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STRUCTURE OF CYCLOCHIVINOSIDE C FROM *Astragalus chivensis*

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*The new cycloartane glycoside cyclochivinoside C, 24*S*-cycloartan-3*β*,6*α*,16*β*,24,25-pentaol 3,16-di*-O-β-*D-glucopyranoside, was isolated from the aerial part of* Astragalus chivensis. *The structures of the isolated compounds were established by chemical transformations and PMR and* ^{13}*C NMR spectra.*

Key words: cycloartanes, cyclocanthogenin, cyclochivinoside C, cyclosiversioside E, cyclosiversigenin.

In continuation of research on cycloartane triterpenoids from plants of the genus *Astragalus* [1], we isolated from the butanol extract of *A. chivensis* Bunge (Leguminosae) cyclosiversioside E (**1**) [2, 3] and a new glycosidic compound that we called cyclochivinoside C (**2**).

The PMR spectrum of **1** contained in the strong-field region resonances for protons of seven methyls at 1.42, 1.40, 1.61, 1.40, 1.11, 1.89, and 1.40 ppm and for two anomeric protons at 4.83 and 4.81 ppm. The ^{13}C NMR spectrum of **1** had resonances for two anomeric C atoms at 107.7 and 105.8 ppm.

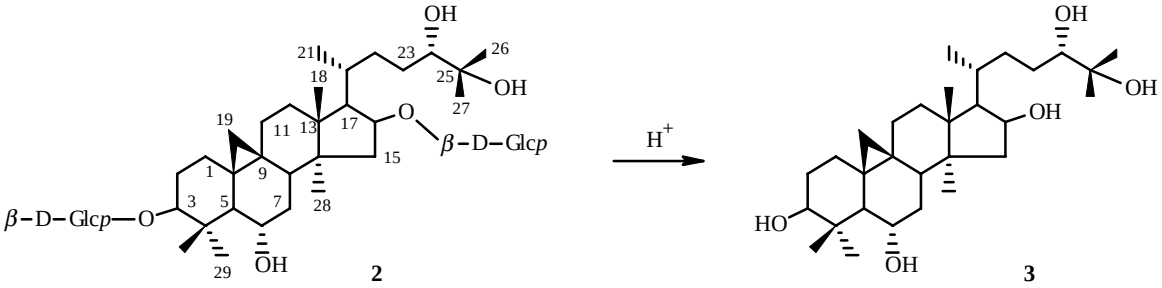
These data indicated that **1** was a bioside.

The structure of **1** was confirmed conclusively using PMR and ^{13}C NMR and two-dimensional spectra. They agreed with those reported for cyclosiversioside E [2, 3].

The presence in the PMR spectrum of glycoside **2** (Table 1) of 1H doublets at 0.22 and 0.54 ppm for an AB system typical of a 1,1,2,2-tetrasubstituted three-membered ring and resonances for seven methyls at high field indicated that this compound was a cycloartane triterpenoid.

The C atoms in the cyclopropane ring, C-9, C-10, and C-19, resonated in the ^{13}C NMR spectrum of **2** at 21.24, 29.37, and 29.60 ppm, respectively. This confirmed the conclusion that this compound was a cyclartane.

Acid hydrolysis of **2** produced the genin, which was identified as cyclocanthogenin (**3**) [4]. TLC and paper chromatography of the carbohydrate part of the hydrolysate detected glucose.



2 **3**

The PMR and ^{13}C NMR spectra of **2** showed clearly resonances for two anomeric protons at 4.98 and 5.02 ppm and for two anomeric C atoms at 106.91 and 106.71 ppm, respectively.

Judging from these data, the new compound was a bioside.

A low-field shift in the ^{13}C NMR spectrum of the resonances for C-3 and C-16 in **2** compared with those in cyclocanthogenin (**3**) determined the sites of attachment of the sugars.

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TABLE 1. PMR and ^{13}C NMR Spectra of Cyclochivinoside C (**2**) and Cyclocanthogenin (**3**) (C_5D_5N, δ, ppm, TMS = 0)

C atom	Cyclochivinoside C		Cyclocanthogenin [4]	C atom	Cyclochivinoside C		Cyclocanthogenin [4]
	^1H	^{13}C	^{13}C		^1H	^{13}C	^{13}C
1	1.57; 1.16	32.53	32.54	23	2.10; 1.68	29.78	27.67
2	2.48; 1.95	30.18	31.17	24	3.91	77.21	76.99
3	3.67	88.92	78.10	25	-	72.56	72.88
4	-	42.71	42.18	26	1.49	25.70	25.48
5	1.75	54.11	53.73	27	1.47	26.54	26.07
6	3.76	68.15	68.04	28	1.04	20.23	19.93
7	1.83; 1.64	38.42	38.33	29	1.99	28.55	29.34
8	1.94	46.36	46.94	30	1.35	16.43	15.87
9	-	21.24	21.02			3-*O*-*β*-D-Glc*p*	
10	-	29.37	29.71	1	5.02	106.91	
11	1.89; 1.24	26.28	26.17	2	4.07	75.82	
12	1.68	33.19	32.95	3	4.24	78.67	
13	-	45.75	45.47	4	4.24	71.72	
14	-	46.12	46.67	5	3.95	78.06	
15	2.15; 1.74	47.53	48.16	6	4.56; 4.39	63.10	
16	4.38	82.15	71.75			16-*O*-*β*-D-Glc*p*	
17	1.85	57.35	57.11	1	4.98	106.71	
18	1.37	18.26	18.03	2	4.02	75.63	
19	0.54; 0.22	29.60	29.09	3	4.29	78.24	
20	2.37	31.11	28.44	4	4.22	71.65	
21	1.12	18.93	18.77	5	3.88	77.98	
22	2.28; 1.43	33.95	32.81	6	4.54; 4.36	62.87	

A comparison of the ^{13}C NMR spectra of cyclochivinoside C and cyclocanthogenin showed that C atoms C-3 and C-16 experienced glycosylation effects in the spectrum of the former. They resonated at 88.92 and 82.15 ppm, respectively.

The configuration of the asymmetric center at C-24 of **2** was determined by comparing ^{13}C NMR spectra of **2** and cyclounifolioside C [4]. The resonance for this C atom in the ^{13}C NMR spectrum of cyclounifolioside C, which has the C-(24*R*)-configuration, occurred at 80.29 ppm whereas in the spectrum of **2** this resonance shifted to strong field by 3.08 ppm (77.21 ppm).

The difference in the chemical shifts for C-24 atoms in ^{13}C NMR spectra of dammarane triterpene glycosides belonging to the 24(*R*) and 24(*S*) series was 2.7-3.3 ppm with C-24 in the *S*-configuration resonating at stronger field [5]. Based on these results, we thought that C-24 in **2** had the *S*-configuration and the hydroxyl was situated in the *α*-orientation.

Based on these data, it can be concluded that **2** is 24*S*-cycloartan-3*β*,6*α*,16*β*,24,25-pentaol 3,16-di-*O*-*β*-D-glucopyranoside.

EXPERIMENTAL

General comments have been published [1].

Separation of the Butanol Fraction. Column chromatography of the butanol fraction using $CHCl_3$:CH_3OH:H_2O (4:1:0.1) isolated **2** (23 mg, 0.0011% based on air-dried raw material).

Cyclosiversioside E (1). $C_{40}H_{66}O_{13}$, mp 252-254°C (MeOH).

PMR spectrum (C_5D_5N, δ, ppm): 1.59, 1.27 (H-1), 2.34, 1.97 (H-2), 3.45 (H-3), 1.87 (H-5), 3.70 (H-6), 2.13, 2.00 (H-7), 2.08 (H-8), 1.75, 1.52 (H-11), 1.69, 1.53 (H-12), 2.31, 1.80 (H-15), 5.05 (H-16), 2.58 (H-17), 1.42 (H-18), 0.15, 0.60 (H-19), 1.40 (H-21), 3.11, 1.68 (H-22), 2.28, 2.04 (H-23), 3.89 (H-24), 1.61 (H-26), 1.40 (H-27), 1.11 (H-28), 1.89 (H-29), 1.40 (H-30); *β*-D-Xyl*p*′: 4.83 (H-1), 4.07 (H-2), 4.13 (H-3), 4.22 (H-4), 4.35, 3.68 (H-5); *β*-D-Xyl*p*″: 4.81 (H1), 4.00 (H-2), 4.16 (H-3), 4.17 (H-4), 4.32, 3.65 (H-5).

^{13}C NMR spectrum (C_5D_5N, δ, ppm): 32.0 (C-1), 30.1 (C-2), 88.4 (C-3), 42.7 (C-4), 52.2 (C-5), 77.9 (C-6), 33.7 (C-7), 44.3 (C-8), 20.8 (C-9), 28.4 (C-10), 26.4 (C-11), 33.6 (C-12), 45.3 (C-13), 46.3 (C-14), 46.0 (C-15), 73.5 (C-16), 58.2 (C-17), 20.6 (C-18), 26.9 (C-19), 87.4 (C-20), 28.7 (C-21), 35.0 (C-22), 26.5 (C-23), 81.8 (C-24), 71.3 (C-25), 28.2 (C-26), 27.2 (C-27), 19.8 (C-28), 28.2 (C-29), 16.7 (C-30); β-D-Xyl*p*″: 107.7 (C-1), 75.7 (C-2), 78.6 (C-3), 71.3 (C-4), 67.1 (C-5); β-D-Xyl*p*″: 105.8 (C-1), 75.4 (C-2), 78.6 (C-3), 71.2 (C-4), 67.0 (C-5).

Literature data for **1** [2]: mp 218-220°C (MeOH), $[\alpha]_D^{20}$ +29.9° (*c* 0.67, MeOH).

Acid Hydrolysis. Glycoside **1** (30 mg) was hydrolyzed by methanolic H_2SO_4 (10 mL, 0.5%) at boiling for 6 h. The mixture was diluted with water. The methanol was distilled. The hydrolysate was cooled and extracted with $CHCl_3$. The $CHCl_3$ extract was washed with water and evaporated to dryness in a rotary evaporator. The solid was chromatographed over a silica-gel column with elution by $CHCl_3$:CH_3OH (25:1) to afford cyclosiversigenin (**4**, 13 mg), $C_{30}H_{50}O_5$, mp 240-242°C (MeOH). The hydrolysate was neutralized with $BaCO_3$ and evaporated. Paper chromatography (PC) using *n*-butanol:pyridine:water (6:4:3) detected xylose by comparison with an authentic sample.

Literature data for **4** [6]: mp 239-241°C (ethylacetate), $[\alpha]_D^{20}$ +44.0 ± 2° (*c* 1.58, MeOH).

Cyclochivinoside C (2), $C_{42}H_{72}O_{15}$, mp 258-260°C (MeOH).

Table 1 gives the PMR and ^{13}C NMR spectra.

Acid Hydrolysis. Glycoside **2** (15 mg) was hydrolyzed as described above. The column was eluted by $CHCl_3$:CH_3OH (25:1) to afford **3** (5 mg). The hydrolysate was neutralized with $BaCO_3$ and evaporated. PC using *n*-butanol:pyridine:water (6:4:3) detected glucose by comparison with an authentic sample.

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