Chemistry of Natural Compounds, Vol. 35, No. 6, 1999

STRUCTURE OF CYCLOGLOBISEPOSIDE C FROM *Astragalus globiceps*

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

UDC 547.918:547.926

A new cycloartane glycoside, cycloglobiseposide C, is isolated from the roots of Astragalus globiceps *Bunge. The structure 3-O-β-D-glucopyranosyl-(1→3)-O-α-L-arabinopyranosyl cycloglobisepogenin is proposed on the basis of NMR spectra.*

In continuation of the investigation of cycloartane triterpenes from *Astragalus globiceps* Bunge (Leguminosae) [1], we isolated a new cycloartane glycoside, cycloglobiseposide C (**1**), from the methanol extract of its roots.

Paper chromatography of the acid hydrolysate of compound **1** detected *D*-glucose and *L*-arabinose. The ^{1}H and ^{13}C NMR spectra indicate that cycloglobiseposide C contains these two units and is therefore a bioside. Table 1 lists the NMR data for compound **1** that were obtained by analyzing one-dimensional and two-dimensional (COSY, HMQC, HMBC) experiments. Table 1 shows that the anomeric protons of the carbohydrate units appear at 4.71 and 4.78 ppm whereas the C atoms appear at 103.34 and 105.59 ppm. Complete analysis of the spectral data of these two units unambiguously demonstrated that they were *L*-arabinose and *D*-glucose.

The ^{1}H NMR spectrum of compound **1** contains two doublets with $^{3}J = 4.1$ Hz in the upfield region at 0.06 and 0.45 ppm. These are characteristic of cyclopropane methylene protons. An absorption band at 2968 cm^{-1} in the IR spectrum of glycoside **1** is also consistent with the presence of this fragment. Furthermore, resonance lines of seven methyl groups clearly appear in the ^{1}H NMR spectrum. Six of these (at 0.85, 1.25, 1.27, 1.34, 1.36, and 1.92 ppm) are singlets. One (at 0.95 ppm) is a doublet with $^{3}J = 6.6$ Hz.

The ^{13}C NMR spectrum of compound **1** has resonances for the C atoms of the seven methyl groups at 17.77, 14.67, 16.42, 24.42, 23.73, 26.70, and 16.30 ppm.

The ^{1}H NMR spectrum of compound **1** in the 3.40-4.80 ppm region consists of multiplets corresponding to 17 protons, 13 of which belong to the two carbohydrate units. The remaining four multiplets at 3.40, 3.68, 3.82, and 4.58 ppm should therefore be assigned to methine protons on the four O-containing C atoms of the bioside genin. Resonance lines at 86.52, 77.10, 75.03, and 69.93 ppm in the ^{13}C NMR spectrum correspond to these. This provides a basis to conclude that glycoside **1** is a cycloartane genin bioside with an open side chain and four secondary hydroxyls.

The presence of only one signal in the downfield region at 86.52 ppm in the ^{13}C NMR spectrum of glycoside **1** indicates only one hydroxyl in the genin part of the bioside is glycosylated. Judging from the magnitude of the chemical shift, the hydroxyl on C-3 is glycosylated. The ^{1}H NMR spectrum shows a doublet of doublets for H-3 at 3.40 ppm with spin—spin coupling constants (SSCC) of 11.7 and 4.4 Hz. This is consistent with the β-equatorial orientation of the glycosylated hydroxyl.

The chemical shift of the other C atom with a free secondary hydroxyl is 69.93 ppm. This corresponds with C-16. The chemical shift of H-16 at 4.58 ppm is consistent with this. The nature of the splitting by three neighboring H atoms on C-15 and C-17, which produces a doublet of doublets of doublets with SSCC 7.7, 7.7, and 4.9 Hz also indicates the β-orientation for the hydroxyl on C-16.

Atoms C-5 and C-8 resonate at 43.55 and 50.46 ppm. These values do not correspond with those of cycloartane glycosides that contain a secondary hydroxyl on C-6 of the genin part [1, 3].

These data suggest that C-7 contains a tertiary hydroxyl. A multiplet at 3.68 ppm that appears with three vicinal SSCC of 8.3, 8.3, and 4.3 Hz corresponds with H-7 and is consistent with the β-equatorial orientation of the hydroxyl on C-7.

Academician S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (99871) 120 64 75. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 763-766, November-December, 1999. Original article submitted September 20, 1999.

 0009-3130/99/3506-0650$22.00

TABLE 1. ^{1}H and ^{13}C NMR Data (δ, ppm, J, Hz) of Cycloglobiseposide C in C_5D_5N, 0 = TMS

Position of C and H	δ_C	δ_H (^nJ)
1	30.91	1.16, 1.50m
2	28.16	1.86, 2.3m
3	86.52	3.40, dd (11.7, 4.4)
4	40.63	-
5	43.55	1.86m
6	30.19	1.85, 2.13m
7	77.10	3.68, ddd (8.3, 8.3, 4.3)
8	50.46	1.82, d (8.3)
9	19.37	-
10	26.53	-
11	24.22	-
12	31.13	1.5m
13	47.75	-
14	44.87	-
15	45.82	1.70m
16	69.93	4.58 (br.ddd), (7.7, 7.7, 4.9)
17	55.12	2.3m
18	17.77	0.85s
19	26.15	0.06 0.45 d (4.1)
20	26.70	-
21	16.30	0.95, d (6.6)
22	32.28	-
23	25.81	1.70, 1.86m
24	75.03	3.82, dd (11.2, 2.6)
25	70.48	-
26	24.42	1.34, s
27	23.73	1.36, s
28	16.42	1.27, s
29	26.70	1.92, s
30	14.67	1.25, s
	3-O-α-*L*-Ara*p*	
1′	103.34	4.71, d (7.5)
2′	73.57	3.93, br.dd (8.8, 7.5)
3′	76.47	4.02, dd (8.7, 8.7)
4′	69.21	4.1
5′	64.99	3.56, dd (11.2, 10.0): 4.23, dd (11.2, 5.2)
	(1-3)-O-β-*D*-Glc*p*	
1″	105.59	4.78, d (7.7)
2″	73.57	3.91, br.dd (8.8, 7.8)
3″	77.10	4.09, dd (8.7, 7.5)
4″	69.85	4.08
5″	76.05	5.38, ddd (9.4, 5.2, 2.6)
6″	61.10	4.18, br.dd (11.7, 5.7): 4.34, dd (11.7, 2.50)

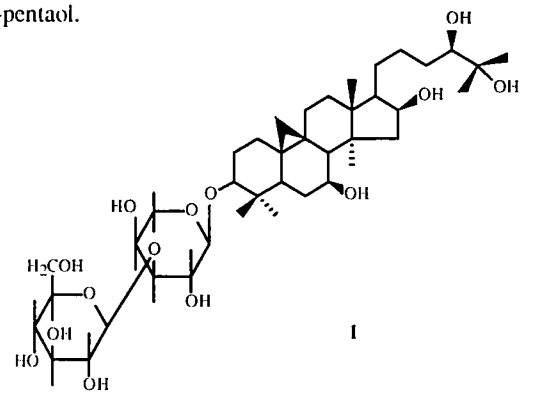
The bridgehead methine proton H-8 resonates at 1.82 ppm, appearing as a doublet with ^3J = 8.3 Hz. The methyl C atom (C-30) in the ^{13}C NMR spectrum of glycoside **1** is located ~2.0 ppm in higher field than that of cycloartane compounds that contain a hydroxyl on C-6. This is yet another indication in favor of a hydroxyl on C-7. A broad multiplet at 3.82 ppm in the ^1H NMR spectrum of compound **1** changes into a pure doublet of doublets with ^3J = 11.2 and 2.6 Hz if the spectrum is recorded in the presence of traces of trifluoroacetic acid.

The signal for the C atom that gives the multiplet at 3.82 ppm is observed at 75.02 ppm among resonance lines of the carbohydrate units in the HMQC spectrum. These data and an analysis of the chemical shifts of C atoms in rings *A* and *C* and the side chain suggested that the fourth secondary hydroxyl is situated on C-24 and has the β-orientation.

A fifth hydroxyl occurs in the genin portion of glycoside **1**. It is tertiary and is located on C-25. This is consistent with the presence of a singlet at 70.48 ppm in the ^{13}C NMR spectrum.

Returning to the placement of the carbohydrate units, we note that a comparative analysis of the chemical shifts of the C atoms indicates that the hydroxyl on C-3 is glycosylated by *L*-arabinose and that the *D*-glucose glycosylates the hydroxyl on the *L*-arabinose C-3 atom. The magnitudes of the chemical shifts of the C atoms in the sugar units indicate that the monosaccharides are in the pyranose form, that the *D*-glucose has the β-configuration, and that the anomeric center of *L*-arabinose has the α-configuration [4].

Thus, the structure 3-O-β-*D*-glucopyranosyl-(1→3)-O-α-*L*-arabinopyranosyl cycloglobisepogenin is proposed for compound **1**. This is a bioside of the new cycloartane genin **2**, which we call cycloglobisepogenin, 24R-cycloartan-3β,7β,16β,24,25-pentaol.



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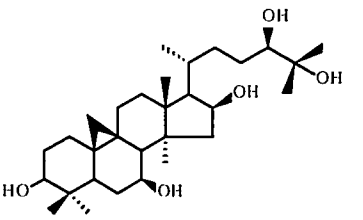

2

EXPERIMENTAL

General comments have been reported [2]. Triterpenes of the butanol fraction of *Astragalus globiceps* were isolated by the literature method [1].

Cycloglobiseposide C (1). Further elution of the column gave **1**, 162 mg, 0.01%, $C_{41}H_{70}O_{15}$, mp 274-275°C (methanol).

IR spectrum (KBr, ν, cm^{-1}): 3394 (OH), 2968 (cyclopropane).

^1H and ^{13}C NMR spectra are listed in Table 1.

Acid Hydrolysis. Cycloglobiseposide C (**1**, 130 mg) was hydrolyzed by methanolic H_2SO_4 (25 ml, 0.15%) with heating on a boiling water bath for 7 h. The reaction mixture was cooled and poured into water (25 ml). The methanol was distilled off. The solid was filtered and washed with water. After neutralization with $BaCO_3$ and evaporation, paper chromatography using butan-1-ol—pyridine—water (6:4:3) detected *D*-glucose and *L*-arabinose that were identical to authentic samples.

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