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Segetoside L, A New Triterpenoid Saponin from *Vaccaria segetalis*

Zeng Hua XIA, Min Liang ZOU, Sheng Min SANG, Ai Na LAO*

Institute of Materia Medica, Shanghai Institutes for Biological Sciences,
Chinese Academy of Sciences, Shanghai 200031

Abstract: A new triterpenoid saponin, named segetoside L, was isolated from the seeds of *Vaccaria segetalis*. On the basis of spectral data and chemical reaction, its structure was established as 28-O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl oleanolic acid 3-O-β-D-glucopyranosyl-(1→3)-[β-D-galactopyranosyl-(1→2)]-β-D-galactopyranoside.

Keywords: *Vaccaria segetalis*, caryophyllaceae, oleanolic acid-type saponin, segetoside L.

Vaccaria segetalis (Neck.) Garcke (caryophyllaceae) is widely distributed in China. The seeds of this plant, Wangbu Liuxing, are used for promoting diuresis, activating blood circulation in traditional Chinese folk medicine[1]. Previously, we have reported the isolation and structural elucidation of segetoside A[2], C[3], D-E[4], F[5], G-I[6], and K[7] from the seeds of *Vaccaria segetalis*. In our continuing investigation of this seeds, a new triterpenoid saponin, named segetoside L, was isolated. This paper deals with the isolation and structural elucidation of segetoside L **1**.

Segetoside L **1** was isolated from the seeds of *Vaccaria segetalis* as the methods described before[2-7].

Segetoside L **1**, a white amorphous powder, had a molecular formula $C_{60}H_{98}O_{28}$, determined from its ESI-MS (at *m/z* 1289 $[M+Na]^+$), ^{13}C NMR and DEPT data. Its spectral features and physicochemical properties suggested **1** to be a triterpenoid saponin. Of the 60 carbons, 30 were assigned to the aglycone part, 30 to the oligosaccharide moiety. The IR absorption bands at 3417 (OH), 1731 (C=O) and 1641cm^{-1} (C=C) were observed. Comparison of the ^{1}HNMR [δ 0.92, 0.95, 0.96, 1.14, 1.19, 1.32, 1.35 (each s, 3H); 5.49, (t-like, 1H)] and the ^{13}CNMR of **1** with those of subcapitatoside B **2** (**Table 1**), isolated from *Aralia subcapitata*[8] in our laboratory, indicated that the aglycone, oleanolic acid, and the sequence of oligosaccharide at C-3 of **1** were the same as those of **2** (**Figure 1**). The pentasaccharide nature of **1** was manifested by its ^{1}HNMR (δ 4.86, d, J=8.2Hz; 5.10, d, J=7.7Hz; 5.37, d, J=7.9Hz; 5.51, d, J=7.6Hz; 6.34, d, J=8.0Hz) and ^{13}CNMR (δ 95.8, 105.1, 105.2, 105.4, 105.5) data. Alkaline hydrolysis of **1** gave a prosaponin, subcapitatoside B **2**, and sugar fraction. Acid hydrolysis of the sugar fraction only gave glucose. Acid hydrolysis of **1** afforded glucose, galactose and oleanolic acid. All

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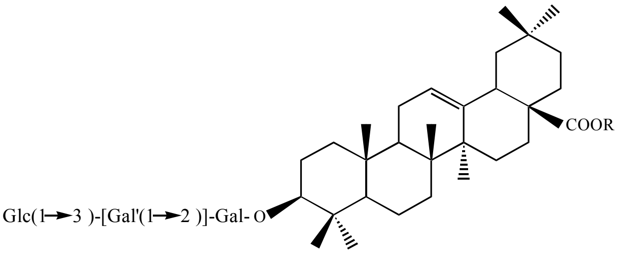
* E-mail: anlao@mail.shcnc.ac.cn

Figure 1 Structures of **1** and **2**



1 R=Glc' (1→6)Glc'' **2** R=H

Table 1 ^{13}CNMR data of **1** and **2,** and ^{1}HNMR data for sugar units of **1** and **2** (C_5D_5N, δ in ppm, J in Hz).

	1	**2**		**1**		**2**	
aglycone	δ_C	δ_C		δ_C	δ_H	δ_C	δ_H
1	38.9 t	38.9 t	C-3 sugars				
2	26.7 t	26.8 t	Gal-1	105.5	4.86, d, (8.2)	105.6	4.88, d, (7.8)
3	89.4 d	89.5 d	2	77.8	4.82, m	77.8	4.83, m
4	39.8 s	39.8 s	3	84.8	4.35, m	84.8	4.37, m
5	56.1 d	56.1 d	4	69.8	4.84, brs	69.8	4.86, brs
6	18.7 t	18.7 t	5	76.2	4.05, m	76.2	4.06, m
7	33.3 t	33.3 t	6	62.5	4.38, m; 4.46, m	62.5	4.46, m; 4.54, m
8	40.0 s	40.0 s	Gal'-1	105.1	5.51, d, (7.6)	105.0	5.50, d, (7.5)
9	48.1 d	48.2 d	2	73.8	4.56, m	73.8	4.56, m
10	37.1 s	37.1 s	3	75.6	4.16, m	75.6	4.18, m
11	23.5 t	23.6 t	4	69.9	4.64, brs	69.9	4.66, brs
12	123.2 d	123.0 d	5	76.4	3.84, m	76.4	3.83, m
13	144.3 s	144.3 s	6	61.6	4.33, m; 4.50, m	61.7	4.35, m; 4.52, m
14	42.3 s	42.3 s	Glc-1	105.2	5.37, d, (7.9)	105.3	5.37, d, (7.6)
15	28.3 t	28.5 t	2	75.5	4.04, m	75.5	4.08, m
16	23.8 t	24.0 t	3	78.5	4.29, m	78.5	4.29, m
17	47.2 s	47.2 s	4	71.7	4.21, m	71.7	4.29, m
18	41.8 d	41.8 d	5	78.6	3.95, m	78.4	3.95, m
19	46.4 t	46.5 t	6	62.6	4.35, m; 4.51, m	62.6	4.35, m; 4.52, m
20	31.3 s	30.9 s	C-28 sugars				
21	34.5 t	34.2 t	Glc'-1	95.8	6.34, d, (8.0)		
22	32.7 t	32.7 t	2	74.0	4.20, m		
24	16.9 q	16.9 q	3	78.9	4.29, m		
25	15.7 q	15.8 q	4	71.1	4.38, m		
26	17.6 q	17.7 q	5	78.1	4.16, m		
27	26.2 q	26.3 q	6	69.6	4.43, m; 4.79,m		
28	176.7 s	176.7 s	Glc''-1	105.4	5.10, d, (7.7)		
29	33.7 q	33.3 q	2	75.3	3.92, m		
30	23.8 q	23.8 q	3	78.6	4.05, m		
			4	71.7	4.21, m		
			5	78.5	3.92, m		
			6	62.8	4.37, m; 4.53,m		

these further suggested that the sequence of oligosaccharide at C-3 of **1** was Glc(1→3)-[Gal'(1→2)]-Gal-. The sugar units at C-28 of **1** should be two glucoses (Glc' and Glc"). Finally, the identity of the monosaccharide and the sequence of oligosaccharide were determined by a combination of ^{1}H-^{1}HCOSY, TOCSY, HMQC and HMBC. In the light of the assigned ^{1}H and ^{13}CNMR data (**Table 1**), the five sugars were identified as pyranose. The β-anomeric configurations of the sugars were judged from their $^3J_{H1\text{-}H2}$ coupling constants (7-9Hz). From the HMBC spectrum we could see that C-3 (δ 89.4) of aglycone with H-1 (δ 4.86) of Gal; C-2 (δ 77.8) of Gal with H-1 (δ 5.51) of Gal', C-3 (δ 84.8) of Gal with H-1 (δ 5.38) of Glc; C-28 (δ 176.7) of aglycone with H-1 (δ 6.31) of Glc' and C-6 (δ 69.6) of Glc' with H-1 (δ 5.08) of Glc" had cross peaks. Thus, segetoside L **1** was determined as: 28-O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl oleanolic acid 3-O-β-D-glucopyranosyl-(1→3)-[β-D-galactopyranosyl-(1→2)]-β-D-galactopyranoside.

The aglycones of triterpenoid saponins isolated from *Vaccaria segetalis* have quillaic acid[4]; gypsogenin[5]; gypsogenic acid[3]; 3, 4-secogypsogenic acid[9]; and olean-12-ene-23, 28-dioic acid 3β, 16α-dihydroxy[7]. It is well known that oleanolic acid is a common aglycone of saponins isolated from many plants, but the oleanolic acid-type saponins have not been isolated from *Vaccaria segetalis* so far. Segetoside L **1** reported here was the first example. It is interesting in chemotaxonomy.

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