride in pyridine led to the formation of a tetraacetate (VI) and a pentaacetate (VII). In the PMR spectrum ($CDCl_3$) of the pentaacetate (VII) the signals of two methyl groups were shifted downfield in comparison with those in the tetraacetate (VI) and appeared at 1.26 and 1.37 ppm (Table 1). This fact indicates that in compound (VI) a tertiary hydroxy group had remained free. This was also shown by the paramagnetic shift of the H-24 signal by 0.42 ppm in the PMR spectrum of the pentaacetate (VII) as compared with the analogous signal in the spectrum of the tetraacetate (VI).

In the PMR spectra (C_5D_5N) of the acetates (VI) and (VII), the H-3 and H-7 signals are observed at 3.17 and 4.82 ppm and 3.18 and 4.82 ppm, respectively. It follows from a comparison of the given values of the chemical shifts of H-3 and H-7 with those of cycloorbicoside A and cycloorbigenin (II) that the D-xylose residue is present at C-3.

In the PMR spectra (C_5D_5N) of the acetates (VI) and (VII) the H-5'a and H-5'e protons of the D-xylose residue resonate in the form of quartets at 3.49 ppm (^2J = 12 Hz, ^3J = 10 Hz) and 4.16 ppm (^2J = 12 Hz, ^3J = 5 Hz). The position of the latter signal scarcely changes on passing from the glycoside (I) to the acetates (VI) and (VII). On the basis of these facts, it must be assumed that the D-xylose residue has the pyranose form.

The signal of the anomeric proton of the D-xylopyranose residue in the PMR spectra of compounds (I), (VI), and (VII) is observed in the form of a doublet with the SSCC ^3J = 6-7.5 Hz. Consequently, the D-xylopyranose has the Cl conformation, which means the β-configuration of the glycosidic bond [5]. The β-configuration of the anomeric center is also shown by the size of the molecular rotation difference between compounds (I) and (II) [6]. (Formulas, top, following page.)

The facts given indicate that cycloorbicoside A is the 3-O-β-D-xylopyranoside of cycloorbigenin.

A similar conclusion was arrived at in a study of the products of the methylation of glycoside (I). Methylation was performed by Hakomori's method [7]. A penta-O-methyl ether (III), a tetra-O-methyl ether (IV), and a tri-O-methyl ether (V) were isolated from the reaction mixture. It was shown by TLC and GLC [8] that the carbohydrate component of the methyl

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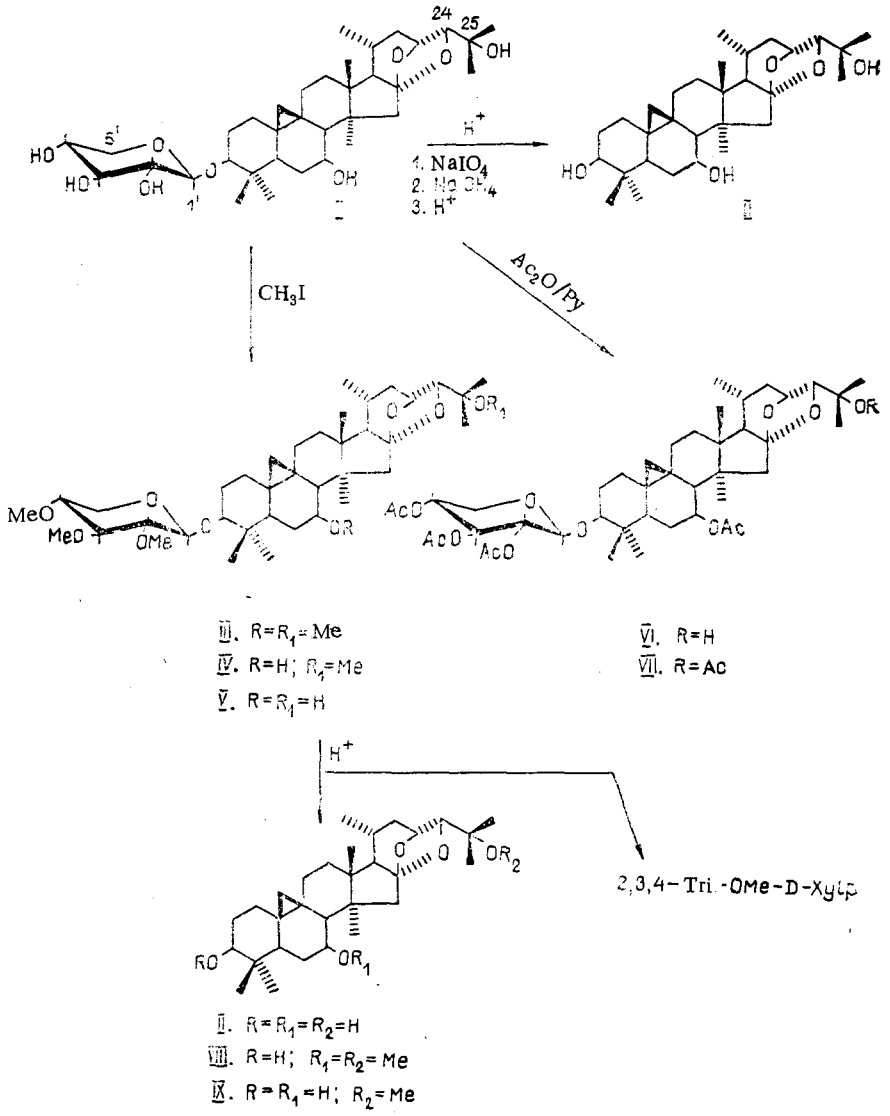

III. R=R$_1$=Me
IV. R=H; R$_1$=Me
V. R=R$_1$=H

VI. R=H
VII. R=Ac

I. R=R$_1$=R$_2$=H
VIII. R=H; R$_1$=R$_2$=Me
IX. R=R$_1$=H; R$_2$=Me

ethers (III-V) was represented by 2,3,4-tri-O-methyl-D-xylopyranose. This was also shown by the peaks of ions with m/z 175, 143, and 115 in the mass spectra of the methyl esters (III-V) which were assigned to a tri-O-methylpentose [9]. As was to be expected, cycloorbigenin (II) was isolated from the genin fraction of a hydrolysate of the tri-O-methyl ether (V), and the monomethyl ether of cycloorbigenin (IX) from the tetra-O-methyl ether (IV). In the mass spectrum of compound (IX) (M^+ 502) the maximum peak was that of an ion with m/z 429 arising on the splitting out of a methoxyisopropyl fragment with the cleavage of the C-24–C-25 bond. This fact permits the assumption that compound (IX) was the 25-monomethyl ether of cycloorbigenin. This conclusion was confirmed by the fact that the values of the chemical shifts of H-3 and H-7 in the PMR spectrum of the monomethyl derivative (IX) practically coincided with those in the spectrum of cycloorbigenin (II).

The acid hydrolysis of the permethylate (III) led to the dimethyl derivative (VIII) (M^+ 516). In the PMR spectrum of compound (VIII), the H-3 and H-7 protons resonated at 3.41 and 2.97 ppm, respectively. The H-3 chemical shift corresponded to the analogous index in the spectrum of cycloorbigenin (II), while the signal of the H-7 proton had undergone a considerable diamagnetic shift. Consequently, compound (VIII) was the 7,25-dimethyl ether of cycloorbigenin. The formation of this substance confirmed the conclusion concerning the attachment of the sugar residue to the hydroxy group at C-3. The SSCC (6-7 Hz) of the anomeric proton in the PMR spectra of the methyl ethers (III-V) [5] also indicated the β-configuration of the glycosidic bond.

Thus, it may be concluded that cycloorbicoside A has the structure (23R,24S)-16β,23:16α, 24-diepoxycycloartane-3β,7β,25-triol 3-O-β-D-xylopyranoside.

EXPERIMENTAL

General Remarks. The following solvent systems were used: 1) butan-1-ol-methanol—water (5:3:1); 2) chloroform—methanol (20:1); 3) benzene—acetone (15:1); 4) benzene—acetone (7:1); 5) benzene—ethyl acetate (5:1); 6) benzene—ethyl acetate (5:2); 7) chloroform—methanol (50:1); 8) benzene—methanol (40:1); 9) chloroform—acetone (15:2); 10) chloroform—methanol (15:1). Silica gels of types KSK and L (Czechoslovakia) with grain sizes of 50-100 μ were used for column chromatography. Thin-layer chromatography (TLC) was performed on Silufol plates.

The monosaccharides and their reducing derivatives were chromatographed on plates impregnated with a 0.3 M solution of sodium dihydrogen phosphate and on Silufol plates. On TLC, the substances were detected by spraying with o-toluidine salicylate followed by heating at 100-110°C for 2-5 min.

Gas—liquid chromatography was performed on a Biokhrom-1 chromatograph; glass capillary column (50 m) with the phase OV-101. The thermostat temperature was 160°C and the carrier gas was helium at a rate of flow of 4 ml/min. Monosaccharides were analyzed in the form of the trimethylsilyl derivatives of the corresponding methyl glycosides [3, 4]. Relative retention times (T_{rel}) were calculated in relation to the retention time of methyl β-D-glucopyranoside.

The methyl glycosides obtained by boiling the methyl ethers of the monosaccharides in 5% methanolic hydrogen chloride solution (4 h) were chromatographed on the same column at a thermostat temperature of 140°C. The relative retention times (T_{rel}) for the methylated methyl glycosides were calculated in relation to methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside.

PMR spectra were recorded in deuteropyridine or deuterochloroform on Varian XL-200 and Tesla BS-567 A instruments (δ, ppm, 0 — HMDS).

For other observations, see [1].

For the isolation of the triterpenoids of *Astragalus orbiculatus*, see [1].

Cycloorbicoside A (I). $C_{35}H_{56}O_9$, mp 267-269°C (from ethanol) $[\alpha]_D^{19}$ + 8.3 ± 2° (s 1.2; methanol). ν_{max}^{KBr}, cm^{-1}: 3610-3200 (OH), 3040 (CH_2 of a cyclopropane ring).

Cycloorbigenin (II) from (I). A solution of 220 mg of glycoside (I) in 100 ml of methanol containing 0.5% of sulfuric acid was boiled for 1.5 h. The reaction products were diluted with water and the methanol was evaporated off. The precipitate that deposited was recrystallized from methanol, giving 90 mg of cycloorbigenin (II), $C_{30}H_{48}O_5$, mp. 217-219°C, $[\alpha]_D^{20}$ + 28.3 ± 2° (s 1.19; ethanol).

The aqueous part of the acid hydrolysate was evaporated to a volume of 20 ml, and heating was continued for another 4 h. Then the reaction mixture was neutralized with ARA-8p anion-exchanger and was evaporated to dryness. The residue was found by TLC in system 1 in comparison with an authentic sample to contain D-xylose. According to the results of GLC, cycloorbicoside A (I) contained one D-xylose residue.

Smith Degradation of Cycloorbicoside A (I). To 0.5 g of cycloorbicoside A (I) in 20 ml of methanol was added 1 g of sodium periodate in 10 ml of water. The reaction was performed at room temperature with stirring for 3 h. Then 30 ml of water containing 2 ml of ethylene glycol was added to the reaction mixture and the reaction product was extracted with chloroform. The residue after the appropriate working up of the chloroform extract and evaporation was dissolved in 30 ml of methanol. In portions, 1 g of sodium tetrahydroborate was added to the solution and the mixture was left at the same temperature for 1.5 h. After this, the reaction mixture was acidified with 12 ml of an aqueous solution containing 2.3 ml of concentrated sulfuric acid and was left for 18 h. The acid solution was diluted with water and was extracted with chloroform. The residue after the evaporation of the chloroform extract was chromatographed on a column with elution by system 2. This gave 280 ml of cycloorbigenin (II), identified by the usual methods.

The Penta-O-methyl Ether (III), Tetra-O-methyl Ether (IV), and Tri-O-methyl Ether (V) of Cycloorbicoside A from (I). At room temperature, with constant stirring, 800 mg of sodium hydride was added in portions to a solution of 807 mg of cycloorbicoside A (I) in 100 ml of

TABLE 1. Chemical Shifts of the Protons of Cycloorbicoside A (I) and Its Derivatives (δ, ppm, 0 — HMDS)

Compound	Positions of protons								
	H-3	H-7	2H-19	H-23	H-24	H-1′	3H-2′; 3′; 4′	2H-5′	CH_3 groups	OAc
I	3,37 q ^3J=11; 4 Hz	3,64 m*	0,15; 0,59 d ^2J=4 Hz	4,58	3,56 s	4,71 d ^3J=6 Hz	3.50—4,30* ; 4,22 m* (H-5′ e)		0,73 d(^3J=6 Hz); 0,93; 1,10; 1,20; 1,24; 1,31; 1,33	—
II	3,38 q ^3J=12; 5 Hz	3,70 td ^3J=10: 10; 3 Hz	0,23; 0,65 d ^2J=4 Hz	4,62 q ^3J=9; 2 Hz	3,58 s	—	—		0,76 d (^3J=6 Hz); 0,99; 1,10 1,13; 1,26; 1,35 (2×CH_3)	—
III	[2,80—3,24*]		[0,18; 0,70 d ^2J=4 Hz	[4,28]	[3,31 s]	[4,19 d ^3J=7 Hz	[2,80—3,80* ; 3,90 m (H-5′ e)]		0,80 d; 0,80; 0,97 (2×CH_3); 1,00(2×CH_3); 1,08; (3,18; 3,22; 3,40; 3,56—2×OCH_3)]	—
IV	[2,80—3,58*]		[0,30; 0,66 d ^2J=4 Hz	[4,28]	[3,30 s]	[4,19 d ^3J=6 Hz	[2,80—3,80* ; 3,89 q, ^2J=10 Hz, ^3J=4 Hz (H-5′ e)]		[0,81 d(^3J=6 Hz); 0,81; 0,96 (2×CH_3); 1,02; 1,08(2×CH_3) 3,18; 3,40; 3,56—2×OCH_3)]	—
V	[2,80—3,60*]		[0,32; 0,67 d ^2J=4 Hz	[4,21**]	[3,31 s]	[4,20 d** ^3J=6 Hz	[2,80—3,80* ; 3,90 q, ^2J=10 Hz, ^3J=4 Hz(H-5′ e)]		[0,82; 0,84 d(^3J=6 Hz); 0,98; 1,04; 1,0,7; 1,10 (2 × CH_3); (3,41; 3,56—2×OCH_3)]	—
VI	3,18 q ^3J=10; 5 Hz	4.82 m*	0,16; 0,56 d ^2J=4 Hz	4,59	3.54 s**	4,72 d* ^3J=7 Hz	5,02—5,66 3,49 q**, ^2J=12 Hz, ^3J= =10 Hz (H-5′ a); 4,16 q , ^2J=12 Hz, ^3J=5 Hz (H-5′e)		0,73 d; 0,78; 0,85; 1,04; 1,11; 1,28; 1,34	1,85; 1.88; 1,90; 1,99
	[3,10 m*]	[4,72 m**]	[0,30 d ^2J=4 Hz	[4,22]	[3.28 s*]	[4,46 d ^2J=7,5 Hz	4,80—5,24** 3,26 m* (H-5′ a); 4,04q , ^2J=12 Hz, ^3J=5 Hz (H-5′e)]		[0,70; 0,81 d; 0,84; 1,02— —1.06 (4×CH_3)]	[1,93; 1,96 (3×OAc)]
VII	3,17 q ^3J=10; 5 Hz	4,82 m*	0,15; 0,55 d ^2J=4 Hz	4,40	3,90 s	4,71 d* ^3J=7 Hz	5,02—5,66 3,49 q, ^2J=12 Hz, ^3J=10 Hz (H-5′ a); 4.16 q. ^2J=12 Hz, ^3J=5Hz (H-5′ e)		0,72 d (^3J=6 Hz); 0,77; 0,84; 1.02; 1,08; 1,43; 1,50	1,85 (2×OAc); 1,90; 1.92; 1.98
	[3,10 m*]	[4,74m**]	[0,31 d ^2J=4 Hz	[4,24]	[3,70 s]	[4,46 d ^3J=7,5 Hz	[4,80—5,24** 3,26 q* , ^2J=12 Hz, ^3J=8 Hz (H-5′ a); 4,04 q, ^2J=12 Hz, ^3J=4 ,5 Hz (H-5′e,]		[0,70; 0,81 d (^3J=6 Hz); 0,84; 1.01; 1.02; 1,26; 1,37]	[1,93 (2×OAc); 1,97 (3×OAc)]
VIII	3,41 q ^3J=9; 5 Hz	2,97 td ^3J=10; 10; 4 Hz	0,10; 0,60 d ^2J=5 Hz	4,43	3,45 s	—	—		0,72 d(^3J=6 Hz); 0,97; 1,02; 1,05; 1,15 (3×CH_3); 3,08 (2×OCH_3)	—
IX	3,40 m*	3,68 td ^3J=10: 10; 4 Hz	0,20; 0,64 d ^2J=4 Hz	4,41	3,44 s	—	—		0,75 d (^3J=6 Hz); 0,96; 0,98 1,10 (3×CH_3); 1,30; 3,08 (OCH_3)	—

The spectra were taken in deuterochloroform or deuteropyridine. The indices given in square brackets were obtained by the use of deuterochloroform. The signals in the horizontal rows marked by asterisks are superimposed upon one another. Where its multiplicity is not shown, the signal of H-23 was observed in the form of a doublet (^3J = 9 Hz) with broadened components ($W_{1/2}$ = 9 Hz). The two H-15 protons of cycloorbicoside A (I) resonate in the spectrum in the form of the doublets of an AB system at 2.43 and 2.66 ppm with the SSCC ^2J = 14 Hz. The signals of the methyl groups appear in the form of singles, with the exception of the CH_3 at C-20, which has a doublet nature; d — doublet; q — quartet; td — triplet of doublets; m — multiplet.

dimethyl sulfoxide. After 40 min, 8 ml of methyl iodide was added dropwise and stirring was continued for another 5 h, after which the reaction mixture was poured into 200 ml of 2% aqueous sodium hyposulfite and was extracted with chloroform. The chloroform extract was washed with water. The residue after the evaporation of the solvent was chromatographed on a column with elution by system 3. This gave 113 mg of the crystalline penta-O-methyl ether (III), $C_{40}H_{66}O_9$, mp 164-166°C (from methanol), $[\alpha]_D^{21}$ + 22 ± 2° (s 0.45; chloroform–methanol (1:1)), ν_{max}^{KBr}, cm^{-1}: 3050 (CH_2 of a cyclopropane ring). There was no band in the region of absorption of hydroxy groups. Mass spectrum, m/z (%): M^+ 690 (4.5), 675 (3.2), 658 (3.6), 617 (48.0), 603 (1.9), 601 (2.3), 585 (11.0), 573 (7.0), 514 (27.0), 499 (14.0), 484 (19.0), 443 (24.0), 441 (38.0), 427 (12.0), 428 (10.0), 411 (46.0), 175 (100), 143 (65.0), 115 (23.0).

Continued elution of the column with the same system led to the isolation of 365 mg of the tetra-O-methyl ether (IV), $C_{39}H_{64}O_9$, mp 194-196°C (from methanol), $[\alpha]_D^{20}$ + 5.9 ± 2° (s 1.0; ethanol), ν_{max}^{KBr}, cm^{-1}: 3520 (OH), 3045 (CH_2 of a cyclopropane ring). Mass spectrum, m/z (%): M^+ 676 (2.0), 661 (2.2), 658 (0.7), 645 (1.6), 632 (0.5), 629 (0.6), 617 (1.5), 603 (40.0), 585 (2.9), 559 (4.3), 502 (5.7), 484 (20.0), 469 (7.9), 429 (11.4), 427 (13.6), 411 (100), 175 (23.6), 143 (22.1), 115 (7.9).

Elution with system 4 gave 257 mg of the tri-O-methyl ether (V), $C_{38}H_{62}O_9$, mp 202-204°C (from methanol), $[\alpha]_D^{20}$ + 8.2 ± 2° (s 0.9; ethanol) ν_{max}^{KBr}, cm^{-1}: 3530-3450 (OH), 3050 (CH_2 of a cyclopropane ring). Mass spectrum, m/z (%): M^+ 662 (0.8), 647 (8.8), 629 (1.1), 603 (23.5), 585 (1.7), 574 (3.8), 559 (2.6), 488 (17.6), 470 (61.8), 455 (26.5), 429 (14.7), 427 (20.6), 411 (91.2), 175 (100), 143 (97.1), 115 (29.4).

The Pentaacetate (VII) and Tetraacetate (VI) of Cycloorbicoside A from (I). Glycoside (I) (504 mg) was acetylated with 3 ml of acetic anhydride in 4 ml of absolute pyridine for 10 days at room temperature. The residue after the evaporation of the solvents was chromatographed on a column with elution by system 5. This gave 221 mg of the pentaacetate (VII), $C_{45}H_{66}O_{14}$, mp 240-242°C (from methanol), $[\alpha]_D^{20}$ + 7.5 ± 2° (s 1.06; benzene). ν_{max}^{KBr}, cm^{-1}: 1770-1730, 1270-1210 (ester groups). M^+ 830.

When elution of the column was continued with system 6, 314 mg of the tetraacetate (VI), $C_{43}H_{64}O_{13}$, was obtained with mp 201-203°C (from methanol), $[\alpha]_D^{20}$ + 8.0 ± 2° (s 1.0; ethanol). ν_{max}^{KBr}, cm^{-1}:3600-3450 (OH), 1770-1725, 1270-1220 (ester groups). M^+ 788.

(23R,24S)-16β,23:16α,24-diepoxycycloartane-3β,7β,25-triol 7,25-Dimethyl Ether (VIII) from (III). The penta-O-methyl ether (III) (83 mg) was boiled in 20 ml of a 0.25% methanolic solution of sulfuric acid for 1 h. Then the reaction mixture was diluted with 30 ml of water and the methanol was evaporated off. The precipitate that deposited was chromatographed on a column with elution by chloroform. This gave 25 mg of the dimethyl ether (VII), $C_{32}H_{52}O_5$, mp 156-158°C (from ethanol), $[\alpha]_D^{20}$ + 40.6 ± 2° (s 0.87; methanol), ν_{max}^{KBr}, cm^{-1}: 3475 (OH), 3030 (CH_2 of a cyclopropane ring). Mass spectrum, m/z (%): M^+ 516 (1.2), 501 (1.7), 484 (2.3), 469 (1.7), 443 (100), 411 (38.9), 393 (5.7), 271 (6.6), 253 (5.2).

(23R,24S)-16β,23:16α,24-diepoxycycloartane-3β,7β,25-triol 25-Monomethyl Ether (IX) from (IV). The tetra-O-methyl ether (IV) (120 mg) was hydrolyzed with 25 ml of a 0.25% methanolic solution of sulfuric acid as described in the preceding experiment. By chromatography of the products so obtained on a column in system 7, 50 mg of compound (IX), $C_{31}H_{50}O_5$, was isolated with mp 166-168°C (from methanol), $[\alpha]_D^{20}$ + 32.5 ± 2° (s 1.1; methanol). ν_{max}^{KBr}, cm^{-1}: 3540-3240 (OH), 3040 (CH_2 of a cyclopropane ring). Mass spectrum, m/z (%): M^+ 502 (0.2), 484 (8.8), 469 (3.4), 466 (3.0), 451 (4.8), 437 (1.8), 429 (100), 411 (52.9), 393 (9.6), 271 (8.8), 253 (7.4).

Cycloorbigenin (II) from (V). The tri-O-methyl ether (V) (20 mg) was boiled in 8 ml of a 0.25% methanolic solution of sulfuric acid for 6 h. The precipitate that formed after dilution with water and evaporation of the methanol was chromatographed on a column in system 8. This yielded 4 mg of cycloorbigenin (II), mp 216-218°C (from methanol). It was also identified from its IR spectrum and from its migration distances on TLC in various solvent systems.

Identification of 2,3,4-tri-O-methyl-D-xylopyranose. The filtrates obtained in the three preceding experiments were evaporated to a volume of 10 ml each, and the concentrated aqueous solutions were heated at 100°C for 5 h. Then they were neutralized with ARA-8p anion-exchanger. In all three cases, 2,3,4-tri-O-methyl-D-xylopyranose was identified by TLC (systems 9 and 10). The presence of a 2,3,4-tri-O-methyl-D-xylopyranose residue in each of compounds (III-V) was shown with the aid of GLC (T_{rel} 0.40, 0.44).

SUMMARY

A new cycloartane glycoside, cycloorbicoside A, has been isolated from the epigeal part of the plant *Astragalus orbiculatus* Ledeb.; it has the structure of (23R,24S)-16β,23:16α,24-diepoxycycloartane-3β,7β,25-triol 3-O-β-D-xylopyranoside.

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ABSOLUTE CONFIGURATION AND CONFORMATIONAL FEATURES OF ALKALOIDS OF THE NITRAMINE GROUP AND THEIR DERIVATIVES

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The absolute configurations of the asymmetric centers in the natural alkaloids nitramine (6R,7eS), isonitramine (6S,7eS), and sibirine (6R,7eR) have been established by the circular dichroism method using the octant rule.

On the basis of the results of x-ray structural analysis (XSA) of crystalline salts the conformations of the cations of nitramine and isonitramine have been found previously [1, 2]. Since the use of the program did not permit antipodes to be distinguished, the suggested diastereomerism of nitramine (I) and isonitramine (II) at the C(7) asymmetric center proved to be erroneous. Later by a comparison of the optical properties of the oxidation products of the two alkaloids we showed that (I) and (II) differed by the configuration of the C(6) spiro carbon atom [3]. In the present paper we give information on the study of the stereochemistry of the molecules of (I) and (II) and their N-methyl derivatives, and also of sibirine [4] by the circular dichroism (CD) method.

The nitramine and isonitramine molecules are fairly mobile. However, in solutions they exist predominantly in conformations fixed by an intramolecular hydrogen bond [1] which is characteristic, in particular, for γ-amino alcohols. Nitramine is conformationally more mobile than isonitramine, and therefore the sign of its specific rotation changed on passing from chloroform ($[\alpha]_D$ + 16°) to methanol ($[\alpha]_D$ − 8°). The conformation of isonitramine is more stable in relation to a change of solvent: $[\alpha]_D$ − 30° ($CHCl_3$) and $[\alpha]_D$ − 37° (CH_3OH).

The oxidation of the hydroxy groups in (I) and (II) to carbonyl groups gave dehydronitramine (III) and dehydroisonitramine (IV) each with one asymmetric center at the C(6) spiro atom. In the CD spectra of compounds (III) and (IV) there were Cotton effects (CEs) in the 300 nm due to the n → π* transition of the carbonyl chromophore with were equal in intensity ($\Delta\varepsilon$ = 0.60) and opposite in sign (Fig. 1, curves 6 and 1, respectively). Similar results were obtained for the specific rotation: $[\alpha]_D$ III −46° (chloroform), $[\alpha]_D$ IV +44° (chloroform). On

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