Chemistry of Natural Compounds, Vol. 35, No. 2, 1999

THE STRUCTURE OF CYCLOGLOBICEPOSIDE B FROM *Astragalus globiceps*

K. K. Uteniyazov, Z. Saatov, M. G. Levkovich, and N. D. Abdullaev

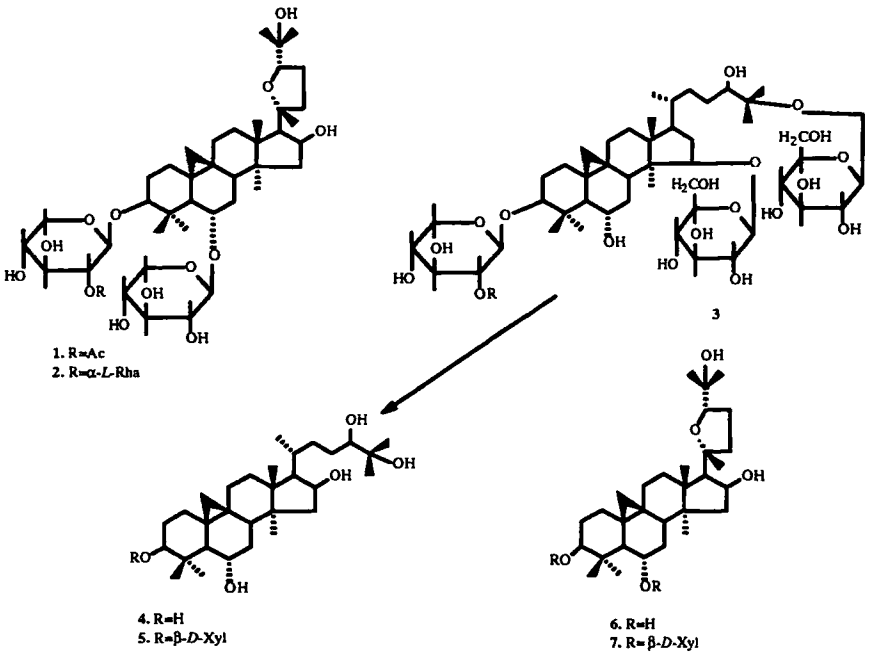
UDC 547.918:547.926

Two known compounds of the cycloartane series — cyclosieversiosides C and G — and the new glycoside cycloglobiceposide B — 24R-cycloartane-3β,6α,16β,24,25-pentaol 16,25-di-O-β-D-glucopyranoside 3-O-β-D-xylopyranoside — have been isolated from the roots of Astragalus globiceps *Bunge. The structures of the glycosides were established on the basis of the results of enzymatic and total hydrolysis and also of ^{1}H and ^{13}C NMR spectra.*

Continuing a study of the cycloartanes of *Astragalus globiceps* Bunge (fam. Leguminosae) [1], from the roots of this plant we have isolated a new cycloartane glycoside — cycloglobiceposide B (**3**) — in addition to the known cyclosieversiosides C (**1**) and G (**2**) [2, 3].

In the PMR spectrum of cycloglobiceposide B (**3**) in the strong field at 0.25 and 0.45 ppm the one-proton doublets of an *AB* system (SSCC ^{2}J = 3.9 Hz) showed the presence of a cyclopropane ring. On this basis, we assigned glycoside (**3**) to compounds of the cycloartane series.

The acid hydrolysis of cycloglobiceposide B showed the presence of xylose and glucose residues in it, together with cycloasgenin C (**4**) [4] as the aglycon.



Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (371) 120 64 75. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 216—219, March-April, 1999. Original article submitted December 28, 1998.

 0009-3130/99/3502-0192$22.00

TABLE 1. Chemical Shifts (ppm) of the Carbon Nuclei in the ^{13}C NMR Spectra of Cyclosieversiosides C (**1**) and G (**2**), Cycloglobiceposide B (**3**), Cycloasgenin C (**4**), and the Monoside (**5**) in C_5D_5N

C atom	1	2	3	4	5
1	34.96	31.85	32.57	32.81	32.61
2	29.86	28.63	30.05	31.48	30.10
3	88.71	87.48	88.77	78.84	88.75
4	42.24	42.54	42.72	42.43	42.71
5	52.15	51.95	54.04	53.88	54.10
6	78.58	78.30	67.91	68.25	67.89
7	34.96	34.91	38.39	38.56	38.40
8	4451	42.54	46.86	47.02	47.00
9	21.25	21.23	21.28	21.17	21.15
10	28.51	27.87	29.60	29.55	29.62
11	26.50	26.50	26.26	26.26	26.25
12	33.50	33.54	32.83	34.37	32.80
13	45.22	45.28	45.63	45.55	45.61
14	46.21	45.44	46.86	46.90	46.92
15	46.04	46.15	47.30	47.82	47.39
16	73.46	73.41	82.84	71.77	71.75
17	58.22	58.00	57.51	57.19	57.15
18	21.26	19.82	18.21	18.08	18.52
19	31.86	30.06	30.37	30.30	30.25
20	87.32	87.35	31.74	31.96	31.95
21	27.17	27.11	19.03	19.18	19.14
22	33.83	32.25	30.22	30.63	30.49
23	26.29	26.29	34.55	34.37	34.57
24	81.72	81.63	78.86	76.96	78.82
25	71.28	71.51	80.79	72.70	72.65
26	28.20	28.18	23.50	25.42	24.83
27	28.26	28.63	22.32	26.39	25.18
28	27.94	27.41	20.20	20.25	20.24
29	16.54	16.90	28.92	29.44	29.04
30	20.66	19.46	16.73	16.23	16.65
1′	104.72	105.84	107.60		107.59
2′	76.31	79.45	75.62		75.63
3′	75.67	77.87	78.04		78.44
4′	71.28	71.27	71.85		71.33
5′	67.15	66.89	67.05		67.05
	6-β-*D*-Xyl	α-*L*-Rha	16-β-*D*-Glc		
1″	105.72	101.94	106.28		
2″	75.43	72.46	75.94		
3″	77.99	72.55	78.86		
4″	71.13	74.20	71.27		
5″	67.03	69.66	78.14		
6″		18.75	69.94		
		6-β-*D*-Xyl	25-β-*D*-Glc		
1‴		105.65	98.75		
2‴		75.46	75.35		
3‴		77.09	78.72		
4‴		71.10	71.85		
5‴		66.89	78.32		
6‴			62.87		
OC=O	170.05				
CH_3	9.76				

The ^1H and ^{13}C NMR spectra of glycoside (3) contained the signals of three protons at 4.78, 4.86, and 5.20 ppm and of three anomeric carbon atoms of monosaccharide residues resonating at 107.60, 106.28, and 98.75 ppm.

The facts given above confirmed that glycoside (3) was a trioside.

It can be seen from Table 1 that in the spectrum of compound (3) the chemical shifts of the carbinol atoms C-3, C-16, and C-25 had undergone glycosylation effects and resonated at 88.77, 82.84, and 80.79 ppm. Thus, it was possible to assume that the sugar residues were attached to the hydroxyls of the genin moiety at the carbon atoms C-3, C-16, and C-25.

The enzymatic hydrolysis of cycloglobiceposide B (3), conducted with the gastric juice of the snail *Helix plectotropis*, led to the formation of monoside (5).

The acid hydrolysis of monoside (5) formed cycloasgenin C (4). *D*-Xylose was detected in the hydrolysate by PC in comparison with an authentic specimen. In the PMR spectrum of monoside (5) the signal of the anomeric proton was observed in the form of a doublet at 4.86 ppm with the SSCC $^3J = 7.7$ Hz. Consequently, monoside (5) contained a *D*-xylose residue attached to the genin part through the hydroxy group at C-3. These results were confirmed by the ^1H and ^{13}C NMR spectra of monoside (5) (see Table 1).

It follows from what has been said above that the two glucose residues in the glycoside (3) molecule are attached to the OH groups at C-16 and C-25. This conclusion was confirmed by the ^1H and ^{13}C NMR spectra of glycoside (3) (see Table 1). The SSCCs of the anomeric protons showed the $^4C_1$ conformation of the pyranose rings and the β- configuration of the glycosidic centers.

Thus, cycloglobiceposide B is 24R-cycloartane-3β,6α,16β,24,25-pentaol 16,25-di-O-β-*D*-glucopyranoside 3-O-β-*D*-xylopyranoside.

EXPERIMENTAL

For general observations, see [1].

Separation of the Butanolic Fraction. The butanolic faction from the roots of *Astragalus globiceps* (5.5 g) was chromatographed on a column of silica gel. Elution by the chloroform—methanol—water (70:23:3) system led to the isolation of 300 mg of cyclosieversioside C (1) (yield 0.02%) and 150 mg of cyclosieversioside G (2) (yield 0.01%). Further elution with the same system gave 100 mg of cycloglobiceposide B (3) (yield 0.08%).

Cyclosieversioside C (1). $C_{42}H_{68}O_{14}$, mp 275—277°C (from methanol).

IR spectrum (KBr, ν, cm^{-1}): 3395 (OH), 2970 (cyclopropane group), 1750, 1260 (ester group).

PMR spectrum (400 MHz, δ, ppm, C_5D_5N): 0.15 and 0.57 (each 1H, d, ^2J=4.5 Hz, 2H-19); 1.09; 1.24; 1.30 (2×CH^3, s); 1.39; 1.59; 1.73)s, each 3H, tertiary methyl griups); 2.05 (Oac); 3.36 (1H, dd, ^3J=11.6 and 4.6 Hz, ^3J=11.1 Hz, H-22); 3.89 (1H, dd, ^3J=8.9 and 5.3 Hz, H-24); 4.78 and 4.90 (each 1H, d, ^3J=7.9 and 7.4 Hz respectively H-1′ and H-1″.

For the ^{13}C NMR spectrum see Table 1.

Acid Hydrolysis. Cyclosieversioside C (1) (50 mg) was hydrolyzed under the conditions described in [1], and 12 mg of cyclosieversigenin (6) was isolated. In the hydrolysate, *D*-xylose was detected by PC in the butanol—pyridine—water (6:4:3) system in comparison with an authentic specimen.

Alkaline Hydrolysis. Cyclosieversioside C (1) (50 mg) was saponified with 20 ml of 0.5% methanolic potassium hydroxide. For the procedure, see [1]. Cyclosieversioside E (7) [1] (37 mg) was isolated.

Cyclosieversioside G (2). $C_{46}H_{76}O_{17}$, mp 222—224°C (from methanol).

PMR spectrum (400 MHz, δ, ppm, C_5D_5N): 0.20 and 0.62 (each 1H, d, ^2J=4.3 Hz, 2H-19); 1.20; 1.29; 1.30; 1.37; 1.43; 1.59; 1.78 (s, each 3H, tertiary methyl groups); 1.74 and 1.76 (3H, d, J=6.0 Hz, Rha); 3.38 (1H, dd, ^3J=11.7 and 4.4 Hz, H-3); 3.80 (1H, m, H-6); 2.62 (1H, d, ^3J=7.6 Hz, H-17); 3.17 (2H, q, ^3J=9.5 Hz, H-22); 3.89 (1H, dd, ^3J=10.9 and 5.2 Hz, H-24); 4.79 and 4.80 (each 1H, d, ^3J=7.3 and 7.4 Hz, respectively, H-1′ and H-1″); 6.60 (1H, d, ^3J=1.5 Hz, H-1‴ of rhamnose).

For the ^{13}C NMR spectra, see Table 1.

Acid Hydrolysis. Cyclosieversioside G (2) (50 mg) was hydrolyzed as described previously [1]. This led to the isolation of 5 mg of cyclosieversioside E (7) and 8 mg of cyclosieversigenin (6). *D*-Xylose and *L*-rhamnose were detected in the hydrolysate by PC in comparison with authentic specimens.

Cycloglobiceposide B (3). $C_{47}H_{82}O_{19}$, mp 285—287°C (from methanol).

IR spectrum (KBr, ν, cm^{-1}): 3394 (OH), 2971 (cyclopropane group).

PMR spectrum (400 MHz, δ, ppm, C_5D_5N): 0.20 and 0.45 (each 1H, d, ^2J=4.0 Hz, 2H-19); 0.97; 1.00 (d, J=6.7 Hz); 1.23; 1.35; 1.52; 1.56; 2.02 (s, each 3H, tertiary methyl groups); 3.65(1H, dd, ^3J=11.6 and 4.6 Hz, H-3); 3.74 (1H, m, H-6); 4.78 (1H, d, ^3J=7.8 Hz, H-1′ of xylose); 4.93 and 5.18 (2H, d, ^3J=7.5 and 7.8 Hz, H-1″, H-1‴ of glucose).

For the ^{13}C NMR spectrum, see Table 1.

Acid Hydrolysis. Compound (**3**) (45 mg) was hydrolyzed as described above [1], and 12 mg of compound (**4**) was isolated. From its physicochemical constants and also by direct comparison with an authentic specimen, compound (**4**) was identified as cycloasgenin C [4]. *D*-Xylose and *D*-glucose were identified in the hydrolysate by PC in comparison with authentic specimens.

Enzymatic Hydrolysis. Compound (**3**) (26 mg) was treated with 2.5 ml of an aqueous solution of the enzymes of *Helix plectotropis*. After being kept at 38°C for three months, the reaction mixture was diluted with 15 ml of water and extracted with butanol (4 × 10 ml). The solvent was evaporated off and the residue was chromatographed on a column of silica gel. Elution with the chloroform—methanol—water (40:7.5:1) system yielded 13 mg of the monoside (**5**), $C_{35}H_{60}O_9$. mp 253—255°C (from methanol).

PMR spectrum: 0.34 and 0.56 (each 1H, d, ^2J=4.0 Hz, 2H-19); 0.99; 1.02 (d, J=6.5 Hz); 1.25; 1.40; 1.47; 1.53; 1.94 (s, each 3H, tertiary methyl groups); 3.70 (1H, dd, ^3J=11.6 and 4.7 Hz, H-3); 3.74 (2H, m, H-6 and H-24); 4.86 (1H, d, ^3J=7.7 Hz, H-1′ of xylose).

Further elution gave 10 mg of the initial substance (**3**).

For the ^{13}C NMR spectrum, see Table 1.

Acid Hydrolysis of Monoside (5). Compound (**5**) (8 mg) was hydrolyzed as described above [1], giving 4 mg of cycloasgenin C (**4**). *D*-Xylose was identified in the hydrolysate by PC in comparison with authentic specimens.

REFERENCES

1. K. U. Uteniyazov, Z. Saatov, N. D. Abdullaev, and M. G. Levkovich, *Khim. Prir. Soedin.*, 509 (1998).
2. A. N. Svechnikova, R. U. Umarov, N. D. Abdullaev, M. B. Gorovits, and N. K. Abubakirov, *Khim. Prir. Soedin.*, 629 (1982).
3. A. N. Svechnikova, R. U. Umarov, M. B. Gorovits, N. D. Abdullaev, and N. K. Abubakirov, *Khim. Prir. Soedin.*, 312 (1983).
4. R. Zh. Karimov, R. U. Umarov, Z. Saatov, M. G. Levkovish, and N. D. Abdullaev, *Khim. Prir. Soedin.*, 670 (1998).