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A New Triterpenoid Saponin from *Aralia subcapitata*

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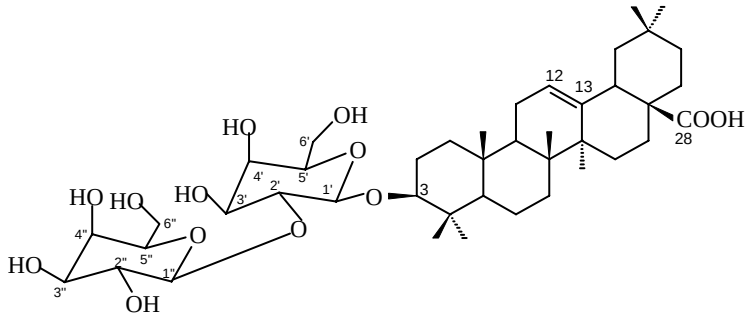
Abstract: A new oleanane-type saponin, named subcapitatoside **A**, has been isolated from the roots of *Aralia subcapitata*. On the basis of chemical and spectral evidence, the structure of subcapitatoside **A** has been established as: 3-O-β-D-galactopyranosyl-(1→2)-β-D-galacto-pyranosyl oleanolic acid.

Key words: *Aralia subcapitata*, oleanane-type saponin, subcapitatoside **A**.

The plants of *Aralia* genus are used as folk medicines for rheumathism, hepatitis and bruise in China [1]. *Aralia subcapitata* Hoo is distributed in Anhui Province of China and also used for the treatment of diabetes. Yang *et al.* [2] reported the isolation of four known triterpenoids from this plant. In this paper, we report the structural elucidation of a new triterpenoid saponin, subcapitatoside **A**, isolated from the roots of this plant.

Figure 1: structure of compound **1**



Subcapitatoside **A** (**1**)**,** an amorphous powder, $[\alpha]_D^{25}$ +40.3 (c 0.23, MeOH), has a molecular formula $C_{42}H_{68}O_{13}$ determined from its ESI-MS(*m/z* 803 $[M+Na]^+$), ^{13}C NMR and DEPT data. The IR absorption bands at 3407 (OH), 1693 (C=O) and 1633cm^{-1} (C=C) were observed. The ^{1}HNMR (δ 0.91, 1.04, 1.08, 1.09, 1.17, 1.39, 1.40, each s, CH_3×7; 5.56 t-like, 1H, olefinic proton; 3.38 m, 1H, CH) and ^{13}CNMR data (**Table 1**) of **1** indicated that the aglycone was oleanolic acid [3]. The disaccharide nature of **1** was manifested by its ^{1}H (δ 4.95 d, J=7.5Hz; 5.18 d, J=7.6Hz) and ^{13}C (δ 105.5, 107.4) NMR

data. On acid hydrolysis, **1** gave D-galactose and oleanolic acid. In the amplified ^{1}HNMR spectrum of **1**, four proton signals (δ 4.63 d, J=2.3; 4.31 dd, J=9.5, 2.3; 4.99 d, J=2.6; 4.16 dd, J=9.5, 2.6) further suggested the presence of two D-galactoses. The chemical shifts of C_3 (δ 89.0) and C_{28} (δ 180.3) revealed that **1** was a monodesmosidic glycoside at C-3 of the aglycone. The identity of the monosaccharide and the sequence of the disaccharide chain were determined by a combination of ^{1}HNMR, ^{13}CNMR, DEPT and 2D-NMR experiments. Starting from the anomeric proton of each sugar unit, the hydrogens within each spin system were delineated using ^{1}H-^{1}HCOSY with the aid of TOCSY. On the basis of the assigned protons, the ^{13}C resonances of each sugar unit were identified by HMQC and further confirmed by HMBC experiments. In the light of the assigned ^{1}H and ^{13}CNMR spectra (**Table 1**), the two galactoses units were identified as pyranoses [4]. The β-anomeric configurations for the sugars were determined from their $^{3}J_{H1H2}$ coupling constants (7-8Hz, **Table 1**). In the 2D-NOESY spectrum, cross peaks were observed between H_3 (δ 3.38) and $H_{1'}$ (δ 4.95), $H_{2'}$ (δ 4.69) and $H_{1''}$ (δ 5.18). The HMBC spectrum showed correlations between C_3 (δ 89.0) and $H_{1'}$ (δ 4.95), $C_{2'}$ (δ 83.2) and $H_{1''}$ (δ 5.18). Thus, subcapitatoside **A** (**1)** was determined to be 3-O-β-D-galactopyranosyl- (1→2) -β-D-galactopyranosyl oleanolic acid (**Figure 1**).

Table 1: ^{13}CNMR data of **1** and ^{1}HNMR (C_5D_5N, δ in ppm, J in Hz) data of sugar moieties of **1**

NO	δ_C		NO	δ_C		NO	δ_C		δ_H	
1	38.9	t	16	23.9	t	1’	105.5	d	4.95	d, 7.5
2	26.9	t	17	46.9	s	2’	83.2	d	4.69	m
3	89.0	d	18	42.2	d	3’	75.6	d	4.31	dd, 9.5, 2.3
4	39.8	s	19	46.7	t	4’	70.0	d	4.63	d, 2.3
5	56.1	d	20	31.1	s	5’	76.6	d	4.12	m
6	18.7	t	21	34.4	t	6’	62.4	t	4.48	m, 4.54 m
7	33.4	t	22	33.4	t	1’’	107.4	d	5.18	d, 7.6
8	39.9	s	23	28.4	q	2’’	74.8	d	4.65	m
9	48.2	d	24	17.0	q	3’’	75.3	d	4.16	dd, 9.5, 2.6
10	37.1	s	25	15.7	q	4’’	69.9	d	4.99	d, 2.6
11	23.9	t	26	17.6	q	5’’	77.0	d	4.01	m
12	122.7	d	27	26.4	q	6’’	61.3	t	4.41	m, 4.44 m
13	145.0	s	28	180.3	s					
14	42.3	s	29	33.4	q					
15	28.5	t	30	23.9	q					

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