Chemistry of Natural Compounds, Vol. 42, No. 3, 2006

CYCLOGALEGINOSIDE D FROM *Astragalus galegiformis* STEMS

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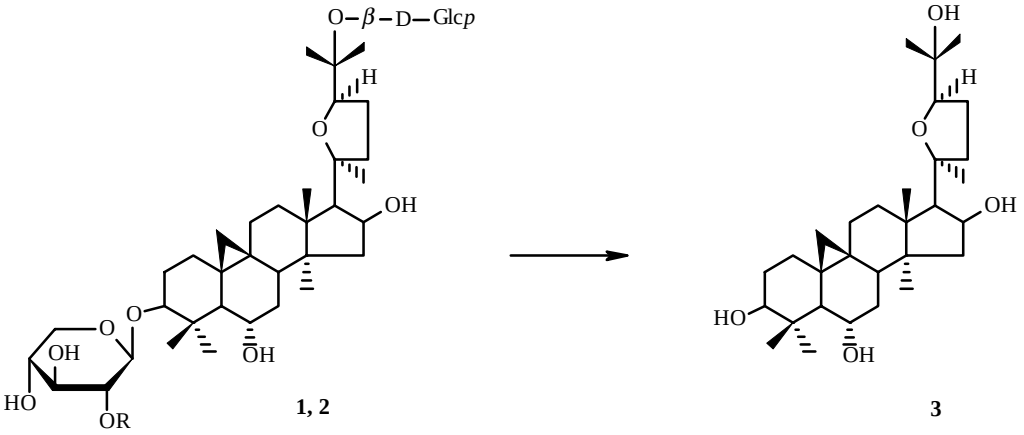
UDC 547.918:547.926

*The new cycloartane glycoside cyclogaleginoside D, which has the structure 25-*O*-β-D-glucopyranoside-20*S*,25*R*-epoxycycloartan-3β,6α,16β,25-tetraol 3-*O*-β-D-(2-*O*-acetyl)xylopyranoside was isolated from* Astragalus galagiformis *stems. The structure of the glycoside was established using chemical transformations and IR, PMR, and ^{13}C NMR spectral data.*

Key words: cyclogaleginoside, cyclogalegigenin, cycloartane, *Astragalus galegiformis* L.

We have previously isolated from *A. galegiformis* L. stems and identified cycloartane glycosides cyclogaleginosides A, B, and E [2, 3]. In continuation of chemical research on isoprenoids from plants of the genus *Astragalus* (Leguminosae) [1], we isolated in addition to the aforementioned glycosides another two polar glycosides C and D. Herein the structure of cyclogaleginoside D (**1**) is examined.

The PMR spectrum of **1** contained a 1H doublet for an AX system at 0.38 and 0.54 ppm with SSCC ^{2}J = 4.5 Hz in addition to signals for seven methyls in the range 0.91-1.41 ppm. This indicated that the compound was a triterpenoid cycloartane [1]. This was consistent with the isolation of cyclogalegigenin (**3**) as the genin from the acid-hydrolysis products of cyclogaleginoside D. Paper chromatography detected D-xylose and D-glucose in the carbohydrate part of the acid-hydrolysis products. The PMR and ^{13}C NMR spectra of **1** (Table 1) contained signals for two carbohydrate units and indicated that the studied glycoside was a bioside.



1, 2

1: R = Ac
2: R = H

3

A 3H singlet at 2.10 ppm in the PMR spectrum of **1** was consistent with one acetic acid moiety. As expected, the ^{13}C NMR spectrum of **1** contained signals for C atoms of one acetyl at 21.1 and 169.5 ppm.

Alkaline hydrolysis of **1** gave glycoside **2**, which was identified as cyclogaleginoside E [3]. Therefore, cyclogaleginoside D is cyclogaleginoside E monoacetate.

The attachment site of the acetyl was found by comparing the ^{13}C NMR spectra of **1** and **2**. Atoms C-6 and C-16 of **1** resonated in the ^{13}C NMR spectrum of **1** at 69.07 and 74.40 ppm, respectively. These values were practically the same as those in the ^{13}C NMR spectrum of **2**. This means that the acetyl is not located on the genin of **1**.

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 0009-3130/06/4203-0310

TABLE 1. Chemical Shifts of C Atoms in **1**, **2**, and **3** (CD_3OD, δ, ppm, 0 = TMS)

C atom	Compound		
	1	**2**	**3***
1	33.05	33.30	32.80
2	30.31	30.58	31.46
3	91.62	89.91	78.30
4	42.70	43.15	42.46
5	54.30	54.66	54.00
6	69.67	69.60	68.40
7	38.85	38.85	38.85
8	48.55	48.50	47.30
9	21.80	21.91	20.99
10	30.46	30.58	29.90
11	27.02	27.17	26.31
12	34.13	34.26	33.45
13	47.72	47.85	45.10
14	47.35	47.47	46.21
15	49.12	49.23	46.81
16	74.40	74.42	72.90
17	56.21	56.31	58.48
18	21.40	21.40	21.63
19	32.23	32.18	31.02
20	88.74	88.93	86.70
21	24.00	24.24	28.60
22	27.92	28.00	34.97
23	24.20	24.27	26.18
24	86.32	86.38	85.00
25	78.89	78.93	70.30
26	24.89	25.01[a]	27.17
27	23.40	23.51[a]	28.21
28	20.82	20.90	20.25
29	28.65	28.73	23.40
30	16.26	16.55	16.05
	β-D-Xyl*p*		
1	104.80	107.48	
2	76.02	75.50	
3	75.00	77.95	
4	71.31	71.29	
5	66.65	66.70	
	β-D-Glc*p*		
1	99.10	99.04	
2	75.05	75.04	
3	77.66	77.63	
4	71.80	71.80	
5	77.63	77.63	
6	62.80	62.84	
C$COCH_3$	169.50		
$COCH_3$	21.10		

*Recorded in C_5D_5N; [a]ambiguous assignment.

Table 1 shows that the chemical shifts of C-1 (-2.68 ppm), C-2 (+0.52 ppm), and C-3 (-2.95 ppm) of the xylopyranose unit changed considerably on going from **2** to **1**. The signs and values of these changes agreed well with the *α*- and *β*-effects of an acetyl situated on C-2 of the *β*-D-xylopyranoside ring [2, 4] and unambiguously determined the site of the acetyl.

Thus, **1** has the structure 25-*O*-β-D-glucopyranoside-20*S*,25*R*-epoxycycloartan-3β,6α,16β,25-tetraol 3-*O*-β-D-(2-*O*-acetyl)xylopyranoside.

EXPERIMENTAL

General comments have been published [3]. We used the following solvent systems: $CHCl_3$:CH_3OH (10:1, 1), $CHCl_3$:CH_3OH:H_2O (70:23.5:2, 2), C_5H_5N:C_6H_6:C_4H_9OH:H_2O (3:5:1:3, 3).

PMR and ^{13}C NMR spectra were recorded on Bruker AM-400 and DRX-500 (CD_3OD) and Tesla BS-567A (C_5D_5N) spectrometers (δ, ppm, 0 = TMS). ^{13}C NMR spectra were obtained with complete C–H decoupling and using J-modulation and DEPT.

Isolation of triterpenoids from *Astragalus galegiformis* L. has been described [1]. Cyclogaleginoside D, $C_{43}H_{70}O_{15}$, mp 215-217°C (CH_3OH). PMR spectrum (500 MHz, CD_3OD, 0 = TMS, δ, ppm, J/Hz): 0.38 and 0.54 (2H-19, d, $^2J = 4.1$), 0.91, 1.02, 1.24, 1.28, 1.29, 1.30, 1.41 (7 × CH_3, s), 2.10 (CH_3COO, s), 2.22 (H-17, d, $^3J = 7.1$), 3.18 (H-3, dd, $^3J_1 = 8.5$, $^3J_2 = 1.40$), 3.45 (H-6, td, $\Sigma J = 18.8$), 3.90 (H-24, dd, $^3J_1 = 9$, $^3J_2 = 5$), 4.11 (D-xylose H-1, d, J = 7.5), 4.43 (D-glucose H-1, d, J = 7.6), 4.65 (D-xylose H-16 and H-2, m). For the ^{13}C NMR spectrum, see Table 1.

Cyclogalegigenin (3) from 1. Cyclogaleginoside D (**1**, 50 mg) was hydrolyzed by methanolic H_2SO_4 (10 mL, 0.25%) at 60°C for 2 h. The reaction mixture was diluted with water. The methanol was evaporated. The precipitate was filtered off and dried. The resulting genin was chromatographed over a silica-gel column with elution by system 1 to isolate **3** (30 mg), mp 196-197°C (CH_3OH), which was identified as cyclogalegigenin.

The aqueous part of the hydrolysate was neutralized with anion-exchanger APA-8p and condensed to a small volume (2-3 mL). Paper chromatography using system 3 detected D-xylose and D-glucose in the carbohydrate part of the hydrolysate.

Cyclogalgeinoside E from 1. Glycoside **1** (20 mg) was saponified by aqueous NaOH (0.1%) at room temperature for 3 h. Work up of the reaction products and chromatography over a silica-gel column using system 2 afforded **2** (13 mg), mp 187-188°C (CH_3OH), which was identified as cyclogaleginoside E [3].

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