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TRITERPENE GLYCOSIDES OF *Zygophyllum eichwaldii*. III. STRUCTURE OF ZYGOEICHWALOSIDE G

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The new triterpene glycoside zygoeichwaloside G was isolated from the roots of Zygophyllum eichwaldii *C.A.M. by column chromatography. Acid hydrolysis and PMR and* ^{13}*C NMR spectroscopy using two-dimensional COSY, TOCSY, and HSQC and analysis of HMBC and ROESY spectra established that glycoside G is 19-α-hydroxyursolic acid 3-O-α-L-(2-O-sulfo)-arabinopyranoside.*

Key words: *Zygophyllum eichwaldii* C.A.M., triterpene glycoside, zygoeichwaloside G, 19-*α*-hydroxyursolic acid, pomolic acid 3-O-*α*-*L*-(2-O-sulfo)-arabinopyranoside.

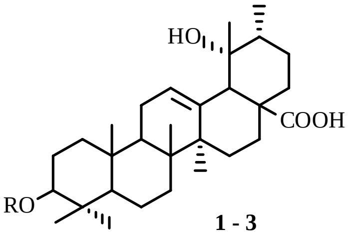
In continuation of studies of triterpene glycosides of *Zygopyllum eichwaldii* C.A.M. (Zygophyllaceae) [1, 2], we isolated the glycoside zygoeichwaloside G (**1**) by column chromatography.

Acid hydrolysis decomposes **1** into pomolic acid (**2**) and arabinose.

The ^{13}C NMR spectrum contains 35 different signals, indicating that **1** is a monoside. This conclusion is confirmed by the presence of signals for anomeric H (5.16 ppm) and carbon (103.59 pm) atoms in the PMR and ^{13}C NMR, respectively. The C atom of the COOH appears at 180.68 ppm, indicating that it is free. Arabinose is bound to one of the hydroxyls in the genin. The genin part of the ^{13}C NMR spectrum of **1** contains a signal at 89.41 ppm that belongs to C-3 and indicates that the hydroxyl on this C atom is glycosylated. Therefore, arabinose is located on the C-3 hydroxyl of pomolic acid.

HMBC and ROESY spectra confirm this conclusion. A correlation in them is seen between the anomeric proton (H-1) of arabinose and C-3 and H-3 of the aglycon. The spin—spin coupling constant (5 Hz) corresponds to the *α*-configuration for the glycoside.

The same structure was found for glycoside C (**3**), which we isolated earlier from the plant. Comparison of the PMR and ^{13}C NMR spectra of **1** and **3** shows that they have the same aglycon. However, the chemical shifts of the protons and C atoms belonging to arabinose differ significantly (Table 1).



1 - 3

1: R = *α*–L-2-O-SO_3H-Ara*p*;
2: R = H;
3: R = α-*L*-Ara*p*

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

Atom	Compound				Atom	Compound			
	1		**3**			**1**		**3**	
	^{13}C	^{1}H	^{13}C	^{1}H		^{13}C	^{1}H	^{13}C	^{1}H
1	38.72	1.48; 0.84	38.52	1.53; 0.96	19	72.75	4.96(OH)	72.41	5.10(OH)
2	26.28	2.05; 1.78	26.38	2.19; 1.92	20	42.40	1.50	42.08	1.53
3	89.41	3.23	88.48	3.35	21	26.97	2.10; 1.35	26.65	2.10; 1.33
4	39.47	-	39.26	-	22	38.52	2.16; 2.05	38.22	2.19; 2.13
5	55.82	0.77	55.64	0.86	23	27.19	1.30	27.95	1.29
6	18.65	1.47; 1.27	18.34	1.53; 1.32	24	16.79	1.03	16.60	0.97
7	33.54	1.55; 1.32	33.23	1.76; 1.37	25	15.46	0.82	15.23	0.89
8	40.37	-	40.07	-	26	17.19	1.06	16.89	1.10
9	47.67	1.76	47.42	1.85	27	24.71	1.73	24.40	1.76
10	37.00	-	36.72	-	28	180.68	-	180.36	-
11	24.03	2.04; 1.96	23.71	2.09; 2.09	29	28.35	1.44	26.86	1.46
12	128.05	5.58	127.73	5.61	30	16.90	1.13	16.48	1.14
13	139.99	-	139.65	-		α-L-Ara*p*			
14	42.133	-	41.81	-	1′	103.59	5.16	107.23	4.78
15	29.31	2.32; 1.28	29.02	2.34; 1.33	2′	77.68	5.40	72.63	4.45
16	26.44	3.14; 2.06	26.10	3.17; 2.1	3′	73.08	4.55	74.34	4.18
17	48.33	-	48.00	-	4′	67.58	4.37	69.23	4.34
18	54.65	3.05	54.31	3.07	5′	68.91	4.29; 3.79	66.43	4.34; 3.84

The two-dimensional methods COSY, TOCSY, and HSQC established that arabinose has in the 2-position a substituent that does not contain C atoms. However, it is rather electronegative. This causes characteristic shifts of the signals for C-1 and C-3 of the sugar. Based on the magnitude of the shifts compared with the unsubstituted unit, we think that the substituent is an SO_3H group [2]. This was confirmed by mass spectrometry. The electrospray mass spectrum exhibits a peak for a molecular ion with *m/z* 683.7, which corresponds with $C_{35}H_{56}O_{11}S$.

Thus, zygoeichwaloside G is the new compound 19-α-hydroxyursolic (pomolic) acid 3-O-α-*L*-(2-O-sulfo)-arabinopyranoside

EXPERIMENTAL

For general comments, see the literature [2].

Mass spectra were recorded in a Finnigan LCQ electrospray instrument.

Isolation of Zygoeichwaloside G (1). Fractions enriched in **1** were rechromatographed over a KSK silica-gel column using $CHCl_3$—CH_3OH—H_2O 65:28:5. Yield 20 mg of amorphous compound.

Acid Hydrolysis. Compound **1** (5 mg) was hydrolyzed by H_2SO_4 (5%) at 95°C for 1 h and cooled. Extraction of the hydrolysate with $CHCl_3$ afforded the genin, which was identified by TLC using $CHCl_3$—C_2H_5OH (25:1) as pomolic acid (19-α-hydroxyursolic acid). Arabinose was detected in the aqueous layer by TLC using BuOH—MeOH—H_2O (5:3:1) after neutralization by $BaCO_3$ and evaporation to the minimal volume.

REFERENCES

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