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TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS. LXX. ORBICOSIDE, THE FIRST LANOSTANE GLYCOSIDE FROM *Astragalus* PLANTS

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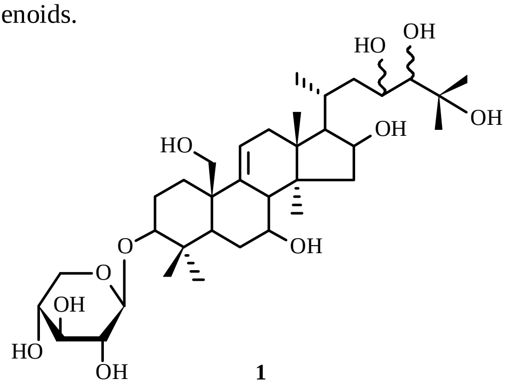
Orbicoside, a new lanostane glycoside and the first from plants of the Astragalus *genus, was isolated from the aerial organs of* Astragalus orbiculatus *Ledeb. (Leguminosae). It has the structure 23ξ,24ξ-lanost-9(11)-en-3β,7β,16β,19,23,24,25-heptaol 3-O-β-D-xylopyranoside. The structure of orbicoside was established using PMR and ^{13}C NMR, which were interpreted using DEPT and 2D NMR spectroscopies ^1H–^1H COSY, HSQC, and HMBC.*

Key words: lanostanoids, triterpenoids, orbicoside, *Astragalus*, Leguminosae, PMR and ^{13}C NMR spectra, DEPT, 2D NMR: ^1H–^1H COSY, HSQC, HMBC.

In continuation of research on isoprenoids of plants from the *Astragalus* genus [1], we isolated from the aerial part of *Astragalus orbiculatus* Ledeb. (Leguminosae) a new glycoside and called it orbicoside (**1**) [2]. The structure determination is presented in this communication.

The PMR and ^{13}C NMR of **1** (Table 1) were interpreted using DEPT and 2D NMR spectroscopy methods (^1H–^1H COSY, HSQC, HMBC), which clearly indicated signals of seven methyls and one hydroxymethyl belonging to the genin. Considering that the lanostane triterpenoid orbigenin (**2**) was isolated from this plant [1, 2], we assigned orbicoside to lanostane tetracyclic triterpenoids.



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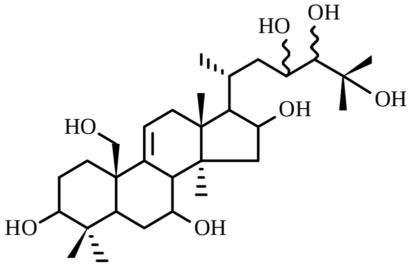

2

In fact, a comparison of the PMR and ^{13}C NMR spectra of **1** and **2** shows that the genin part of orbicoside and orbigenin are completely similar with the exception of C-3, which is glycosylated. Therefore, orbigenin is the aglycon of **1**.

The chemical shifts of the C and H atoms of the carbohydrate part and the spin—spin coupling constants (SSCC) indicate that **1** is a monoside that contains *β*-D-xylopyranose [3-10]. These parameters are consistent with the $^4C_1$-conformation of the pentose in orbicoside.

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TABLE 1. Chemical Shifts of C and H in Orbicoside (**1**), Data from DEPT and 2D NMR Spectra: ^{1}H–^{1}H COSY, HSQC, and HMBC and Chemical Shifts of C Atoms in Orbigenin (**2**) (δ, ppm, J/Hz, C_5D_5N, 0 = TMS)

C atom	**1**				**2**
	δ_C	DEPT	δ_H (J)	HMBC (C atom)	δ_C
1	30.87	CH_2	*α* 1.35		30.99
			β 2.62 dt (13.6; 3.4)		
2	27.22	CH_2	2.13; 2.40		28.66
3	88.87	CH	3.50 dd (11.8; 4)	4, 29, 30, X1	78.20
4	39.84	C	-		39.71
5	50.44	CH	1.36		50.34
6	31.85	CH_2	1.98; 2.25		32.22
7	71.79	CH	4.09 td (10; 4)		71.84
8	50.87	CH	2.87 dm	7, 9, 11, 13	50.87
9	141.86	C	-		142.01
10	44.93	C	-		45.30
11	121.58	CH	5.62 dt (6.2; 2)	8, 10, 12, 13	121.57
12	37.54	CH_2	2.16; 2.26	9, 11, 13, 14, 18	37.54
13	45.37	C	-		45.37
14	45.37	C	-		45.38
15	49.52	CH_2	2.48 dd (14; 5)	8, 13, 14, 16, 28	49.56
			3.00 dd (14; 8)	13, 14, 17, 28	
16	72.63	CH	4.83 td (8; 5)	13, 14	72.63
17	55.50	CH	1.93 dd (11.3; 7.3)		55.50
18	15.69	CH_3	1.43 s		15.72
19	60.54	CH_2	4.09; 4.22 d (10)		60.54
20	27.42	CH	2.62		27.42
21	20.47	CH_3	1.23 d (6.4)		20.47
22	43.03	CH_2	2.20; 2; 20		43.03
23	73.20	CH	4.32 td (8.4; 3)		73.21
24	79.14	CH	3.78 d (8.4)		79.13
25	74.25	C	-		74.24
26	24.70	CH_3	1.73 s		24.69
27	28.89	CH_3	1.69 s		28.90
28	19.28	CH_3	1.15 s		19.28
29	28.57	CH_3	1.37 s		29.18
30	18.10	CH_3	1.10 s		17.70
			β-D-Xyl*p* (X)		
1	107.73	CH	4.88 d (7.6)	3, X4	
2	75.48	CH	4.02 dd (8.6; 7.8)	X3	
3	78.60	CH	4.18 t (8.6)	X2, X4	
4	71.23	CH	4.23 m		
5	67.14	CH_2	4.41 dd (11.3; 5)	X1, X3, X4	
			3.81 dd (11.3; 9.9)	X1, X3, X4	

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

The signal for C-3 in the ^{13}C NMR spectrum of **1** undergoes a low-field shift by $\Delta\delta$ +10.67 ppm compared with that in **2** and is observed at δ 88.87. This unambiguously determines the bonding site of the carbohydrate as C-3 of the genin. In agreement with this, correlation peaks occurred between the anomeric proton, observed at δ 4.88 as a doublet with SSCC ^3J = 7.6 Hz, and C-3 of the genin and between H-3, found at δ 3.50 as a doublet of doublets with SSCC $^3J_1$ = 11.8 Hz and $^3J_2$ = 4 Hz, and the anomeric C atom observed at δ 107.73.

Thus, the spectral data lead to the conclusion that the new lanostane glycoside orbicoside has the structure 23ξ,24ξ-lanost-9(11)-en-3β,7β,16β,19,23,24,25-heptaol 3-O-β-D-xylopyranoside. Orbicoside is the first lanostane glycoside isolated from plants of the *Astragalus* genus [2, 11].

EXPERIMENTAL

General comments have been published [12]. The following solvent systems were used: $CHCl_3$:CH_3OH:H_2O (70:23:4, 1).

PMR and ^{13}C NMR spectra were recorded on a UNITY 400plus spectrometer in C_5D_5N (δ, ppm, 0 = TMS); ^{13}C NMR spectra, with full C—H decoupling and also under DEPT conditions. 2D NMR spectra were recorded using standard Varian programs.

Isolation and Separation of *Astragalus orbiculatus* Ledeb. Triterpenoids. Fractions with compound 8 that accumulated after elution of cycloorbicoside G [13] were rechromatographed over a column with elution by system 1 to isolate 8 (98 mg), called by us orbicoside (**1**).

Orbicoside (1), $C_{35}H_{60}O_{11}$, mp 281-283°C (CH_3OH).

For PMR and ^{13}C NMR spectra, see Table 1.

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