Chinese Chemical Letters Vol. 11, No. 1, pp. 49–53, 2000

A New Triterpenoid Saponin from the Seeds of *Vaccaria segetalis*

Sheng Min SANG[1], Min Liang ZOU[1], Ai Na LAO[1]*, Zhong Liang CHEN[1], Jun UZAWA[2], and Yasuo FUJIMOTO[3]

[1]Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 200031
[2]The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan
[3]College of Pharmacy, Nihon University, 7-7-1 Narashinodai, Funabashi, Chiba 274-8555, Japan

Abstract: A new triterpenoid saponin, named segetoside **k**, has been isolated from the seeds of *Vaccaria segetalis*. On the basis of chemical reaction and spectral analysis, the structure of segetoside K was established as: olean-12-ene-23α , 28β-dioic acid 3β, 16α-dihydroxy-28-O-[β-D-glucopyranosyl-(1→3)]-β-D-glucopyra-nosyl-(1→2)-β-D-glucopyrano syl-(1→6)-β-D-gluco-pyranoside(**1**).

Keywords: *Vaccaria segetalis*, Triterpenoid saponin, Segetoside **K**.

The seeds of *Vaccaria segetalis* (Neck) Garcke, which is distributed all over China, except southern China, are used in Chinese folk medicine for promoting diuresis, activating blood circulation and relieving carbuncles [1]. Previous studies on the seeds of this plant have led to the isolation of seven cyclic peptides [2-5] and several saponins [6-10]. We have reported the isolation and structural elucidation of Segetosides **A, C-E** from the seeds of *Vaccaria segetalis* [11-13]. Further investigation of the seeds led to the isolation of a new triterpenoid saponin, named Segetoside **K (1)**.

The *n*-butanol fraction from the ethanolic extract of the seeds of *Vaccaria segetalis* was chromatographed on Diaion HP-20, silica gel (CH_2Cl_2-MeOH-H_2O 2.5:1:0.15) and RP-18 silica gel (70% MeOH) to afford segetoside **K**

Segetoside **K,** an amorphous solid, $[\alpha]_D^{24}$ –20.53 (c 0.28, MeOH), had a molecular formula of $C_{54}H_{86}O_{26}$ determined by ESIMS (at *m/z* 1174 $[M+Na]^+$) as well as ^{13}C and DEPT NMR data. Its spectral features and physicochemical properties suggested **1** to be a triterpenoid saponin. Its IR spectrum showed characteristic absorptions for hydroxyl (3400cm^{-1}), ester (1726cm^{-1}) and a glycosidic linkage (1000-1100cm^{-1}). The ^{1}HNMR spectrum showed the signals of six methyl groups at δ 1.01, 1.10, 1.12, 1.19, 1.69, 1.82 ppm, and one olefinic proton at δ 5.59ppm. The ^{13}CNMR spectroscopic data revealed six methyl groups at δ 12.4, 16.4, 17.6, 24.0, 27.3, 33.3 ppm, a pair of olefinic carbon

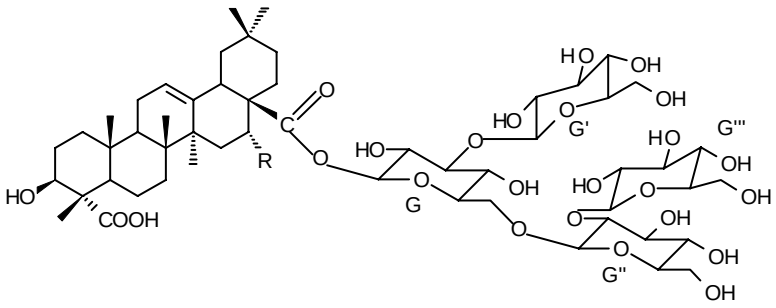
Table 1 ^{13}CNMR data of compounds **1**、**2**，and **3**, and ^{1}HNMR data of the sugar part of **1** (C_5D_5N, δ in ppm, J in Hz)

aglycon moiety				sugar moiety			
position	1	2	3	position	1		2
1	39.4 t	39.0 t	39.2 t		δ_C	δ_H	δ_C
2	28.0 t	27.7 t	26.2 t	G			
3	75.7 d	75.5 d	75.6 d	1	95.2 d	6.21 d, 7.7	94.8 d
4	54.6 s	54.3 s	54.4 s	2	73.3 d	4.29 m	73.1 d
5	52.2 d	51.8 d	52.0 d	3	88.2 d	4.32 m	87.9 d
6	21.9 t	21.6 t	21.8 t	4	69.4 d	4.35 m	69.1 d
7	33.4 t	32.9 t	33.3 t	5	77.0 d	4.18 m	76.8 d
8	40.6 s	40.2 s	40.4 s	6	69.1 t	4.35 m	68.8 t
9	47.7 d	48.3 d	42.6 d			4.56 m	
10	37.0 s	36.8 s	37.0 s	G’			
11	24.0 t	23.8 t	23.9 t	1	106.0 d	5.38 d, 7.9	105.6 d
12	122.8 d		123.0 d	2	75.8 d	4.13 m	75.5 d
13	144.5 s	144.0 s	145.3 s	3	78.3 d	4.22 m	78.0 d
14	42.2 s	42.0 s	42.2 s	4	71.4 d	4.23 m	71.2 d
15	36.2 t	28.2 t	36.2 t	5	78.6 d	3.99 m	78.3 d
16	74.2 d	23.1 d	74.7 d	6	62.6 t	4.52 m	62.4 t
17	49.2 s	46.9 s	49.0 s			4.61 m	
18	41.4 d	41.6 d	41.5 d	G’’			
19	47.3 t	46.1 t	47.3 t	1	102.8 d	4.97 d, 7.7	102.5 d
20	30.9 s	30.6 s	31.0 s	2	83.8 d	4.11 m	83.5 d
21	36.0 t	33.8 t	36.2 t	3	78.1 d	4.33 m	77.9 d
22	32.2 t	32.2 t	32.7 t	4	71.0 d	4.23 m	70.8 d
23	180.8 s	180.8 s	180.6 s	5	78.5 d	3.85 m	78.2 d
24	12.4 q	12.3 q	12.3 q	6	62.3 t	4.45 m	62.1 t
25	16.4 q	16.0 q	16.2 q			4.49 m	
26	17.6 q	17.3 q	17.5 q	G’’’			
27	27.3 q	26.0 q	27.3 q	1	106.0 d	5.37 d, 7.7	105.6 d
28	176.0 s	176.3 s	180.8 s	2	76.5 d	4.13 m	76.2 d
29	33.3 q	33.0 q	33.4 q	3	78.1 d	4.22 m	77.9 d
30	24.0 q	23.6 q	24.8 q	4	71.3 d	4.23 m	71.0 d
				5	78.7 d	3.99 m	78.4 d
				6	62.5 t	4.36 m	62.3 t
						4.40 m	

atoms at δ 122.8 and 144.5ppm, and two carbonyl carbons at δ 176.0 and 180.7 ppm. All these proved that the aglycon of **1** was an oleanic acid triterpene. Comparison of the signals from the aglycon moiety of **1** in the ^{13}CNMR spectra with those from compound **3** (olean-12-ene-23α，28β-dioic acid 3β，16α-dihydroxy) [14] showed that the aglycon

moiety of **1** was the same as **3** (**Table 1**). Acid hydrolysis of **1** produced sugar components identified as all D-glucose. The β anomeric configurations for the glucoses were judged from their large $^{3}J_{H1,H2}$ coupling constants (7-8Hz). Comparing the ^{13}CNMR signals of the sugar part of **1** with those of vaccaroside **A** (**2**) which has been isolated from this plant[10,12] revealed that **1** has the same sugar part as those of **2**. Moreover, from the HMBC spectrum of compound **1**, cross peaks were observed between C_{28} (δ 176.0) and H_{G1} (δ 6.21), C_{G3} (δ 88.2) and $H_{G'1}$ (δ 5.38), C_{G6} (δ 69.1) and $H_{G''1}$ (δ 4.97), and $C_{G''2}$ (δ 83.8) and $H_{G'''1}$ (δ 5.37). These results further confirmed that the sugar chain was located at C-28 of the sapogenin. Thus, segetoside **K** was determined to be: olean-12-ene-23α, 28β-dioic acid 3β, 16α-dihydroxy-28-O-[β-D-glucopyranosyl-(1→3)]-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside(**1**).

Figure 1 Segetoside **K** (**1**): R=OH,Vaccaroid **A** (**2**) : R=H



References

1. Jiangsu New Medical College, *Zhong-yao-da-ci-dian*, Shanghai Science and Technology Publisher, **1986**, p, 311.
2. H. Morita, Y.S. Yun, and H. Itokawa, *Tetrahedron*, **1995**, *51*(21), 5987.
3. H. Morita, Y.S. Yun, and H. Itokawa, *Tetrahedron*, **1995**, *51*(21), 6003.
4. H. Morita, Y.S. Yun, and H. Itokawa, *Phytochemistry*, **1996**, *42*(2), 439.
5. Y.S. Yun, H. Morita, and H. Itokawa, *J. Nat. Prod.*,**1997**, *60*(3), 216.
6. V.I. Litvinenko, K. Amanmuradov, and N.K. Abubakirov, *Khim. Prir. Soed*.**1967**, *3*(2), 159.
7. K. Amanmuradov, N.K. Abubakirov, *Khim. Geol. Nauk*.,**1964**, *6*(1), 104.
8. H. Morita, Y.S. Yun, and H. Itokawa, *Bioorg. Med. Chem. Letters*, **1997**, *7*(8), 1095.
9. Y.S. Yun, K. Shimizu, H. Morita, and K. Takeya, *Phytochemistry*, **1998**, *47*(1), 143-144.
10. K. Koike, Z. H. Jia, and T. Nikaido, *Phytochemistry*, **1998**, *47* (7), 1343.
11. S. M. Sang, A. N. Lao, H. C. Wang, Z. L. Chen, J. Uzawa, and Y. Fujimoto, *Phytochemistry*, **1998**, *48* (3), 569.

12. S. M. Sang, A. N. Lao, H. C. Wang, Z. L. Chen, J. Uzawa, and Y. Fujimoto, *J. Asian. Nat. Prod. Res.* , **1999**, *1* (3) , 199.
13. S. M. Sang, A. N. Lao, H. C. Wang, Z. L. Chen, J. Uzawa, and Y. Fujimoto, *Nat. Prod. Sci.* , **1998**, *4* (4) , 268.
14. H. Y. Li, K. Koike, *J. Nat. Prod.* , **1993**, *56* (6), 1065

Received 6 July 1999