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TRITERPENE GLYCOSIDES OF PLANTS OF THE *Astragalus* GENUS. IV. STRUCTURE OF CYCLOUNIFOLIOSIDE D FROM *Astragalus unifoliolatus*

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*The new cycloartane glycoside cyclounifolioside D (**1**) was isolated from roots of* Astragalus unifoliolatus *Bunge. The structure of 16-O-acetyl-24R-cycloartan-3β,6α,16β,24,25-pentaol 3-O-β-D-glucopyranoside was established using chemical transformations and spectral data.*

Key words: *Astragalus unifoliolatus*, triterpene glycoside, cycloartane, cyclounifolioside C, cyclounifolioside D, cycloasgenin C.

In continuation of studies of cycloartane triterpenoids and their glycosides, we isolated the new compound called cyclounifolioside D (**1**) from roots of *Astragalus unifoliolatus* Bunge (Leguminosae) [1-3].

The IR spectrum of **1** has absorption bands characteristic of hydroxyl, methylene, and ester groups at 3465, 3048, 1718, and 1273 cm^{-1}.

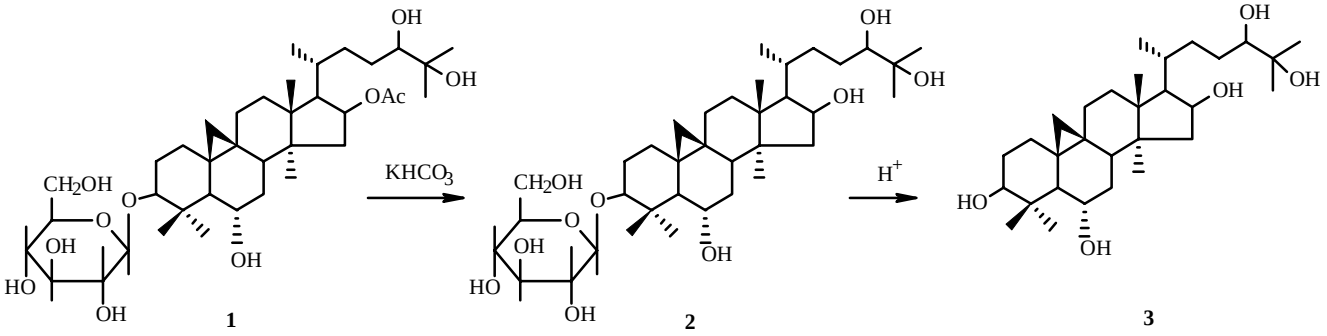
The PMR spectrum of **1** exhibits at strong field (0.57 and 0.25 ppm) 1H doublets of an AB system belonging to methylene H atoms of a cyclopropane ring and clearly visible peaks for resonances of seven methyls at 0.95, 1.05, 1.20, 1.37, 1.51, 1.54, and 2.01 ppm.

The C atoms C-9, C-10, and C-19 of the cyclopropane ring resonate in the ^{13}C NMR spectrum at 20.80, 28.66, and 29.08 ppm, respectively. Therefore, **1** is a cycloartane triterpenoid.

The PMR and ^{13}C NMR spectra of **1** contain one 3H singlet at 2.21 ppm and signals of C atoms at 21.21 and 170.6 ppm. These are consistent with the presence of one acetyl.

The PMR and ^{13}C NMR spectra of **1** exhibit signals of one anomeric proton at 4.99 ppm and one anomeric C atom at 106.68 ppm. These indicate that **1** is a monoside.

Alkaline hydrolysis of **1** produces **2**, identified as cyclounifolioside C [3].



1 **2** **3**

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TABLE 1. Chemical Shifts in PMR and ^{13}C NMR Spectra of Cyclounifolioside D (**1**), Cyclounifolioside C (**2**), and Cycloasgenin C (**3**), (δ, ppm, 0 = TMS, C_5D_5N)

Atom	Chemical shifts					
	1		**2**		**3**	
	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H
1	32.19	1.58; 1.15	32.16	1.57; 1.17	32.96	1.54; 1.13
2	29.74	2.49; 1.89	32.91	2.49; 1.87	31.36	2.49; 179
3	88.84	3.665	88.81	3.68	78.12	3.60
4	42.42	-	42.36	-	42.19	-
5	53.8	1.74	53.83	1.77	53.75	1.74
6	67.63	3.79	67.70	3.78	68.09	3.67
7	32.56	1.64; 1.62	38.16	1.59; 1.66	38.37	1.69; 1.67
8	45.68	1.836	46.76	1.847	47.02	1.84
9	20.89	-	21.02	-	21.05	-
10	28.66	-	29.91	-	30.16	-
11	25.97	1.81; 1.27	26.06	1.83; 1.24	26.13	1.86; 1.27
12	33.19	1.65; 1.39	32.91	1.68; 1.47	32.55	1.67; 1.39
13	46.82	-	45.45	-	45.48	-
14	45.68	-	46.64	-	46.69	-
15	46.51	2.12; 1.31	48.43	2.139; 1.28	48.54	2.19; 1.27
16	75.42	5.53	71.47	4.09	71.51	4.73
17	55.26	1.93	56.99	1.93	57.05	1.93
18	18.23	1.20	18.51	1.35	18.53	1.37
19	29.08	0.57; 0.25	29.14	0.56; 0.23	29.36	0.61; 0.34
20	31.59	1.94	31.35	1.98	31.86	1.98
21	18.33	1.04	18.69	1.12	18.85	1.12
22	33.95	2.09; 1.12	34.58	2.16; 1.13	31.18	2.06; 1.13
23	30.13	2.15; 1.46	29.70	2.16; 1.55	34.62	2.07; 1.54
24	79.18	3.68	80.29	3.69	80.31	3.81
25	72.59	-	72.46	-	72.49	-
26	25.74	2.01	25.62	2.01	25.65	1.89
27	25.68	1.54	25.86	1.52	25.88	1.52
28	19.76	0.95	19.95	1.04	20.03	1.04
29	27.41	1.51	28.66	1.49	29.18	1.49
30	16.51	1.37	16.44	1.40	15.89	1.40
Ac(16)	21.21; 170.6	2.21	-	-	-	-
			β-D-Glc*p*(1→3)Agl			
1	106.68	4.99	106.66	4.99	-	-
2	75.69	4.08	75.66	4.08	-	-
3	78.50	4.26	78.48	4.26	-	-
4	71.66	4.22	71.61	4.23	-	-
5	77.93	3.97	77.89	3.97	-	-
6	62.83	4.58; 4.40	62.79	4.579; 4.40	-	-

The acetyl group replaces the C-16 hydroxyl of the aglycon according to a correlation peak found in the ROESY spectrum for coupling of the CH_3 with chemical shift 2.21 ppm and H-23. The presence of the C-16 acetyl also explains the weak-field shift of H-16 (5.53 ppm) (Table 1).

Acid hydrolysis of compound **2** produced genin **3**, identified as cycloasgenin C [2, 3]. Paper chromatography (PC) of the hydrolysate detected D-glucose by comparison with authentic samples.

The anomeric proton of D-glucose resonates at 4.99 ppm as a doublet with spin—spin coupling constant ^{3}J = 7.2 Hz

and indicates that the monosaccharide has the pyranose form, $^4C_1$-conformation, and β-configuration.

The signal of C-3 in the ^{13}C NMR spectrum of compound **1** is significantly (+10.72 ppm) shifted to weak field compared with signals of cycloasgenin C (**3**) and resonates at 88.84 ppm. This unambiguously defines the attachment site of β-D-glucopyranose as C-3.

Thus, the structure 16-O-acetyl-24*R*-cycloart-3β,6α,16β-24,25-pentaol 3-O-β-D-glucoyranoside is established for cyclounifolioside D (**1**).

EXPERIMENTAL

For general comments, see the literature [1].

Separation of the Ethylacetate Fraction. The ethylacetate fraction was chromatographed over a silica-gel column with elution by $CHCl_3$—CH_3OH—H_2O (9:1:0.05) to afford 1.38 mg (0.0063%) of **1**.

Cyclounifolioside D (1). $C_{38}H_{64}O_{11}$, mp 171-173°C (MeOH), $[\alpha]_D$ 36°, IR spectrum (KBr, ν, cm^{-1}): 3465 (OH), 3048 (cyclopropane ring), 1718 and 1273 (ester).

Table 1 lists the PMR and ^{13}C NMR spectra.

Alkaline Hydrolysis of Cyclounifolioside D (1). Compound **1** (80 mg) was saponified by $KHCO_3$ (25 mL, 0.5%). The reaction mixture was left at room temperature for 1 d, diluted with water, neutralized by acetic acid, and extracted with butanol. The solid obtained after removal of butanol was chromatographed over a silica-gel column with elution by $CHCl_3$—CH_3OH (4:1) to afford **2**, identified by TLC as cyclounifolioside C.

Acid Hydrolysis of 2. Compound **2** (10 mg) was hydrolyzed by methanolic H_2SO_4 (5 mL, 0.5 %) at 70°C for 1 h, cooled, and diluted with water. The methanol was distilled off. The resulting solid was filtered off to afford **3**, identified as cycloasgenin C.

D-Glucose was detected in the hydrolysate by PC and comparison with authentic samples.

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