Chemistry of Natural Compounds, Vol. 43, No. 3, 2007

TRITERPENE GLYCOSIDES FROM *Astragalus* AND THEIR GENINS. LXXV. STEROLS AND TRITERPENOIDS FROM *Astragalus orbiculatus*

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UDC 547.918:547.926

In continuation of research on isoprenoids from plants of the genus *Astragalus* (Leguminosae), we isolated and identified from the aerial part of *A. orbiculatus* Ledeb. 12 triterpenoids of the cycloartane and lanostane types [1, 2]. One of these, cycloartane glycoside cycloorbicoside A (**3**), is an effective interferon inductor [3]. Therefore, we studied roots of *A. orbiculatus* for isoprenoid content.

Air-dried ground roots (4 kg) that were collected during fruiting near Aktash of Tashkent District (Ugam ridge) were exhaustively extracted by methanol (5 × 15 L). Evaporation of the methanol afforded dry extract (109.92 g) that was chromatographed over a column of silica gel (grade L) with elution successively by $CHCl_3$, $CHCl_3$:CH_3OH (20:1), and $CHCl_3$:CH_3OH:H_2O (70:12:1). Repeated rechromatography of fractions containing isoprenoids using various solvent systems isolated three pure compounds: **1** (145 mg, 0.0036%), **2** (93 mg, 0.0023%), and **3** (839 mg, 0.021%). These were identified as *β*-sitosterol (**1**) [4], *β*-sitosterol *β*-D-glucopyranoside (**2**) [4], and cycloorbicoside A (**3**) [5] based on PMR (see below) and ^{13}C NMR spectra (Table 1) and direct comparison with authentic samples.

The yield of cycloorbicoside A from aerial parts of *A. orbiculatus* was 0.6% [6]. This is 30 times greater than the yield from roots. Therefore, consideration of roots of this plant as a source of cycloorbicoside A is unwarranted.

***β*-Sitosterol (1)**, $C_{29}H_{50}O$, mp 131-132°C (MeOH). Mass spectrum (*m*/*z*): 414 (100) $[M]^+$, 399 (37.5), 396 (50), 381 (31.3), 329 (37.5), 303 (56.3), 273 (31.3), 255 (37.5), 231 (25), 213 (43.8).

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = TMS): 0.70 (s, CH_3-18), 0.88 and 0.90 (d, ^3J = 6.8, CH_3-26 and CH_3-27), 0.91 (t, ^3J = 7.6, CH_3-29), 1.01 (d, ^3J = 6.6, CH_3-21), 1.08 (s, CH_3-19), 2.69 (m, 2H-4), 3.90 (m, H-3), 5.49 (br.d, H-5).

Table 1 lists the ^{13}C NMR spectrum.

***β*-Sitosterol *β*-D-glucopyranoside (2)**, $C_{35}H_{60}O_6$, mp 276-279°C (MeOH).

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = TMS): 0.67 (s, CH_3-18), 0.87 and 0.89 (d, ^3J = 6.8, CH_3-26 and CH_3-27), 0.91 (t, ^3J = 7.6, CH_3-29), 0.95 (s, CH_3-19), 1.00 (d, ^3J = 6.4, CH_3-21), 2.50 and 2.75 (m, 2H-4), 3.94-4.04 (m, H-3 and D-glucose H-5), 4.09 (dd, $^3J_1$ = 9, $^3J_2$ = 7.8, D-glucose H-2), 4.29-4.36 (m, D-glucose H-3 and D-glucose H-4), 4.45 (dd, ^2J = 11.7, ^3J = 5.3, D-glucose H-6), 4.60 (dd, ^2J = 11.7, ^3J = 2.5, D-glucose H-6′), 5.09 (d, ^3J = 7.6, D-glucose H-1), 5.37 (m, H-5).

Table 1 lists the ^{13}C NMR spectrum.

Cycloorbicoside A (3), $C_{35}H_{56}O_9$, mp 267-269°C (EtOH).

PMR spectrum (100 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.20 and 0.62 (d, ^2J = 4, 2H-19), 0.76 (d, ^3J = 5, CH_3-21), 0.94, 1.10, 1.22, 1.24, 1.30, 1.34 (s, 6 × CH_3), 2.54 (AB q, ^2J = 14, 2H-15), 3.40 (dd, $^3J_1$ = 11, $^3J_2$ = 4, H-3), 3.56 (s, H-24), 4.59 (br.d, ^3J = 9, H-23), 4.72 (d, ^3J = 7, D-xylose H-1).

Table 1 lists the ^{13}C NMR spectrum.

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TABLE 1. Chemical Shifts of C Atoms in **1-3** (δ, ppm, C_5D_5N, 0 = TMS)

C atom	Compound			C atom	Compound		
	1	**2**	**3**		**1**	**2**	**3**
1	37.89	37.60	32.01	20	36.46	36.47	23.81
2	32.69	30.36	29.71	21	19.66	19.51	20.06
3	71.32	78.51	88.35	22	34.27	34.34	38.46
4	43.56	39.46	41.10	23	26.47	26.58	71.75
5	142.03	141.04	46.63	24	46.10	46.19	90.57
6	121.24	121.97	31.83	25	29.52	29.63	71.12
7	32.28	32.27	70.18	26	19.07	19.11	27.89*
8	32.22	32.18	55.35	27	19.26	19.33	24.75*
9	50.54	50.48	19.78	28	23.44	23.52	18.97[a]
10	36.96	37.03	27.20	29	12.06	12.07	25.83
11	21.42	21.38	26.80	30	-	-	15.39
12	40.08	40.07	33.13			*β*-D-Glc*p*	*β*-D-Xyl*p*
13	42.57	42.60	44.27	1		102.69	107.50
14	56.97	56.95	46.84	2		75.41	75.50
15	24.59	24.60	48.87	3		78.69	78.58
16	28.60	28.61	115.30	4		71.85	71.21
17	56.33	56.38	60.62	5		78.26	67.10
18	12.21	12.25	18.97[a]	6		62.98	
19	20.03	20.04	30.00				

*Signals assigned unambiguously; [a]signals superimposed.

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