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TRITERPENE GLYCOSIDES FROM *Astragalus* AND THEIR GENINS. LXXXII. CYCLOMACROSIDE B, A NEW GLYCOSIDE*

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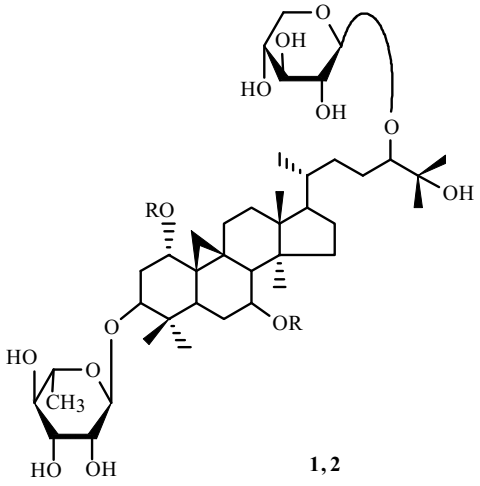
The structure of the new cycloartane glycoside cyclomacroside B that was isolated from Astragalus macropus *Bunge (Leguminosae) was shown to be 1,7-di-*O*-acetyl-24*R*-cycloartan-1α,3β,7β,24,25-pentaol 3-*O*-α-L-rhamnopyranoside-24-*O*-β-D-xylopyranoside.*

Key words: cyclomacroside B; cyclomacroside D; cyclomacrogenin B; cycloartane triterpenoids; *Astragalus macropus* Bunge; Leguminosae; PMR, ^{13}C NMR, DEPT, COSY, HSQC, and HMBC spectra.

In continuation of research on cycloartane triterpenoids and their glycosides from plants of the genus *Astragalus* (Leguminosae), we determined the structure of the new compound F that was isolated from *A. macropus* Bunge [1] and was called by us cyclomacroside B (**1**).



1, 2

1: R = Ac; **2:** R = H

Examination of the PMR and ^{13}C NMR spectra of **1** indicated that it was a cycloartane triterpenoid [2–5]. Its PMR spectrum (Table 1) had at strong field 1H doublets for an AX system at δ 0.35 and 0.82 with SSCC ^{2}J = 5 Hz that belonged to the methylene group of a 1,1,2,2-tetrasubstituted cyclopropane. The same PMR spectrum had resonances of eight methyls at δ 0.73–1.49, seven of which belonged to the cycloartane skeleton. Therefore, the eighth methyl should belong to the methylpentose included in the carbohydrate part of the glycoside. In fact, the PMR and ^{13}C NMR spectra of **1** contained two sets of resonances for the monosaccharide units. Considering biogenetic factors suggesting that glycosides isolated from this plant contained L-rhamnose and D-xylose units, the chemical shifts, multiplicity, and SSCC of these resonances indicated that α-L-rhamnopryanosyl and β-D-xylopyranosyl units were present in the $^{1}C_{4}$- and $^{4}C_{1}$-conformations in cyclomacroside B.

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TABLE 1. Chemical Shifts of C and H Atoms and Parameters of DEPT, $^1H–^1H$ COSY, HSQC, and HMBC Spectra of Cyclomacroside B (**1**) (C_5D_5N, δ, ppm, J/Hz)

C atom	DEPT	δ_C	δ_H	HMBC (C atoms)	NOESY (H atoms)
1	CH	75.92	4.81 t (2.9)		2*β*, 19 (δ 0.35)
2	CH_2	32.57	1.83, 2.42 dt (14.4, 3.5, 3.5)		
3	CH	82.74	3.65 dd (12, 4.5)		
4	C	40.34	–		
5	CH	39.46	2.14 dd (13.2, 4.2)		
6	CH_2	26.81	1.02 q (11), 1.90		
7	CH	72.48	4.98 td (10.9, 5.5)		5, 6*α*
8	CH	49.40	1.93		
9	C	20.94	–		
10	C	29.26	–		
11	CH_2	26.53			
12	CH_2	33.02			
13	C	45.65	–		
14	C	48.58	–		
15	CH_2	36.17			
16	CH_2	28.95			
17	CH	51.83			
18	CH_3	16.94	0.84 s		
19	CH_2	25.65	0.35 d (5), 0.82 d (5)		1
20	CH	36.45			
21	CH_3	18.76	0.80 d (6.4)		
22	CH_2	33.30			
23	CH_2	28.37			
24	CH	89.54	3.72 dd (8, 1.9)		
25	C	71.92	–		
26	CH_3	24.98	1.37 s	24, 25, 27	
27	CH_3	26.75	1.30 s	24, 25, 26	
28	CH_3	18.50	0.86 s		
29	CH_3	25.65	0.79 s	3	
30	CH_3	14.09	0.73 s	3	
			α-L-Rha*p* (R)		
1	CH	104.43	5.19 d (1)	3, R5	3, R2
2	CH	72.22	4.44 dd (3, 1)		R1
3	CH	72.83	4.31 dd (9, 3.5)		
4	CH	73.82	4.12		
5	CH	70.00	4.14		
6	CH_3	18.28	1.49 d (5.6)	R4, R5	R4, R5
			β-D-Xyl*p* (X)		
1	CH	106.12	4.90 d (7.7)	24	24
2	CH	75.10	3.87 t (8.4)	X3	
3	CH	78.06	4.01 t (8.7)		
4	CH	70.88	4.07 td (9, 9, 4.2)		
5	CH_2	67.22	3.59 t (10), 4.17 dd (11, 4.8)		
Ac	C	170.14	–		
	C	170.06	–		
	CH_3	21.60[a]	1.97 s		
	CH_3	21.00[a]	1.93 s		

Chemical shifts given without multiplicities and SSCC were found from 2D spectra. [a]Resonances are mutually interchangeable.

A comparison of NMR spectra showed that cyclomacroside B was a glycoside of cyclomacrogenin B [1] in which C-3 and C-24 were glycosylated. The HMBC spectrum of **1**, which contained correlation peaks for coupling of the anomeric

proton of α-L-rhamnopyranose (δ 5.19), C-3 (δ 82.74), the anomeric proton of β-D-xylopyranose (δ 4.90), and C-24 (δ 89.54), was consistent with 6-deoxyhexose and pentose on C-3 and C-24, respectively.

PMR and ^{13}C NMR spectra of **1** also showed resonances for two acetyl groups (δ 1.93, 1.97, 21.00, 21.60, 170.06, 170.14). Therefore, cyclomacroside B was an ester. As expected, **1** was hydrolyzed by base to form cyclomacroside D (**2**) [6], the formation of which from new glycoside **1** confirmed the conclusion about the location, size of the oxide ring, and conformation and configuration of the monosaccharide units.

The acetyl groups should have been located on the genin part of the molecule because the monosaccharide units were unsubstituted. The chemical shifts of C-25 (δ 71.92) and CH_3-26 and CH_3-27 (δ 1.37, 1.30) indicated that the tertiary hydroxyl group was unsubstituted. Therefore, the secondary hydroxyls at C-1 and C-7 were acetylated in **1**.

The conclusion about the location of the acetyls was confirmed by the weak-field shift of resonances for H-1, H-7, C-1, and C-7 in the PMR and ^{13}C NMR spectra of **1** (observed at δ_H 4.81 and 4.98 and δ_C 75.92 and 72.48, respectively) as compared with those in the spectra of cyclomacroside D.

Thus, the results led to the conclusion that the new cyclomacroside B had the structure 1,7-di-*O*-acetyl-24*R*-cycloartan-1α,3β,7β,24,25-pentaol 3-*O*-α-L-rhamnopyranoside-24-*O*-β-D-xylopyranoside.

EXPERIMENTAL

General comments have been published [7]. We used the following solvent systems: $CHCl_3$:CH_3OH:H_2O (70:23:4). NMR spectra were recorded in Py-d_5 on Bruker AM 300 and UNITYplus 400 spectrometers. ^{13}C NMR spectra were obtained with full C–H decoupling and under DEPT conditions. 2D spectra were recorded using standard Bruker and Varian programs. Spectra on the Bruker AM 300 spectrometer were obtained without an internal standard; on the UNITYplus 400 spectrometer, with HMDS internal standard. Chemical shifts of protons are given relative to HMDS. ^{13}C NMR chemical shifts are given relative to the β-C atoms of Py-d_5 (δ 123.493 relative to TMS).

Cyclomacroside B (1) was compound F [1], $C_{45}H_{74}O_{15}$, mp 155–156°C (MeOH).

Table 1 gives the PMR and ^{13}C NMR, DEPT, ^1H–^1H COSY, HSQC, and HMBC spectra.

Alkaline Hydrolysis of 1. Cyclomacroside B (**1**, 50 mg) was hydrolyzed by methanolic NaOH (5 mL, 1%) for 3 d at room temperature and then diluted with water. The MeOH was evaporated. The products were extracted with *n*-BuOH. After the usual work up and evaporation of solvents, the solid was chromatographed over a column of silica gel using $CHCl_3$:CH_3OH:H_2O (70:23:4) to afford **2** (28 mg), which was identified as cyclomacroside D [6] by direct comparison with an authentic sample and NMR spectra.

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