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TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS. XCII. CYCLOARTANE GLYCOSIDES FROM *A. oldenburgii*

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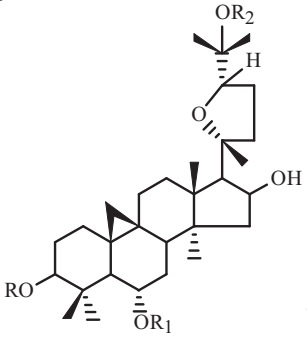
In continuation of research on cycloartane triterpenoids from plants of the genus *Astragalus*, we studied *A. oldenburgii* B. Fedtsch. (Leguminosae). Ground air-dried aerial parts (1.5 kg) of the plant collected in June 2004 in Surkhandar′ya Oblast (Babatag) were extracted exhaustively with MeOH (5 × 8 L). The combined MeOH extracts were concentrated to a syrupy mass, diluted with twice the volume of H_2O, and extracted first with $CHCl_3$ and then with *n*-BuOH. The BuOH extract was evaporated to dryness to afford total extracted substances (58 g) that were chromatographed over a column of silica gel with elution first by $CHCl_3$:MeOH (9:1) and then (6:1).

Elution of the column by $CHCl_3$:MeOH (6:1) isolated cyclosiversioside F (**1**, 92 mg, 0.0061%, yield here and henceforth is calculated per air-dried raw material), which was identified based on PMR and ^{13}C NMR spectral characteristics (Table 1) [1] and by direct comparison with an authentic sample.



1: R = β-D-Xyl*p*, R_1 = β-D-Glc*p*, R_2 = H
2: R = α-L-Rha*p*(1→4)-β-D-Glc*p*, $R_1 = R_2$ = H
3: R = β-D-Xyl*p*, $R_1 = R_2$ = β-D-Glc*p*

1 - 3

PMR spectrum of cyclosiversioside F (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.07 and 0.46 (d, ^2J = 4, 2H-19), 0.81, 1.16, 1.17, 1.24, 1.28, 1.45, 1.91 (s, 7 × CH_3), 2.39 (d, ^3J = 7.8, H-17), 3.00 (q, $^2J = {}^3J_1 = {}^3J_2$ = 9.4, H-22), 3.39 (dd, $^3J_1$ = 11.6, $^3J_2$ = 4.4, H-3), 3.57 (dd, ^2J = 11.2, ^3J = 10, β-D-xylopyranose H-5a), 3.66 (td, $^3J_1 = {}^3J_2$ = 8.4, $^3J_3$ = 3.8, H-6), 3.75 (dd, $^3J_1$ = 8.9, $^3J_2$ = 5, H-24), 3.76 (m, β-D-glucopyranose H-5), [3.91 (t, $^3J_1 = {}^3J_2$ = 8.5) and 3.92 (dd, $^3J_1$ = 8.8, $^3J_2$ = 7.6) β-D-xylopyranose and β-D-glucopyranose 2H-2], 4.00–4.13 (β-D-xylopyranose and β-D-glucopyranose 2H-3, 2H-4), 4.19 (dd, ^2J = 11.4, ^3J = 5, β-D-glucopyranose H-6), 4.23 (dd, ^2J = 11.2, ^3J = 5, β-D-xylopyranose H-5e), 4.36 (dd, ^2J = 11.6, ^3J = 2.7, β-D-glucopyranose H-6′), 4.72 (d, ^3J = 7.5, β-D-xylopyranose H-1), 4.77 (d, ^3J = 7.8, β-D-glucopyranose H-1), 4.86 (q, $^3J_1 = {}^3J_2 = {}^3J_3$ = 7.5, H-16). Table 1 lists the ^{13}C NMR spectrum of cyclosiversioside F.

Continued elution of the column by the same solvent system isolated glycoside **2** (28 mg, 0.0018%). Interpretation of the PMR and ^{13}C NMR spectra of **2** (Table 1) indicated that it was identical to astraverrucin IV [2].

PMR spectrum of astraverrucin IV (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = HMDS): 0.09 and 0.42 (d, ^2J = 4, 2H-19), 0.87, 1.17, 1.19, 1.20, 1.29, 1.45 (s, 6 × CH_3), 1.58 (d, ^3J = 6.4, α-L-rhamnopyranose CH_3) 1.89 (s, CH_3), 2.40 (d, ^3J = 7.8, H-17), 2.97 (q, $^2J = {}^3J_1 = {}^3J_2$ = 11.4, H-22), 3.47 (dd, $^3J_1$ = 11, $^3J_2$ = 4, H-3), 3.60 (m, β-D-glucopyranose H-6 and H-5), 3.75 (dd, $^3J_1$ = 8.9, $^3J_2$ = 5.5, H-24), 3.89 (dd, $^3J_1$ = 8.9, $^3J_2$ = 7.8, β-D-glucopyranose H-2), 4.03 (dd, ^2J = 12.8, ^3J = 3.7, β-D-glucopyranose H-6), 4.06 (t, $^3J_1 = {}^3J_2$ = 8.9, β-D-glucopyranose H-3), 4.17 (dd, ^2J = 12.3, ^3J = 2.1, β-D-glucopyranose H-6′), 4.21 (t, $^3J_1 = {}^3J_2$ = 9.4, α-L-rhamnopyranose H-4), 4.32 (t, $^3J_1 = {}^3J_2$ = 9.4, β-D-glucopyranose H-4), 4.45 (dd, $^3J_1$ = 9.1, $^3J_2$ = 3.4, α-L-rhamnopyranose H-3), 4.58 (dd, $^3J_1$ = 3.4, $^3J_2$ = 1.6, α-L-rhamnopyranose H-2), 4.79 (d, ^3J = 7.8, β-D-glucopyranose H-1), 4.88 (m, α-L-rhamnopyranose H-16 and H-5), 5.77 (d, ^3J = 1.6, α-L-rhamnopyranose H-1). Table 1 lists the ^{13}C NMR spectrum of astraverrucin IV.

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TABLE 1. Chemical Shifts of C Atoms of **1**–**3** (100 MHz, C_5D_5N, δ, ppm, 0 = TMS)

C atom	DEPT	Compound			C atom	DEPT	Compound		
		1	**2**	**3**			**1**	**2**	**3**
1	CH_2	32.18	32.32	32.12	27	CH_3	28.56[d]	28.52	25.64
2	CH_2	28.82	30.04	28.51	28	CH_3	21.07[a]	20.13	19.68
3	CH	88.50	89.10	88.47	29	CH_3	28.56[d]	28.94	28.48
4	C	42.63	42.56	42.64	30	CH_3	16.62	16.65	16.55
5	CH	52.52	53.99	52.41			*β*-D-Xyl*p*	*β*-D-Glc*p*	*β*-D-Xyl*p*
6	CH	79.28	67.97	79.25	1	CH	107.66	106.70	107.67
7	CH_2	34.61	38.61	34.05	2	CH	75.56[e]	76.03	75.59
8	CH	45.69	47.04	45.35	3	CH	78.51	76.80	78.02
9	C	21.07[a]	20.91	21.02[a]	4	CH	71.24[c]	78.35	71.23
10	C	28.96	29.47	28.87	5	$CH(CH_2)$	67.03	76.92	67.03
11	CH_2	26.13	26.40	26.13	6	CH_2		61.70	–
12	CH_2	33.35	33.35	33.40			*β*-D-Glc*p*	*α*-L-Rha*p*	*β*-D-Glcp_6
13	C	45.01	44.99	45.18	1	CH	105.22	102.62	104.99
14	C	46.18[b]	46.10	46.08	2	CH	75.56[e]	72.60	75.54
15	CH_2	46.18[b]	46.62	45.46	3	CH	78.11	72.76	78.54[b]
16	CH	73.35	73.40	73.49	4	CH	71.79	73.98	71.76
17	CH	58.14	58.33	57.91	5	CH	79.14	70.29	78.54[b]
18	CH_3	19.81	21.49	21.02[a]	6	$CH_3(CH_2)$	63.04	18.50	62.95
19	CH_2	30.19	30.57	30.18					*β*-D-Glcp_{25}
20	C	87.21	87.19	87.14	1	CH			98.86
21	CH_3	28.18	27.09	27.73	2	CH			75.14
22	CH_2	34.85	34.88	35.01	3	CH			78.17
23	CH_2	26.44	26.18	25.99	4	CH			71.31
24	CH	81.64	81.64	82.00	5	CH			79.03
25	C	71.24[c]	71.22	78.58	6	CH_2			62.69
26	CH_3	27.06	28.14	22.90					

Resonances denoted by the same letters are mutually overlapped.

Continued elution of the column by $CHCl_3$:MeOH (4:1) led to the isolation of glycoside **3** (126 mg, 0.0084%), which was identified as astragaloside VII by interpretation of the PMR and ^{13}C NMR spectra [3, 4] and comparison with an authentic sample.

PMR spectrum of astragaloside VII (400 MHz, C_5D_5N, δ, ppm, *J*/Hz, 0 = HMDS): 0.05 and 0.45 (d, $^2J = 4.4$, 2H-19), 0.78, 1.13, 1.20, 1.25, 1.29, 1.54, 1.92 (s, $7 \times CH_3$), 1.78 (d, $^3J = 8.8$, H-5), 2.29 (d, $^3J = 7.7$, H-17), 2.67 (q, $^2J = {}^3J_1 = {}^3J_2 = 11$, H-22), 3.40 (dd, $^3J_1 = 11$, $^3J_2 = 4.5$, H-3), 3.58 (dd, $^2J = 11.3$, $^3J = 10$, *β*-D-xylopyranose H-5a), 3.68 (td, $^3J_1 = {}^3J_2 = 8$, $^3J_3 = 4$, H-6), 3.76 (dd, $^3J_1 = 8.8$, $^3J_2 = 6.4$, H-24), 3.79 (m, *β*-D-glucopyranose $2 \times$ H-5), 4.73 (d, $^3J = 7.5$, *β*-D-xylopyranose H-1), 4.75 (m, H-16), 4.78 (d, $^3J = 7.6$, C-6 *β*-D-glucopyranose H-1), 4.95 (d, $^3J = 7.6$, C-25 *β*-D-glucopyranose H-1). Table 1 lists the ^{13}C NMR spectrum of astragaloside VII.

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