TRITERPENE GLYCOSIDES FROM *Astragalus* AND THEIR GENINS. LXXIX. STRUCTURE OF CYCLOMACROSIDE C

D. A. Iskenderov, I. M. Isaev, and M. I. Isaev

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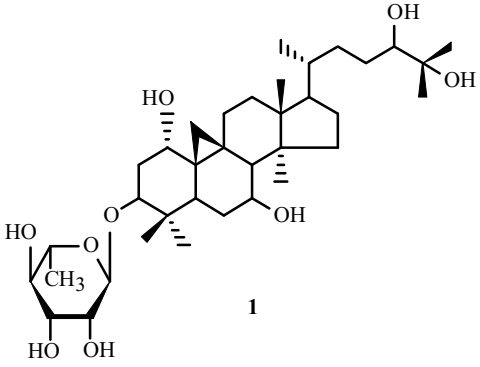
In continuation of the study of isoprenoids from plants of the genus *Astragalus* (Leguminosae) [1], we present results from a structure determination of substance G [2], which was isolated from *A. macropus* Bunge and which we called cyclomacroside C (**1**), $C_{36}H_{62}O_9$, mp 281-283°C (CH_3OH).

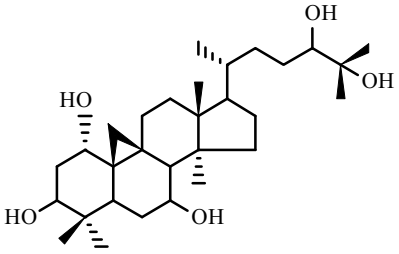
The PMR spectrum of **1** (Table 1) contained two 1H doublets of an AX system at δ 0.45 (^2J = 4 Hz) and 0.87 (^2J = 4.1 Hz) in addition to resonances for seven methyls at high field. This enabled us to classify the compound as a cycloartane triterpenoid [3-6].

The PMR and ^{13}C NMR spectra of **1** contained also a set of resonances from one monosaccharide unit. Therefore, **1** was glycosidic in nature and a monoside. The chemical shifts of C and H atoms in addition to the SSCC identified the monosaccharide as α-L-rhamnopyranose with the $^1C_4$-conformation [7-9].

A comparison of the PMR and ^{13}C NMR spectra of **1** and cyclomacrogenin B (**2**) [2] showed that the latter was the genin of **1**.



1



2

The peak for H-3 (δ 4.14) in the HMBC spectrum of **1** was correlated with that for the anomeric C atom (δ 104.48), indicating that the α-L-rhamnose was attached at C-3. This was also consistent with the ^{13}C NMR spectrum in which the resonance for C-3 underwent a low-field shift compared with that of cyclomacrogenin B and was observed at δ 84.22.

Thus, **1** had the structure 3-*O*-α-L-rhamnopyranoside-24*R*-cycloartan-1α,3β,7β,24,25-pentaol.

S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax: (99871) 120 64 75, e-mail: m_isaev@rambler.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 113-114, January-February, 2009. Original article submitted October 13, 2008.

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TABLE 1. Chemical Shifts of C and H Atoms and DEPT, ^{1}H-^{1}H COSY, HSQC, and HMBC Correlation Spectra of **1** and Chemical Shifts of C Atoms of **2** (C_5D_5N,δ, ppm, J/Hz, 0 = TMS)

C atom	Compound				
	1				**2** [2]
	DEPT	δ_C	δ_H	HMBC (C atoms)	δ_C
1	CH	72.40	3.81 br.s	3	72.65
2	CH_2	37.07	2.50 m, 2.02		38.95
3	CH	84.22	4.14 dd (11.9, 4.1)	R1	72.96
4	C	40.80	-		40.98
5	CH	39.18	2.61 (13.5, 4.3)		39.36
6	CH_2	32.08	2.03, 1.28		32.31
7	CH	70.02	3.95 td (9.3)		70.14
8	CH	55.32	1.90 d (9.1)	7, 14, 28	55.21
9	C	21.00	-		21.00
10	C	30.94	-		31.32
11	CH_2	26.37	2.56, 1.41		26.47
12	CH_2	33.23	1.64, 1.80		33.30
13	C	45.99	-		45.99
14	C	49.06	-		49.13
15	CH_2	37.92	1.54, 1.96		37.86
16	CH_2	28.99[a]	2.01, 1.82		28.98[a]
17	CH	52.37	1.65		52.38
18	CH_3	17.98	1.12 s	12, 13, 14, 17	17.91
19	CH_2	28.99[a]	0.45 d (4), 0.87 d (4.1)		28.98[a]
20	CH	36.43	1.62		36.43
21	CH_3	18.67	1.00 d (5.7)	17, 20	18.68
22	CH_2	34.21	1.63, 1.80		34.22
23	CH_2	28.27	1.82, 1.82		28.20
24	CH	79.06	3.77 d* (7.7)		79.06
25	C	72.72	-		72.72
26	CH_3	25.92	1.50 s	24, 25, 27	25.94
27	CH_3	26.04	1.52 s	24, 25, 26	26.19
28	CH_3	18.98	1.22 s	8, 13, 14, 15	19.02
29	CH_3	25.67	0.96 s	3, 4, 5, 30	26.03
30	CH_3	14.41	0.92 s	3, 4, 5, 29	13.98
			α-L-Rha*p* (R)		
1	CH	104.48	5.34 s	3, R2, R3, R5	
2	CH	72.31	4.55 br.d (3)		
3	CH	72.86	4.48 dd (8.5, 3)		
4	CH	74.06	4.28 t (8.6)	R5	
5	CH	69.75	4.29 m		
6	CH_3	18.36	1.56 d (5.4)	R4, R5	

Chemical shifts given without multiplicities and SSCC were found from 2D spectra.
[a]Resonances overlap; *Broad doublet. Spectra were recorded on a Bruker AM 300 spectrometer.

ACKNOWLEDGMENT

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