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TRITERPENE GLYCOSIDES FROM *Astragalus* AND THEIR GENINS. LXXI. CYCLOORBICOSIDE D, A NEW GLYCOSIDE FROM *Astragalus orbiculatus*

R. P. Mamedova, M. A. Agzamova, and M. I. Isaev

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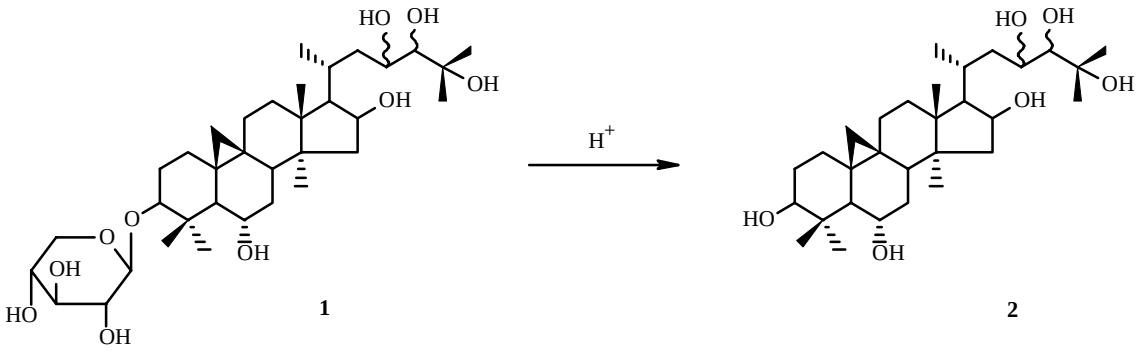
The new cycloartane glycoside cycloorbicoside D, which has the structure 23ξ,24ξ-cycloartan-3β,6α,16β,23,24,25-hexaol 3-O-β-D-xylopyranoside, was isolated from the aerial part of Astragalus orbiculatus *Ledeb. (Leguminosae).*

Key words: triterpenoids, cycloartanes, cycloorbicoside D, *Astragalus*, Leguminosae, ^{1}H and ^{13}C NMR spectra, J-modulation, 2D NMR: ^{1}H—^{1}H COSY, TOCSY, ROESY, HSQC, HMBC.

In continuation of research on triterpenoids from plants of the genus *Astragalus* [1], we isolated from the methanol extract of *A. orbiculatus* Ledeb. (Leguminosae) the new glycosidic compound **6** [2], which we called cycloorbicoside D (**1**). The proof of structure of this glycoside is examined in the present article.

The PMR spectrum of **1** (Table 1) exhibits at strong field a 1H doublet for an AX system at δ 0.17 and 0.45 with characteristic geminal SSCC ^{2}J = 4 Hz, indicative of the presence of a 1,1,2,2-tetrasubstituted cyclopropane ring. Signals for seven methyls are also seen in the same spectrum. These facts indicate that the examined compound is a cycloartane triterpenoid [3-5]. In fact, the acid hydrolysis products of **1** contained the genin, which was identified as cycloorbigenin C (**2**) [6].

Paper chromatography (PC) detected D-xylose in the carbohydrate part of the hydrolysate. The PMR and ^{13}C NMR spectra of **1** exhibit signals from one unit of this monosaccharide. This means that **1** is a monoxyloside.



1 **2**

A comparison of the ^{13}C NMR spectra of cycloorbicoside D and cycloorbigenin C (Table 1) shows that C-3 experiences a glycosylation effect in the spectrum of the former. Therefore, the D-xylose is bonded to this C atom.

The chemical shifts and SSCC of the monosaccharide protons are consistent with the pyranose form, the $^4C_1$-conformation and the β-configuration of D-xylose. This same conclusion is reached based on the chemical shifts of the corresponding C atoms.

Thus, we correctly conclude that cycloorbicoside D is 23ξ,24ξ-cycloartan-3β,6α,16β-23,24,25-hexaol 3-O-β-D-xylopyranoside.

S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (99871) 120 64 75, e-mail: m_isaev@rambler.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 345-346, July-August, 2005. Original article submitted March 10, 2005.

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TABLE 1. Chemical Shifts of C and H Atoms in **1** (δ, ppm, J/Hz, C_5D_5N, 0 = HMDS) and **2** (δ, ppm, J/Hz, C_5D_5N, 0 = TMS)

C atom	Compound			
	1		**2**	
	δ_C	δ_H (J)	δ_C	δ_H (J)
1	32.43		32.85	1.28, 1.65
2	29.17		31.49	1.95, 2.05
3	88.67	3.53 dd (12, 4)	78.41	3.67 dd (11.5, 4.5)
4	42.80		42.51	-
5	53.98		54.01	1.75 d (9.2)
6	67.87	3.66 m	68.29	3.81 td (9.3, 3.4)
7	38.30		38.62	1.75, 2.05
8	46.90		47.19	1.97
9	21.24		21.30	-
10	30.26		29.64	-
11	26.16		26.36	1.25, 1.95
12	32.95		33.05	1.65, 1.65
13	45.57		46.18	-
14	46.72		46.90	-
15	47.70		47.78	1.80, 2.15
16	72.07	4.60 td (7.5, 5)	72.20	4.72 td (7.2, 5.2)
17	57.34		57.51	1.86
18	18.70	1.27 s	18.94	1.40 s
19	30.00	0.17, 0.45 d (4)	30.11	0.33, 0.61 d (4)
20	27.25		27.41	2.61 m
21	20.15	1.10 d (6.5)	20.36	1.21 d (7)
22	42.64		42.97	2.15, 2.20
23	73.01	4.22 m	73.17	4.33 t (8.5)
24	79.07	3.67 d (9)	79.19	3.77 d (8.2)
25	74.27		74.37	-
26	24.54	1.62 s	24.70	1.72 s
27	28.80	1.59 s	28.98	1.68 s
28	20.04	0.91 s	20.25	1.03 s
29	28.77	1.88 s	29.41	1.89 s
30	16.62	1.23 s	16.20	1.37 s
	β-D-Xyl*p*			
1	107.48	4.80 d (8)		
2	75.51	3.96 dd (9, 8)		
3	78.39	4.06 t (9)		
4	71.17	4.14 td (10, 5)		
5	66.93	3.62 dd (11, 10)		
		4.26 dd (11, 5)		

Chemical shifts of protons are given without multiplicities and SSCC found using 2D spectra.

EXPERIMENTAL

General comments have been published [7]. We used the following solvents: $CHCl_3$:CH_3OH:H_2O (70:12:1, 1), $CHCl_3$:CH_3OH (15:1, 2), *n*-C_4H_9OH:C_5H_5N:H_2O (6:4:3, 3).

PC was performed on FN-11 paper in descending mode using system 3. Monosaccharides in PC were detected by spraying with anilinium phthalate followed by heating for 5-10 min at 100-110°C.

PMR and ^{13}C NMR spectra were obtained on Bruker DRX-500 and Bruker WM-250 spectrometers in C_5D_5N. ^{13}C NMR spectra were recorded with full C–H decoupling and with J-modulation. 2D NMR spectra were recorded using standard Bruker programs.

Cycloorbicoside D (1). Intermediate fractions containing **6** that accumulated during isolation of cycloorbicosides A [8] and G [9] were rechromatographed over a column using system 1 to isolate **1**, $C_{35}H_{60}O_{10}$, mp 285-287°C (CH_3OH).

PMR spectrum (250 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = TMS): 0.27 and 0.55 (2H-19, d, $^2J = 4$), 1.00 (CH_3, s), 1.19 (CH_3-21, d, $^3J = 6$), 1.31 (CH_3, s), 1.34 (CH_3, s), 1.63 (CH_3, s), 1.67 (CH_3, s), 1.98 (CH_3, s), 4.90 (H-1, D-xylose, d, $^3J = 7$).

Table 1 lists the PMR spectrum obtained at 500 MHz with HMDS internal standard.

^{13}C NMR spectrum (62.5 MHz, C_5D_5N, δ, ppm, 0 = TMS): 32.51 (C-1), 29.37 (C-2), 88.67 (C-3), 42.73 (C-4), 54.07 (C-5), 67.96 (C-6), 38.18 (C-7), 46.90 (C-8), 21.41 (C-9), 30.10 (C-10), 26.37 (C-11), 33.19 (C-12), 45.76 (C-13), 46.79 (C-14), 47.70 (C-15), 72.84 (C-16), 57.54 (C-17), 18.65 (C-18), 30.01 (C-19), 27.37 (C-20), 20.12 (C-21), 42.53 (C-22), 72.13 (C-23), 79.45 (C-24), 73.93 (C-25), 24.90 (C-26), 28.43 (C-27), 20.17 (C-28), 28.72 (C-29), 16.56 (C-30), 107.06 (C-1′), 74.98 (C-2′), 77.60 (C-3′), 70.99 (C-4′), 66.30 (C-5′).

Table 1 lists the ^{13}C NMR spectrum obtained at 125 MHz.

Acid Hydrolysis of Cycloorbicoside D. Glycoside **1** (800 mg) was hydrolyzed by methanolic H_2SO_4 (60 mL, 0.25%) at 70°C for 3 h. The reaction mixture was diluted with water. The methanol was evaporated. The resulting solid was filtered off and washed with water. The dried solid was chromatographed over a column with elution by system 2 to isolate cycloorbigenin C (**2**, 450 mg), mp 256-258°C (MeOH).

Table 1 lists the PMR and ^{13}C NMR spectra.

The aqueous filtrate was concentrated to 30 mL and boiled for 1 h. The cooled reaction mixture was neutralized with ARA-8p anion-exchanger. After removing the anion-exchanger and evaporating the solution to a small volume, PC using system 3 detected in the concentrated solution D-xylose. The PMR and ^{13}C NMR spectra indicate that cycloorbicoside D contains one D-xylose unit.

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