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TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS
LX. CYCLODISSECTOSIDE — A NEW DIXYLOSIDE OF CYCLOCEPHALOGENIN

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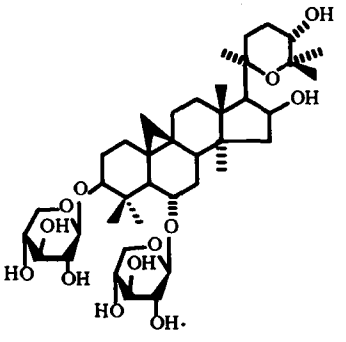
Two more glycosides isolated from the plant Astragalus dissectus *B. Fedtsch. et N. Ivanova (Leguminosae) have been identified on the basis of ^1H and ^{13}C NMR spectra. One of them proved to be cyclosieversioside E, while the other was a new dixyloside of cyclocephalogenin, namely 20R,25-epoxy-24S-cycloartane-3β,6α,16β,24-tetraol 3,6-di-O-β-*D*-xylopyranoside.*

We are pursuing an investigation into a series of 9β,19-cyclolanostane methylsteroids and their glycosides [1]. Earlier [2], from a methanolic extract of the roots with stems of the plant *Astragalus dissectus* B. Fedtsch. et N. Ivanova (Leguminosae) we isolated and identified six individual substances of steroid and triterpenoid natures: β-sitosterol, cyclosieversigenin, β-sitosterol β-*D*-glucopyranoside, cyclosieversigenin 3-O-β-*D*-xylopyranoside, cyclosieversioside F, and cyclocanthoside E. A chromato-graphically homogeneous substance was obtained from the fractions that had accumulated between cyclosieversigenin 3-O-β-*D*-xylopyranoside and cyclosieversioside F. The present paper is devoted to the identification of the components of this fraction.

A consideration of the ^1H and ^{13}C NMR spectra of the fraction under study showed that it consisted of a mixture of two cycloartane glycosides [3, 4] the quantitative ratio of which was approximately 1:1.

The signals of four anomeric protons were observed in the ^1H NMR spectrum at (ppm) 4.80 (2H, d, ^3J = 8 Hz), 4.83 (d, ^3J = 7.5 Hz), and 4.85 (d, ^3J = 7.5 Hz). In agreement with this, the signals of the carbon atoms of four pentose residues were traced in the ^{13}C NMR spectrum (Table 1). The chemical shifts of the carbon atoms of the carbohydrate part of the glycosides showed that all four pentose residues consisted of terminal β-*D*-xylopyranose. The anomeric carbon atoms of two of the β-*D*-xylopyranose residues resonated at 107.61 ppm, and the other two at 105.74 and 105.64 ppm. The chemical shifts of the first pair of anomeric carbon atoms (107.61 ppm) showed that the corresponding *D*-xylopyranose residues were each attached to a hydroxy group at C-3 of a genin [1]. As was to be expected, the resonance signals of the glycosylated C-3 atoms of the genins were observed at 88.42 and 88.32 ppm.



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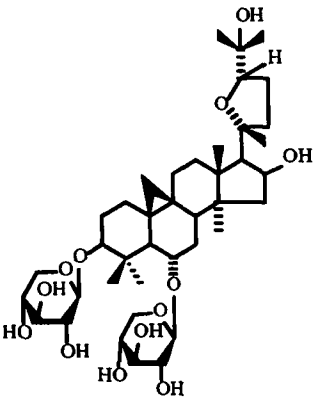

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TABLE 1. Chemical Shifts of the Carbon Atoms of Cyclodissectoside (1) and Cyclosieversioside E (2) (δ, ppm, C_5D_5N, 0 — TMS)

C atom	Compound			C atom	Compound		
	1	2	2*		1	2	2*
1	32.11	31.94	31.87	22	26.79	34.92	34.82
2	30.11	30.11[a]	29.93[a]	23	24.11	26.29	26.17
3	88.42	88.32	88.26	24	68.77	81.67	81.57
4	42.60	42.60	42.45	25	75.25	71.26[d]	71.21
5	52.35	52.13	52.03	26	28.63	27.13	26.95
6	78.55[a]	78.55[b]	78.30[b]	27	28.16	27.99[c]	27.99[c]
7	34.24	33.57	33.50	28	19.96	19.68	19.57
8	44.91	44.21	44.22	28	28.16	28.63	28.45
9	21.19	21.19	21.07	30	16.71	16.71	16.54
10	28.16	27.99[c]	27.99[c]			3-O-β-D-Xylp	
11	26.70	26.41	26.33	1	107.61	107.61	107.38
12	34.14	33.48	33.35	2	75.60	75.60	75.38
13	46.03	45.20	45.09	3	78.55[a]	78.55[b]	78.30[b]
14	46.80	45.91	45.72	4	71.26	71.26[d]	71.09
15	47.24	46.18	46.07	5	67.05	67.05	66.77
16	73.98	73.43	73.37			6-O-β-D-Xylp	
17	60.76	58.15	58.02	1	105.74	105.64	105.52
18	20.43	20.49	20.41	2	75.36	75.36	75.19
19	29.59	30.11[a]	29.93[a]	3	78.29	77.84	77.80
20	79.00	87.30	87.20	4	71.10	71.10	70.93
21	28.84	28.40	28.38	5	66.99	66.99	66.76

Signals labeled with the same letter within a column and also those having the same chemcial shifts in columns 1 and 2 are superposed on one another.

*The spectrum of the sample of cyclosieversioside E was obtained on a Bruker AC 200 spectrometer.

Attention is attracted by the signals of the C-5 and C-7 atoms, which were located at 52.35 (52.13) and 34.24 (33.57) ppm. These facts unambiguously determined the positions of the other pair of monosaccharides at C-6 of the genins [1]. Consequently, the two glycosides had identical structures of the carbohydrate components: 3-O-β-*D*-xylopyranoside 6-O-β-*D*-xylopyranoside. This permitted us to assume that the glycosides concerned were twin glycosides of different genins.

The signal of a tertiary carbon atom linked to an oxygen atom, at 87.30 ppm, and the signal of a secondary carbon atom also linked to oxygen, at 81.67 ppm, belong to the C-20 and C-24 atoms of a genin having a 20R,24S-epoxy-16β,25-diol structural fragment [4]. This was also shown by the signals of the protons H-16 (5.03 ppm, q, $^3J_1 = {}^3J_2 = {}^3J_3 = 8$ Hz), H-22 (3.11 ppm, m), and H-24 (3.86, dd, $^3J_1 = 10$, $^3J_2 = 5$ Hz) observed in the ^{1}H NMR spectrum. This meant that one of the glycosides was a dixyloside of the genin cyclosieversigenin, which is very widely distributed in plants of the *Astragalus* genus and is known under the name of cyclosieversioside E (2) [4].

By screening out the signals of the carbon atoms and protons of cyclosieversioside E using the ^{1}H and ^{13}C NMR spectra of an authentic specimen, we obtained the ^{1}H and ^{13}C NMR spectra of the glycoside (1) that had remained unidentified.

In the ^{13}C NMR spectrum taken under J-modulation conditions two signals from tertiary carbon atoms bearing oxygen functions stood out, at 79.00 and 75.25 ppm. These parameters practically coincide with the values of the chemical shifts of the C-20 and C-25 atoms of cyclocephalogenin [1]. This fact enabled us to assume that the latter was the genin of glycoside (1). In agreement with this, in the same ^{13}C NMR spectrum we observed two signals from secondary alcoholic carbon atoms

at 73.98 and 68.77 ppm, relating to the C-16 and C-24 atoms. The signals of H-16 (4.93 ppm, m) and H-22 (3.11 ppm, m) observed in the ^{1}H NMR spectrum served as additional confirmation of the conclusion that glycoside (1) was in fact a bioside of cyclocephalogenin.

Thus, glycoside (1) has the structure of 20R,25-epoxy-24S-cycloartane-3β,6α,16β,24-tetraol 3,6-di-O-β-*D*-xylopyranoside. This compound is the third glycoside of cyclocephalogenin, after cyclocephaloside I [5] and cyclocanthoside F [1], and we have called it cyclodissectoside.

EXPERIMENTAL

General Observations. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM 400 spectrometer in deuteropyridine with the internal standard TMS (δ, ppm). The ^{13}C NMR spectra were recorded with complete suppression of C—H interactions and also under J-modulation conditions. Spectra of a specimen of cyclosieversioside E (2) were taken under analogous conditions on a Bruker AC 200 instrument.

The Isolation and Separation of the Isoprenoids of *Astragalus dissectus* are described in [2]. In the intermediate fractions that had accumulated between cyclosieversigenin 3-O-β-*D*-xylopyranoside and cyclosieversioside F we detected a chromatographically homogeneous fraction coinciding with cyclosieversioside E (2) (6 mg).

Cyclodissectoside (1), $C_{40}H_{66}O_{13}$. PMR spectrum (δ, ppm, J, Hz): 0.14 and 0.58 (2H-19, d, ^{2}J = 4 Hz), 1.09; 1.27; 1.31; 1.44; 1.56; 1.65; 1.93 (7×CH_3, s), 2.13 (H-17, d, ^{3}J = 7.5 Hz), 3.11 (H-22, m), 3.46 (H-3, dd, $^3J_1$ = 12, $^3J_2$ = 4 Hz), 4.80 (2 anomeric protons, ^{3}J = 8 Hz), 4.93 (H-16, m). For the ^{13}C NMR spectrum, see Table 1.

Cyclosieversioside E (2), $C_{40}H_{66}O_{13}$. PMR spectrum (δ, ppm, J, Hz): 0.12 and 0.57 (2H-19, d, ^{2}J = 4 Hz), 1.05; 1.24; 1.26; 1.26; 1.38; 1.55; 1.89 (7×CH_3, s), 2.56 (H-17, d, ^{3}J = 8 Hz), 3.11 (H-22, m), 3.44 (H-3, dd, $^3J_1$ = 12, $^3J_2$ = 4 Hz), 3.86 (H-24, dd, $^3J_1$ = 10, $^3J_2$ = 5 Hz), 4.83 and 4.85 (2 anomeric protons, ^{3}J = 7.5 Hz), 5.03 (H-16, Hz , $^3J_1 = {}^3J_2 = {}^3J_3$ = 8 Hz). For the ^{13}C NMR spectrum, see Table 1.

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