Pergamon

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A PHENYLPROPANOID GLYCOSIDE FROM *VACCARIA SEGETALIS*

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Key Word Index—*Vaccaria segetalis*; Caryophyllaceae; phenylpropanoid glycoside; segetoside A.

Abstract—A new phenylpropanoid glycoside, named segetoside A, and a known compound, allantoin, have been isolated from the seeds of *Vaccaria segetalis*. On the basis of chemical and spectral data, the structure of segetoside A has been established as α-D-(6-*O*-dihydroferuloyl)glucopyranosyl(1 → 2)-β-D-fructofuranoside.
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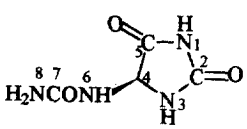
INTRODUCTION

The seeds of *Vaccaria segetalis* V. wolf, a plant 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 have led to the isolation of five cyclic peptides [2–4] and several saponins [5, 6]. From this source, we have isolated the known compound allantoin (**1**) and a new phenylpropanoid glycoside, named segetoside A (**2**).



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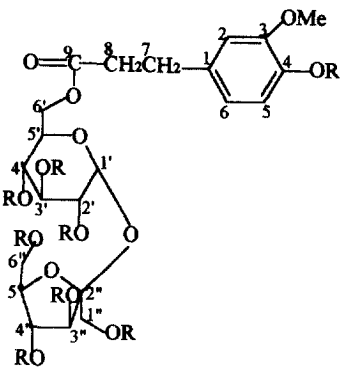
RESULTS AND DISCUSSION

Dried and powdered seeds of *V. segetalis* yielded the phenylpropanoid glycoside (**2**) and allantoin (**1**).

Compound **1** was identified as allantoin by comparing its spectral data (^{1}H- and ^{13}C-NMR) directly. This is the first time that allantoin has been isolated from this plant.

Compound **2** was assigned the molecular formula $C_{22}H_{32}O_{14}$ (FAB-MS, $[M+H]^+ = m/z$ 521). The IR spectrum showed absorption bands due to hydroxyl (3391 cm^{-1}) and ester (1724 cm^{-1}) groups, and aromatic rings (1603, 1518, 993 cm^{-1}). The ^{1}H NMR spectrum of **2** (Table 1) contained the signals for one methoxyl group (δ 3.87, 3H, *s*), three aromatic protons (δ 7.02, 1H, *d*, J = 1.5 Hz; δ 7.23, 1H, *d*, J = 7.9 Hz; and δ 6.91, 1H, *dd*, J = 7.9; 1.5 Hz), and four methylene protons (δ 3.04, 2H, *t*, J = 7.5 Hz, and δ 2.84, 2H, *t*, J = 7.5 Hz), suggesting that **2** contained one dihydroferuloyl moiety. Fourteen proton signals aground δ_H 4.0–6.2 and assignable to methine and methylene and 12 carbon signals around δ_C 65–106, suggested the presence of a disaccharide moiety, most probably sucrose in view of the characteristic doublet



2 R=H

3 R=Ac

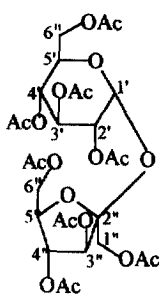


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Table 1. ^{1}H NMR spectral data of compounds **2** (C_5D_5N) and **3** ($CDCl_3$) (500 MHz)

H	2	3
Dihydroferuloyl		
2	7.02 (1H, *d*, *J** = 1.5)	6.84 (1H, *d*, *J* = 1.3)
3-OMe	3.87 (3H, *s*)	3.81 (3H, *s*)
5	7.23 (1H, *d*, *J* = 7.9)	9.93 (1H, *d*, *J* = 8.2)
6	6.91 (1H, *dd*, *J* = 6.9; 1.5)	6.79 (1H, *dd*, *J* = 8.2; 1.3)
7	3.04 (2H, *t*, *J* = 7.5)	2.94 (2H, *t*, *J* = 7.6 Hz)
8	2.84 (2H, *t*, *J* = 7.5)	2.70 (2H, *m*)
Glucose		
1′	6.23 (1H, *d*, *J* = 3.6)	5.67 (1H, *d*, *J* = 3.7)
2′	4.25 (1H, *dd*, *J* = 3.7; 9.5)	4.86 (1H, *dd*, *J* = 3.6; 8.6)
3′	4.77 (1H, *t*, *J* = 9.6)	5.45 (1H, *m*)
4′	4.16 (1H, *t*, *J* = 9.4)	5.07 (1H, *t*, *J* = 9.7)
5′	4.95 (1H, *m*)	4.29 (1H, *m*)
6′	4.82 (1H, *dd*, *J* = 5.7; 11.7)	4.16 (1H, *m*)
	5.06 (1H, *m*)	4.29 (1H, *m*)
Fructose		
1″	4.39 (1H, *d*, *J* = 11.9)	4.15–4.22 (2H, *m*)
	4.44 (1H, *d*, *J* = 11.9)	
3″	5.20 (1H, *m*)	5.44 (1H, *m*)
4″	5.30 (1H, *m*)	5.36 (1H, *t*, *J* = 5.8)
5″	4.61 (1H, *m*)	4.20 (1H, *m*)
6″	4.56 (1H, *dd*, *J* = 6.0; 12.0)	4.27 (1H, *m*)
	4.47 (1H, *dd*, *J* = 2.9; 12.0)	4.37 (1H, *dd*, *J* = 9.8; 4.5)

* *J* in Hz.

signal with a small coupling constant at δ_H 6.23 (1H, *d*, *J* = 3.6 Hz) assignable to the anomeric proton in the α-D-glucopyranose unit [7, 8].

Acetylation of **2** and sucrose with acetic anhydride in pyridine at room temperature afforded the peracetyl derivatives **3** and **4**. On comparing the ^{13}C NMR spectra of **3** and **4** (Table 2), the presence of sucrose in **2** was confirmed. The position of the linkage of the dihydroferuloyl and the sucrose unit was assigned by HMBC. In the HMBC spectrum of **2**, correlations between the H_2-6′ (δ_H 4.82; 5.06) of the glucose unit and the carbonyl carbon (δ_C 173.2) of the dihydroferuloyl group, were observed, so the dihydroferuloyl group was located at C-6′ of glucose. Based on these spectroscopic data and chemical evidence, compound **2** was determined to be α-D-(6-*O*-dihydroferuloyl)glucopyranosyl(1 → 2)-β-D-fructofuranoside, named segetoside A. The assignments of the protons and carbons of **2** (Tables 1 and 2) were based on the results of its DQFCOSY, HMQC, HMBC, and total correlation spectroscopy (TOCSY).

Table 2. ^{13}C NMR spectral data of **2** (C_5D_5N), **3** ($CDCl_3$) and **4** ($CDCl_3$) (425 MHz)

C	2	3	4
Dihydroferuloyl			
1	132.2 *s*	139.4 *s*	
2	112.7 *d*	120.4 *d*	
3	148.6 *s*	150.8 *s*	
3-OMe	55.9 *q*	55.8 *q*	
4	146.6 *s*	138.1 *s*	
5	116.5 *d*	122.6 *d*	
6	121.4 *d*	112.6 *d*	
7	30.9 *t*	30.5 *t*	
8	36.6 *t*	35.3 *t*	
9	173.2 *s*	172.4 *s*	
Glucose			
1′	93.4 *d*	89.9 *d*	89.9 *d*
2′	73.3 *d*	70.3 *d*	70.2 *d*
3′	74.9 *d*	69.6 *d*	69.6 *d*
4′	71.8 *d*	68.1 *d*	68.1 *d*
5′	71.7 *d*	68.5 *d*	68.4 *d*
6′	64.8 *t*	61.7 *t*	61.7 *t*
Fructose			
1″	64.8 *t*	62.8 *t*	62.8 *t*
2″	105.8 *s*	104.1 *s*	103.9 *s*
3″	79.7 *d*	75.7 *d*	75.6 *d*
4″	75.9 *d*	75.0 *d*	74.9 *d*
5″	84.5 *d*	79.1 *d*	79.1 *d*
6″	63.6 *t*	63.6 *t*	63.5 *t*

EXPERIMENTAL

General

CC: silica gel 60H and TLC (HSGF254) (Qingdao Haiyang Chemical Group Co. of China); ^{1}H (500 Hz, 600 Hz) and ^{13}C (125 Hz, 150 Hz) NMR: JEOL GSX-

500 with NM-EFG type field gradient unit and JEOL α600 with NM-AFG type field gradient unit, TMS as int. standard. FAB-MS: MAT-95 Mass spectrometer.

Plant material

The seeds of *Vaccaria segetalis* were purchased at Shijia Zhuang, Herbei Province (China) in 1994. The botanical identification was made by Xuesheng Bao (Shanghai Institute of Drug Control). A voucher specimen has been deposited at the Herbarium of the Department of Phytochemistry, Shanghai Institute of Materia Medica, Chinese Academy of Sciences.

Extraction and isolation

The powdered seeds of *V. segetalis* (50 kg) were extracted successively with petrol and 95% EtOH. After evaporation of the EtOH *in vacuo*, the residue was suspended in water and then extracted successively with CH_2Cl_2, EtOAc and *n*-BuOH. The EtOAc fraction (10 g) was subjected to silica gel CC using a CH_2Cl_2–MeOH gradient system (1:0–0:1). The fraction eluted by 20% MeOH was subjected to silica gel CC with a CH_2Cl_2–MeOH–H_2O (4:1:0.1) solvent system to give compound **2** (40 mg) and **1** (200 mg). Compound **2** was further purified by Sephadex LH-20 CC eluted by 90% EtOH.

Compound **1**. Needles, mp 232–35°. HR-MS *m/z*: 158.0446 $[M]^+$, $C_4H_6O_3N_4$ requires: 158.1152; EI-MS *m/z*: 158 $[M]^+$ (47), 130 (55), 87 (81), 60 (100); IR ν_{max}^{KBr} cm^{-1}: 3438, 1780, 1712, 1655, 1529, 1431, 1327, 1016; ^1H NMR (600 MHz, DMSO): δ 5.24 (1H, *d*, $J = 8.2$ Hz, H-4), 5.78 (1H, *s*, H-8), 6.89 (1H, *d*, $J = 8.2$ Hz, H-6), 8.04 (1H, *s*, H-3), 10.54 (1H, *s*, H-1); ^{13}C NMR (150 MHz, DMSO): δ 173.4 (*s*, C-5), 157.21 (*s*, C-7), 156.6 (*s*, C-2), 62.2 (*d*, C-4).

Compound **2**. Oil, $[\alpha]_D^{24}$ +38.21° (MeOH, *c* 0.56). IR ν_{max}^{KBr} cm^{-1}: 3391, 1724, 1604, 1518, 1275, 1051, 993; ^1H NMR (500 MHz, C_5D_5N) and ^{13}C NMR (125 MHz, C_5D_5N): Tables 1 and 2, respectively; FAB-MS *m/z*: 521 $[M+H]^+$ (5), 358 (9), 341 (13), 323 $(M-H-$dihydroferuloyl$]^+$ (8), 259 (3), 196 (3), 179 (10), 137 (18), 93 (100).

Acetylation of **2** *and sucrose*. Each (5 mg) was dissolved in pyridine (0.2 ml) and treated with excess Ac_2O (0.2 ml) at room temp. overnight; then the product was poured into iced water and extracted with $CHCl_3$ to give compounds **3** and **4**, respectively.

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