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TRITERPENE GLUCOSIDES OF *Astragalus* AND THEIR GENINS. LXXIV. CYCLOTRISECTOSIDE, THE FIRST TRISDESMOSIDE OF CYCLOCEPHALOGENIN*

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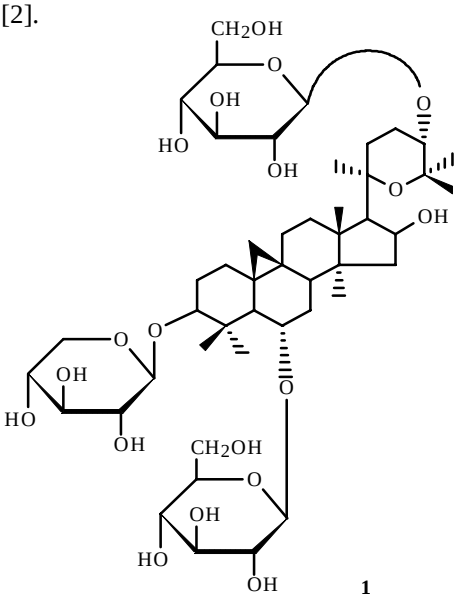
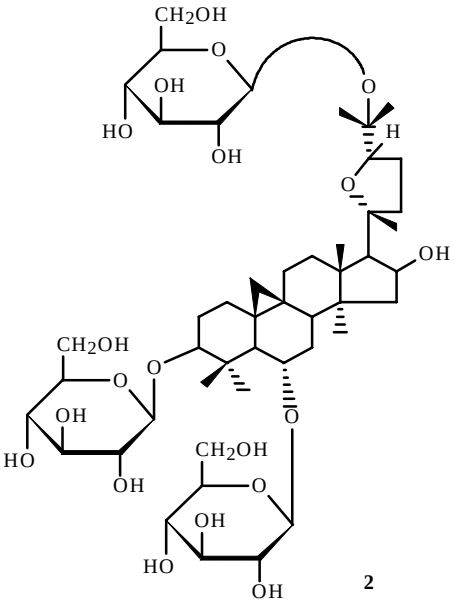
The two trisdesmoside cycloartane glycosides astragaloside VII and cyclotrisectoside were isolated from Astragalus dissectus *(Leguminosae) and identified. The latter was 20R,25-epoxy-24S-cycloartan-3β,6α,16β,24-tetraol 3-O-β-D-xylopyranoside-6,24-di-O-β-D-glucopyranoside and was a new natural compound.*

Key words: triterpenoids, cycloartanes, cyclotrisectoside, astragaloside VII, *Astragalus*, Leguminosae, PMR and ^{13}C NMR spectra, J-modulation.

In continuation of research on cycloartane triterpenoids [1], we identified another two components (**1** and **2**) from *Astragalus dissectus* B. Fedtsch. et Ivanova (Leguminosae) that were isolated from the methanol extract of roots and stems of this plant [2].



1



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Fractions containing a chromatographically homogeneous crystalline compound of glycosidic nature that was chromatographically similar to astragaloside VII (**2**) were accumulated after isolation of cyclocanthoside E. Judging from the PMR spectrum, the compound was a mixture of two cycloartane glycosides [3-5] in a 1:1 ratio. An analogous mixture consisting of cyclosiversioside E and cyclodissectoside, which are paired glycosides of cyclosiversigenin and cyclocephalogenin, was isolated previously by us from this same plant [6].

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TABLE 1. Chemical Shifts of C Atoms of **1** and **2** (δ, ppm, C_5D_5N, 0 = TMS)

C atom	Compound			C atom	Compound		
	1	**2**	**2***		**1**	**2**	**2***
1	32.20	32.20	32.22	26	28.76	22.93	22.96
2	29.35	29.03	28.97	27	27.95	25.64	25.67
3	88.59	88.52	88.56	28	19.92	19.74	19.78
4	42.66	42.66	42.69	29	28.72	28.54	28.42
5	52.66	52.44	52.49	30	16.59	16.59	16.63
6	79.28	79.28	79.28			*β*-D-Xyl*p*	
7	34.07	34.07	34.13	1	107.67	107.63	107.65
8	45.66	45.38	45.59	2	75.58	75.58	75.61
9	21.08	21.08	21.12	3	77.99	77.99	78.02
10	30.18	30.18	30.19	4	71.25	71.25	71.28[a]
11	26.20	26.18	26.22	5	67.04	67.04	67.06
12	33.93	33.46	33.50			6-*O*-*β*-D-Glc*p*	
13	45.93	45.26	45.30	1	105.01	105.01	105.02
14	46.51	45.53	45.45	2	75.18	75.58	75.61
15	46.68	46.15	46.19	3	78.54	78.54	78.16
16	74.13	73.53	73.57	4	71.66	71.66	71.91[a]
17	60.70	57.97	58.02	5	78.13	78.13	78.96
18	21.00	21.00	21.04	6	63.03	63.03	63.08
19	28.92	28.54	28.58		24-*O*-*β*-D-Glc*p*	25-*O*-*β*-D-Glc*p*	
20	78.62	87.18	87.22	1	100.67	98.89	98.93
21	28.76	27.74	27.77	2	74.24	75.30	75.22
22	26.67	35.07	35.10	3	78.54	78.54	78.56[b]
23	18.89	26.02	26.06	4	71.36	71.36	71.42
24	79.50	82.07	82.11	5	79.04	79.04	79.08[b]
25	74.62	78.62	78.65	6	63.11	62.74	62.80

Signals with the same chemical shifts in columns 1 and 2 are mutually overlapping; those denoted with the same letters, arbitrarily assigned. 2* are ^{13}C NMR spectra of astragaloside VII.

The PMR spectrum of the studied compound (see Experimental) showed signals for six anomeric protons at δ 4.83, 4.834, 4.88, 4.888, 4.894, and 5.04 as doublets with SSCC ^{3}J = 8 Hz. The ^{13}C NMR spectrum contained signals of six terminal monosaccharides (Table 1). The set of signals for the C atoms indicated that the carbon composition of these glycosides consisted of two D-xyloses and four D-glucoses. Therefore, the glycosides were trisdesmoside triosides including *β*-D-xylopyranose and *β*-D-glucopyranose in a 1:2 ratio. Analysis of the monosaccharide composition of the glycosides by GC confirmed this conclusion.

The chemical shifts for C-3 of δ 88.59 (88.52, chemical shifts of C atoms of **2** are given in parentheses), C-5 52.66 (52.44), and C-7 34.07 (34.07) in the ^{13}C NMR spectrum indicated that C-3 and C-6 in these glycosides were glycosylated [6, 7]. The set of signals at δ 73.53 (C-16), 87.18 (C-20), 82.07 (C-24), and 78.62 (C-25) defined the structural fragment of **2**, including the side chain, as 20*R*,24*S*-epoxy-16*β*,25-diol glycosylated at C-25. This was consistent with the signals of H-17 (2.43, d, ^{3}J = 8 Hz) and H-22 (2.77, q, J = 11 Hz) in the PMR spectrum of **2**. The D-glucose, the anomeric C atom of which resonated at δ 98.89, was located on C-25. Two other signals for anomeric C atoms at δ 107.63 and 105.01 belonged to D-xylopyranose and D-glucopyranose on C-3 and C-6, respectively [7].

Thus, the structure of **2** was identical to that of astragaloside VII, which is 20*R*,24*S*-epoxycycloartan-3*β*,6*α*,16*β*,25-tetraol 3-*O*-*β*-D-xylopyranoside-6,25-di-*O*-*β*-D-glucopyranoside [8, 9]. By using the spectrum of astragaloside VII, its signals were separated from those of the mixture and the PMR and ^{13}C NMR spectra of glycoside **1** were obtained.

Signals of tertiary C atoms bonded to an O atom in the J-modulated ^{13}C NMR spectrum of **1** were observed at δ 78.62 and 74.62 and belonged to C-20 and C-25. This indicated that a 20*R*,25-epoxy was present. A multiplet at δ 4.75 in the PMR spectrum and a doublet at δ 74.14 in the ^{13}C NMR spectrum of this same glycoside indicated that it contained a 16*β*-hydroxyl. A doublet for the resonance of H-17 at δ 2.09 confirmed this conclusion.

One of the H-22 protons in the PMR spectrum of **1** resonated at δ 2.98, like in spectra of cyclocephalogenin glycosides [6, 7]. This indicated that C-24 in **1** was singly bonded to an O atom and that C-24 had the *S*-configuration [7]. This C atom gave a signal at δ 79.50, proving that it was glycosylated. Atom C-24 of cyclodissectoside and cyclocanthoside F had a free hydroxyl and resonated in the ^{13}C NMR spectra at δ 68.77 and 68.84, respectively [6, 7]. In fact, the chemical shift of the anomeric C atom of a single D-glucopyranose is δ 100.67 and confirms that the hexose was located on C-24 [10].

Taking into account the chemical shifts of anomeric C atoms of the remaining monosaccharides, *β*-D-xylopyranose (δ 107.67) and *β*-D-glucopyranose (δ 105.01) [7], and biogenetic considerations that six cycloartane glycosides with a C-3 D-xylose, the C-1 atom of which resonates in the range δ 107.38-107.65 [2, 6], have been isolated from *A. dissectus*, it can be concluded that the pentose was located on C-3 and the hexose on C-6.

Thus, the new glycoside **1**, which we called cyclotrisectoside, was a trisdesmoside trioside of cyclocephalogenin with the structure 20*R*,25-epoxy-24*S*-cycloartan-3*β*,6*α*,16*β*,24-tetraol 3-*O*-*β*-D-xylopyranoside-6,24-di-*O*-*β*-D-glucopyranoside.

EXPERIMENTAL

General Comments. PMR and ^{13}C NMR spectra in deuteropyridine with TMS internal standard (δ, ppm) were obtained on a Bruker AM 400 spectrometer. ^{13}C NMR spectra were recorded with full suppression of C–H coupling and under J-modulation conditions. Spectra of **2** were recorded under analogous conditions on a UNITYplus400 instrument.

Isolation and Separation of *A. dissectus* Isoprenoids have been published [2]. After isolation of cyclocanthoside E, fractions containing a chromatographically homogeneous crystalline compound (1.03 g, 0.066%) that behaved like astragaloside VII (**2**) on TLC were accumulated. GC [11] showed that the glycosides contained D-glucose and D-xylose in a 1.00:0.44 ratio.

Cyclotrisectoside (1), $C_{47}H_{78}O_{19}$. PMR spectrum (400 MHz, C_5D_5N, δ, J/Hz, 0 = TMS): 0.05 and 0.51 (2H-19, d, $^2J = 4$), 0.87, 1.20, 1.34, 1.37. 1.47, 1.55, 1.99 (7 × CH_3, s), 2.09 (H-17, d, $^3J = 8$), 2.98 (H-22, td, $^3J_1 = {}^2J = 13$, $^3J_2 = 5$), 3.51 (H-3, dd, $^3J_1 = 12$, $^3J_2 = 4$), 4.75 (H-16, m), 4.834, 4.888, 4.894 (three anomeric protons, d, $^3J = 8$). Table 1 gives the ^{13}C NMR spectrum.

Astragaloside VII (2), $C_{47}H_{78}O_{19}$. PMR spectrum (400 MHz, C_5D_5N, δ, J/Hz, 0 = TMS): 0.16 and 0.56 (2H-19, d, $^2J = 4$), 0.90, 1.25, 1.32, 1.36, 1.40, 1.63, 2.02 (7 × CH_3, s), 2.43 (H-17, d, $^3J = 8$), 2.77 (H-22, q, $^2J = {}^3J_1 = {}^3J_2 = 11$), 3.50 (H-3, dd, $^3J_1 = 12$, $^3J_2 = 4$), 4.83 (H-1 of Xylp, d, $^3J = 8$), 4.85 (H-16, m), 4.88 (H-1 of Glcp on C-6, d, $^3J = 8$), 5.04 (H-1 of Glcp on C-25, d, $^3J = 8$). Table 1 gives the ^{13}C NMR spectrum.

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