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NEW CYCLOARTANE GLYCOSIDES FROM *Astragalus caucasicus* AND *A. galegiformis*

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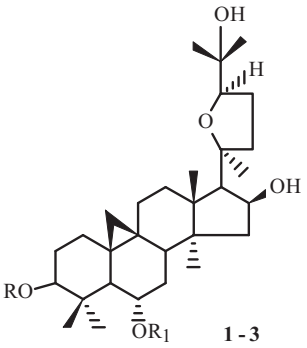
In continuation of research on cycloartane triterpenoids from leaves of *Astragalus caucasicus* Pall. and stems of *A. galegiformis* (Leguminosae L.), one compound from each was isolated and called D (**1**) and C (**2**) [2], respectively, in addition to previously isolated compounds [1, 2] from enriched fractions. Based on IR, PMR, and ^{13}C NMR spectral data, these compounds were assigned to the cycloartane series [3] (Table 1).



1 - 3

1: R = Glc*p*-(6→1)-Rha*p*, R_1 = H
2: R = (2′-OAc)-Xyl*p*, R_1 = Xyl*p*
3: R = R_1 = H

Compound 1, white needle-like crystals, MW 798.3 g/mol (mass spectrometry), $C_{42}H_{70}O_{14}$, mp 220–222°C (MeOH). IR spectrum (KBr, ν_{max}, cm^{-1}): 3600–3200 (OH), 3050 (cyclopropane ring CH_2),

Acid hydrolysis of **1** and **2** produced a genin (**3**), 490 $[M]^+$, $C_{30}H_{50}O_5$, mp 194–196°C (MeOH). A solution of the genin in acetone in the presence of H_2SO_4 did not give an acetonide, indicating the absence of an α-diol group in the side chain. The genin was identified by direct comparison with an authentic sample on TLC and ^{13}C NMR data as cyclogalegigenin [2]. Paper chromatography of the aqueous part of the hydrolyzate of **1** detected D-glucose and L-rhamnose; of **2**, D-xylose.

Glycoside **1** was hydrolyzed by rhamnodiastase into cyclogalegigenin and rutinose [4].

According to a comparison of ^{13}C NMR spectral data for **1** and **3**, the carbohydrate unit in **1** was located on C-3 of the genin (Table 1). The SSCC of the anomeric protons indicated that the monosaccharides had the pyranose form and the β-configuration for D-glucose and the α-configuration for L-rhamnose [5].

Based on the analysis of the results, **1**, which was isolated for the first time from *A. caucasicus*, was cyclogalegigenin 3-*O*-β-D-rutinoside, which we called cycloascauloside D.

Compound 2, white needle-like crystals, mp 184–188°C (aq. MeOH), $[M]^+$ 796.25 (mass spectrometry), $C_{42}H_{68}O_{14}$. IR spectrum (KBr, ν_{max}, cm^{-1}): 3600–3220 (OH), 3050 (cyclopropane ring CH_2). The PMR spectrum showed at 2.01 ppm a resonance for an acetyl (Table 1). Acid cleaved **2** on cyclogalegigenin and D-xylose. Base gave a less polar glycoside, acid hydrolysis of which produced **3** and D-xylose.

Enzymatic hydrolysis of the glycoside by *Helix plectotropis* gave D-xylose and a monoside with mp 226–227°C ($CHCl_3$:MeOH, 1:1), which was identified as cyclogaleginoside A [6].

A comparison of chemical shifts for C′ and C″ atoms of **2** showed that C-1′ underwent a diamagnetic shift by 2.69 ppm [$\Delta\delta$ = δ(C-1″) 107.49 – δ(C′) 104.80]. This indicated that the acyl group was located in D-xylose bonded to C-3 of the aglycon. The strong-field shift of C-1′ by 2.69 ppm indicated that the acetyl was located on the neighboring C atom (C-2′) [7].

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TABLE 1. PMR and ^{13}C NMR Spectral Data for Cycloascualoside D (**1**), Cyclogaleginoside C (**2**), and the Genin (**3**) (400 MHz, C_5D_5N, δ, ppm, J/Hz, 0 = TMS)

C atom	**1**		**2**		**3**
	δ_C	δ_H	δ_C	δ_H	δ_C
1	32.70	1.53; 1.23	32.69	1.61; 1.29	32.50
2	29.60	2.29; 1.95	29.62	2.35; 1.90 dq	30.98
3	88.00	2.60 (dd, J = 11.7; 4.4)	88.10	3.50	78.20
4	42.65	–	42.65	–	42.40
5	53.81	1.88 (d, J = 8.6)	52.80	1.90	53.30
6	68.41	3.78 (td, J = 8.6; 3.9)	79.20	3.80 (td, J = 8.6; 3.9)	68.20
7	37.80	2.26; 1.84	34.40	1.95	37.90
8	46.30	2.0	45.68	–	47.10
9	20.31	–	21.50	–	20.80
10	29.60	–	28.80	1.80; 1.29	29.90
11	26.25	1.80; 1.44	26.25	1.60	26.30
12	33.70	1.85; 1.71	33.20	–	33.45
13	45.52	–	45.55	–	45.32
14	46.30	–	46.35	2.38 (dd, J = 13.5; 7.8)	46.60
15	47.41	2.40 (dd, J = 2.7; 8.1), 1.28	47.43	1.81 (dd, J = 3.5; 4.6)	47.10
16	73.32	4.90 m	72.98	4.72 (d, J = 7.8; 7.1; 4.0)	73.02
17	58.82	2.26 (d, J = 7.5)	58.80	1.79 (d, J = 7.1)	58.15
18	21.65	1.68 s	21.65	1.40	21.63
19	30.22	0.20; 0.52	30.22	0.39; 0.20 (d, J = 4.0)	30.91
20	86.90	–	86.90	2.37	86.70
21	28.80	1.5 s	28.80	1.09 (d, J = 6.3)	28.40
22	34.69	3.12 (td, J = 13. 9)	34.70	2.30; 1.47	34.80
23	26.17	2.19 m; 1.98 м	26.17	1.80; 1.90	26.15
24	85.10	3.90 (dd, J = 8.8; 6.3)	85.10	3.90	85.00
25	70.12	–	70.12	–	70.10
26	27.50	1.24 s	27.52	1.42 s	27.20*
27	28.10	1.30 s	28.15	1.47 s	28.00*
28	20.30	0.95 s	20.35	1.97 s	20.17
29	29.12	1.29 s	29.12	1.37 s	29.40
30	16.00	1.02 s	16.00	0.99 s	16.20
$CO\text{-}CH_3$			170.10		
$CO\text{-}CH_3$			19.75	2.01	
		3-*O*-D-Glc*p*		3-*O*-D-Xyl*p*	
1′	105.60	4.92 (d, J = 13.0)	104.80	4.30 (d, J = 7.5)	
2′	75.50	4.13 (dd, J = 9.3; 7.7)	75.02	4.09 (dd, J = 8.5; 7.5)	
3′	79.00	4.25	78.20	4.18 (td, J = 8.5; 5.2)	
4′	71.70	3.91 m	71.31	4.19 (d, J = 8.5)	
5′	78.12	4.55 (dd, J = 11.7; 3.2)	66.65	4.29 (dd, J = 11.4; 5.2; 3); 3.60 (dd, J = 11.8; 8.5)	
6′	67.50	4.40; 4.27 (dd, J = 11.7; 4.5)			
		6′-*O*-L-Rha*p*		6-*O*-D-Xyl*p*	
1″	101.80	5.71 (d, J = 8.0)	107.49	4.82 (d, J = 7.5)	
2″	72.20	4.83 (dd, J = 4.0; 1.3)	75.50	4.00 (dd, J = 8.5; 7.5)	
3″	72.50	4.70–4.40 (J = 10.0)	77.90	4.10 (t, J = 9.0)	
4″	73.90	4.40 (J = 10.0)	71.31	4.19 (dd, J = 8.5; 5.2)	
5″	69.63	4.80 (dq, J = 10.6)	66.65	4.34 (d, J = 11.4); 3.68 (d, J = 5.3)	
6″	18.70	1.71 (d, J = 6.0)			

*Ambiguous assignment.

A comparison of ^{13}C NMR spectra of **2** and **3** showed that the carbohydrate groups in **2** were located on C-3 and C-6 of the genin (Table 1). Therefore, **2** was a bisdesmoside of cyclogalegigenin. The SSCC of the anomeric protons indicated that D-xylose had the pyranose form and the *β*-configuration.

Thus, **2**, which was isolated for the first time from stems of *A. galegiformis*, was 20*S*,24*R*-epoxycycloartan-3β,6α,16β,25-tetraol 3-*O*-β-D-(2′-*O*-acetyl)xylopyranosyl-6-*O*-β-D-xylopyranoside, which we called cyclogaleginoside C.

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