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TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS.
LXII. GLYCOSIDES OF *Astragalus stipulosus*

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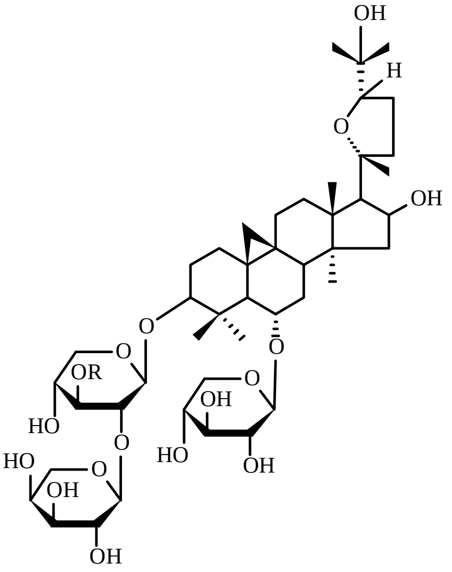
We are continuing research on triterpene glycosides of the cycloartane series that are produced by plants of the *Astragalus* genus (Leguminosae) [1]. In the present communication, compounds of stipular astragalus (*Astragalus stipulosus* Boriss.) are described. The cycloartane glycosides askendoside B (**1**) [2, 3], D (**2**) [3, 4], G (**3**) [5], and saccharose were isolated from the roots of this plant. The glycosides were identified by direct comparison with authentic samples and on the basis of ^{1}H and ^{13}C NMR spectra, which were interpreted using 2D NMR ^{1}H—^{1}H COSY, HMQC, and results from DEPT and J-modulation experiments.

The ^{1}H and ^{13}C NMR spectra of askendosides B and D have been partially examined [2, 4, 6]. Therefore, we present the complete interpretation of these spectra (Table 1).

Air-dried ground roots of stipular astragalus (600 g) that were stored in October 1997 in Baisun region of Surkhandar′ya district of the Republic of Uzbekistan were extracted with CH_3OH (3×2 L). A compound (420 mg) that was identified as saccharose by paper chromatography (*n*-butanol—pyridine—water, 6:4:3) crystallized out of the first CH_3OH extract on standing. Judging from the intensity of the spot on TLC, saccharose is the predominant component in the CH_3OH extract. However, we did not attempt to isolate quantitatively saccharose or even determine its content.

A dry solid (58.5 g) was obtained after evaporating the CH_3OH extracts. The CH_3OH extract (4 g) was chromatographed on a column using $CHCl_3$—CH_3OH—H_2O (70:23:4). Yield of askendoside B (**1**), 174 mg, 0.42% of dry roots; askendoside D (**2**), 15 mg, 0.037%; askendoside G (**3**), 414 mg, 1.01%.



1. R=Ac
2. R=H

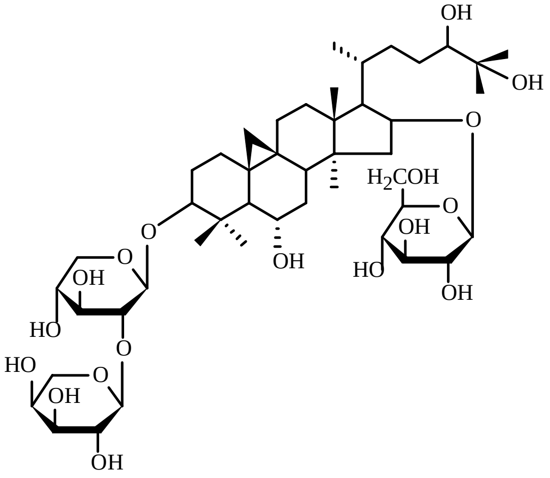


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TABLE 1. ^{1}H and ^{13}C NMR Spectra of Askendosides B (**1**) and D(**2**) and ^{13}C NMR Spectrum of Askendoside G (**3**) (δ, ppm, J, Hz, C_5D_5N, TMS = 0)

C atom	Compound				
	1		**2**		**3 [5]**
	δ_C	$\delta_H(J)$	δ_C	$\delta_H(J)$	δ_C
1	31.70	1.26 and 1.50 m	31.76	1.25; 1.50	32.64[a]
2	29.69	1.93 and 2.20 m	29.93	1.92; 2.22	29.21
3	88.26	3.22 dd(11.6; 4.5)	87.59	3.31 dd(11;5)	88.59
4	42.57	-	42.56	-	42.80
5	51.77	1.79 d (7.6)	51.64	1.78 d (8)	54.01
6	77.19	3.76 m	77.18	3.73 m	67.98
7	32.92	1.66 and 2.13 m	32.88	1.65; 2.03	38.40
8	43.16	2.12 d (7.6)	43.11	2.03	46.84
9	21.29	-	21.24	-	21.29
10	27.99	-	27.93	-	30.33[b]
11	26.51	1.50 and 2.06 m	26.41	1.50; 2.03	26.30[c]
12	33.52	1.50 and 1.66 m	33.45	1.50; 1.65	34.44
13	45.25	-	45.18	-	45.57
14	46.16	-	46.09	-	46.84
15	45.62	1.84 dd (12.5; 7.5) 2.38 dd (12.5; 7.9)	45.54	1.78 dd (12; 8) 2.29 dd (12; 8)	47.73
16	73.43	5.08q (7.3)	73.37	4.99 q (8)	83.14
17	58.04	2.61 d (7.8)	57.97	2.54 d (8)	57.52
18	20.11	1.39 s	20.05	1.33 s	18.08
19	25.40	0.09 and 0.61 d (4.4)	25.43	0.07 and 0.57 d (4)	30.33[b]
20	87.35	-	87.26	-	31.97
21	28.63	1.31 s	28.55	1.26 s	19.05
22	34.92	1.66;3.15q (10.6)	34.85	1.63; 3.05 k (11)	30.33[b]
23	26.31	2.06 and 2.33 m	26.22	2.02; 2.25	32.64[a]
24	81.66	3.89 dd (9; 5.3)	81.58	3.83 dd (9; 6)	80.00
25	71.28	-	71.23	-	72.76
26	27.12	1.31 s	27.04	1.26 s	25.40
27	28.18	1.60 s	28.08	1.53 s	26.30[c]
28	19.53	1.17 s	19.48	1.10 s	20.17
29	27.59	1.65 s	27.48	1.72 s	28.69
30	16.37	1.32 s	16.26	1.28 s	16.36
3-O-β-*D*-Xyl*p*					
1	104.05	4.89 d (5.5)	105.21	4.73 d (7)	105.70
2	75.47[a]	4.29 dd (7.4; 5.5)	83.54	4.02 dd (9; 7)	83.66
3	77.04	5.66t (7.4)	77.37	4.08	77.76
4	68.48	4.14 td (7.6; 4.4)	70.91	4.08	71.04
5	65.00	3.71 dd (11.3; 9.5) 4.33 dd(11; 5)	66.47	3.53 dd (12; 9) 4.23	66.71
α-*L*-Ara*p*					
1	105.22	5.01 d (7)	106.67	5.12 d (6.6)	106.74[d]
2	72.48	4.41 dd (9; 7)	73.63	4.53 dd (8.4; 6.6)	73.65
3	74.46	4.19 dd (10; 4.5)	74.18	4.15 dd (9; 3.5)	74.32
4	69.31	4.29 m	69.07	4.25	69.17
5	67.12	4.35 dd (12; 2.9) 3.76 dd (12.3; 2)	67.01	4.36 dd (12; 3.5) 3.74 dd (12; 2)	67.08

TABLE 1. (continued)

C atom	Compound				
	1		2		3 [5]
	δ_C	δ_H (J)	δ_C	δ_H (J)	δ_C
		6-O-β-*D*-Xyl*p*			β-*D*-Glc*p*
1	105.73	4.83 d (7)	105.61	4.76 d (7.2)	106.74[d]
2	75.47[a]	4.00 t (7.5)	75.31	3.91 t (8)	75.82
3	78.39	4.16 t (8)	78.20	4.05	78.81
4	71.12	4.14 td (7.6; 4.4)	71.01	4.08	71.79
5	66.92	3.72 dd (11.5; 8) 4.37 dd (11.7; 4.6)	66.77	3.61 dd (12; 9) 4.25	78.13
6	-	-	-	-	62.90
CH_3	21.41	2.17 s	-	-	-
COO	170.61	-	-	-	-

Signals denoted by the same letters overlap each other. Chemical shifts of protons that are given without multiplicity and SSCC were found using two-dimensional spectra.

Askendoside B (1), $C_{47}H_{76}O_{18}$, mp 215-218°C (CH_3OH), $[\alpha]_D^{25}$ -45.5 ± 2° (*c* 1.1, pyridine) [2, 3]. For the ^{1}H and ^{13}C NMR spectra, see Table 1.

Askendoside D (2), $C_{45}H_{74}O_{17}$, mp 235-236°C (CH_3OH), $[\alpha]_D^{25}$ -9.1 ± 2° (*c* 1.1, pyridine) [3, 4]. For the ^{1}H and ^{13}C NMR spectra, see Table 1.

Askendoside G (3), $C_{46}H_{78}O_{18}$, mp 273-275°C (CH_3OH), $[\alpha]_D^{25}$ +11 ± 2° (*c* 0.9, pyridine) [5]. PMR spectrum (500 MHz, C_5D_5N, δ, ppm, TMS = 0, J, Hz): 0.27 and 0.50 (2H-19, d, ^2J = 4 Hz), 1.00 (CH_3-21, d, ^3J = 7.5 Hz), 0.95, 1.21, 1.44, 1.45, 1.50, 2.00 ($6\times CH_3$, s), 4.83 (H-1, D-glucopyranose, d, ^3J = 7.5 Hz), 4.93 (H-1, D-xylopyranose, d, ^3J = 7.5 Hz), 5.25 (H-1, L-arabinopyranose, ^3J = 7.5 Hz). For the ^{13}C NMR spectrum, see Table 1.

NMR spectra were recorded on UNITYplus 400, Bruker AM-400, and Bruker DRX-500 spectrometers with the exception of the ^{13}C NMR spectrum of **3**, which was obtained on a Tesla BS-567 A instrument.

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