Chemistry of Natural Compounds, Vol. 43, No. 2, 2007

CYCLOCHIVINOSIDE B FROM THE AERIAL PART OF *Astragalus chivensis*

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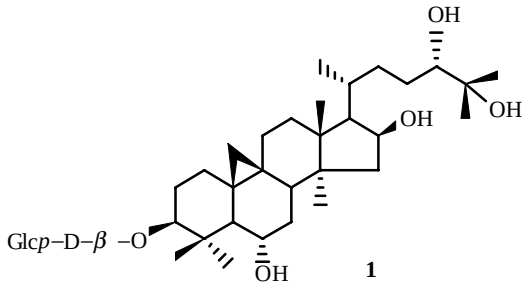
UDC 547.918:547.926

The known glycoside aleksandroside I and the new cycloartane glycoside cyclochivinoside B, 24S-cycloartan-3β,6α,16β,24,25-pentaol 3,25-di-O-β-*D-glucopyranoside, were isolated from the aerial part of* Astragalus chivensis. *Their structures were established using chemical transformations and two-dimensional spectra (TOCSY, ROESY, HMBC, HSQC, COSY).*

Key words: cycloartanes, cyclocanthogenin, cyclochivinoside B, aleksandroside I.

In continuation of research on triterpene glycosides from plants of the genus *Astragalus* growing in the Republic of Karakalpakstan [1], the known glycoside aleksandroside I (**1**) [2] and the new cycloartane glycoside cyclochivinoside B (**2**) were isolated from the butanol fraction of the methanol extract of the aerial part of *Astragalus chivensis* Bunge (Leguminosae). Herein we report the structures of these glycosides.

The PMR spectrum of **1** contained at strong field of 0.23 and 0.55 ppm 1H doublets of an AB splitting system belonging to the methylene protons of the cyclopropane ring and signals for seven methyls. This enabled us to classify **1** as a cycloartane triterpenoid.



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The PMR and ^{13}C NMR spectra of **1** contained signals for one anomeric proton that resonated at 5.00 ppm and one C atom that resonated at 106.97 ppm, consistent with one carbohydrate in **1**. Comparison of the physical chemical constants and PMR and ^{13}C NMR spectra of **1** with the literature showed that they were in complete agreement with those of aleksandroside I [2] (Table 1). Thus, the structure of **1** was 24*S*-cycloart-3*β*,6*α*,16*β*,24,25-pentaol 3-*O*-*β*-D-glucopyranoside.

The PMR spectrum of **2** contained two 1H doublets of an AB system at 0.23 and 0.56 ppm that were unambiguously assigned to an isolated methylene of a cyclopropane ring and signals for seven methyls at 1.03, 1.10, 1.35, 1.39, 1.52, 1.56, and 2.01 ppm at strong field (Table 1).

The C atoms of the cyclopropane ring, C-9, C-10, and C-19, resonated in the ^{13}C NMR spectrum of **2** at 21.33, 29.29, and 30.02 ppm, respectively (Table 1). These data and the elemental formula $C_{42}H_{72}O_{15}$ enabled us to classify unambiguously **2** as a cycloartane triterpenoid.

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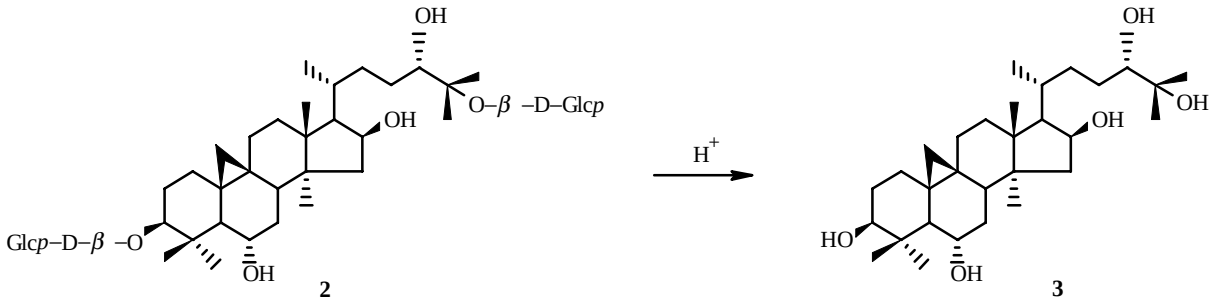
 0009-3130/07/4302-0166

TABLE 1. PMR and ^{13}C NMR Data for Aleksandroside I (**1**), Cyclochivinoside B (**2**), and Cyclocanthogenin (**3**) (C_5D_5N, δ, ppm, TMS = 0)

C atom	Compound				
	1		**2**		**3** [4]
	^1H	^{13}C	^1H	^{13}C	^{13}C
1	1.57; 1.15	32.48	1.56; 1.15	32.46	32.54
2	2.48; 1.93	30.23	2.46; 1.96	30.22	31.17
3	3.67	89.11	3.66	89.12	78.10
4	-	42.67	-	42.67	42.18
5	1.74	54.13	1.73	54.14	53.73
6	3.77	67.97	3.75	68.01	68.04
7	1.82; 1.65	38.45	1.82; 1.64	38.49	38.33
8	1.95	47.01	1.96	47.06	46.94
9	-	21.32	-	21.33	21.02
10	-	29.29	-	29.29	29.71
11	1.90; 1.24	26.50	1.92; 1.20	26.37	26.17
12	1.67	33.23	1.67	33.21	32.95
13	-	45.77	-	45.73	45.47
14	-	46.85	-	46.90	46.67
15	2.18; 1.76	48.38	2.14; 1.73	48.68	48.16
16	4.74	71.94	4.68	71.75	71.75
17	1.83	57.39	1.80	57.38	57.11
18	1.41	18.94	1.39	18.84	18.03
19	0.55; 0.23	29.95	0.56; 0.23	30.02	29.09
20	2.39	28.71	2.30	31.57	28.44
21	1.10	18.39	1.10	18.84	18.77
22	2.29; 1.48	33.08	2.44; 1.34	35.01	32.81
23	1.97; 1.84	27.96	1.95; 1.67	29.30	27.67
24	3.89	77.26	3.91	78.99	76.99
25	-	72.05	-	80.97	72.88
26	1.48	26.33	1.56	24.28	25.48
27	1.46	26.50	1.52	21.59	26.07
28	1.04	20.18	1.03	20.23	19.93
29	2.00	28.96	2.01	28.98	29.34
30	1.34	16.94	1.35	16.75	15.87
	3-*O*-*β*-D-Glc*p*		3-*O*-*β*-D-Glc*p*		
1	5.00	106.97	5.00	106.97	
2	4.08	75.98	4.08	75.97	
3	4.23	78.80	4.24	78.79	
4	4.23	71.94	4.24	71.92	
5	3.96	78.20	3.89	78.20	
6	4.55; 4.41	63.13	4.57; 4.42	63.11	
			25-*O*-*β*-D-Glc*p*		
1			5.20	98.76	
2			4.02	75.41	
3			4.22	78.79	
4			4.18	71.85	
5			3.89	78.27	
6			4.53; 4.28	62.85	

Acid hydrolysis of **2** gave the genin, which was identified using spectral data and the literature as cyclocanthogenin (**3**) [3, 4].



2 **3**

Paper chromatography (PC) of the acid hydrolysis products of **2** detected glucose by comparison with an authentic sample. The PMR and ^{13}C NMR spectra clearly showed signals for two anomeric protons at 5.00 and 5.20 ppm and two anomeric C atoms at 106.97 and 98.76 ppm, respectively. These data were consistent with two glucoses in **2**. Therefore, it was a bioside.

According to Table 1 for **2**, carbinol atoms C-3 and C-25 of the aglycon, which resonated at 89.12 and 80.97 ppm, respectively, underwent a glycosylation effect. This unambiguously determined the attachment site of the carbohydrates in **2** as C-3 and C-25 of the genin.

Thus, **2**, which we called cyclochivinoside B, was a new compound. The experimental data showed that **2** was 24*S*-3*β*,6*α*,16*β*,24,25-pentaol 3,25-di-*O*-*β*-D-glucopyranoside.

EXPERIMENTAL

General Comments. Silica gel plates (KSK, 0.005-0.043 mm) containing gypsum (10%) and Silufol UV-254 plates (Czech Rep.) were used for TLC. Column chromatography (CC) was carried out over silica gel (KSK, 0.1-0.08, 0.16-0.1 mm). Cycloartanes and their derivatives were detected on TLC by spraying with methanolic phosphotungstic acid (20%) with subsequent heating at 120°C for 5-10 min. PMR and ^{13}C NMR spectra in Py-d_5 were recorded on a Bruker DRX-500 instrument at working frequencies 500.13 and 125.27 MHz, respectively, at 30°C with TMS standard. Two-dimensional spectra were recorded using standard Bruker methods. The mixing time for recording TOCSY and ROESY spectra was 0.2 s. The following solvent systems were used: $CHCl_3$:CH_3OH:H_2O (4:1:0.1), $CHCl_3$:CH_3OH (25:1), and *n*-butanol:pyridine:water (6:4:3).

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

Isolation of Cycloartanes. Dried and ground aerial part (2.0 kg) of *A. chivensis* that was collected in June 2003 in Kegeiliisk region of the Republic of Karakalpakstan was extracted with methanol (5 × 10 L). The methanol extract was evaporated to a thick syrupy consistency. The aqueous residue was extracted first with ethylacetate and then with butanol to separate polar and slightly polar cycloartanes. Solvents were evaporated in vacuo to afford butanol (80.0 g) and ethylacetate (50.0 g) fractions. The butanol fraction was chromatographed over a column using system 1.

Aleksandroside I (1), $C_{36}H_{62}O_{10}$, 1.2 g (0.06%, here and henceforth yields are given based on air-dried raw material), mp 292-294°C. Table 1 gives the PMR and ^{13}C NMR spectra (500 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = TMS).

Cyclochivinoside B (2), $C_{42}H_{72}O_{15}$, 152 mg (0.0076%), mp 254-256°C. Table 1 gives the PMR and ^{13}C NMR spectra (500 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = TMS).

Acid Hydrolysis. Compound **2** (40 mg) was hydrolyzed by methanolic H_2SO_4 (15 mL, 0.25%) at 70°C for 4 h. The mixture was cooled and treated with water (30 mL). The methanol was removed. The resulting solid was filtered off and chromatographed over a column with elution by system 2 to afford **3** (12 mg), $C_{30}H_{52}O_5$, mp 192-193°C (methanol).

After neutralization with $BaCO_3$ and evaporation, glucose was detected in the hydrolysate by PC in system 3 and comparison with an authentic sample.

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