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## Journal of Asian Natural Products Research

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713454007>

### Two new sucrose esters from *Sparganium stoloniferum*

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Online publication date: 27 July 2010

**To cite this Article** Xiong, Ying , Deng, Ke-Zhong , Guo, Yuan-Qiang , Gao, Wen-Yuan and Zhang, Tie-Jun(2008) 'Two new sucrose esters from *Sparganium stoloniferum*', Journal of Asian Natural Products Research, 10: 5, 425 — 428

**To link to this Article:** DOI: 10.1080/10286020801892334

**URL:** <http://dx.doi.org/10.1080/10286020801892334>

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## Two new sucrose esters from *Sparganium stoloniferum*

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(Received 29 August 2007; final version received 28 November 2007)

Two new sucrose esters,  $\beta$ -D-(1-*O*-acetyl-3-*O*-*trans*-feruloyl)fructofuranosyl- $\alpha$ -D-2',4',6'-*O*-triacylglucopyranoside (**1**) and  $\beta$ -D-(1-*O*-acetyl-3-*O*-*trans*-feruloyl)fructofuranosyl- $\alpha$ -D-2',3',6'-*O*-triacylglucopyranoside (**2**), together with two known sucrose esters have been isolated from *Sparganium stoloniferum*. Their structures were elucidated by spectroscopic methods.

**Keywords:** *Sparganium stoloniferum*; Sparganiaceae; rhizome; sucrose esters

### 1. Introduction

*Sparganium stoloniferum* Buch.-Hamil. (Sparganiaceae) is a plant of monotype genus and has been used as an emmenagogue, a galactagogue, and an antispasmodic agent in Chinese folk medicine for a long time.<sup>1</sup> Previous phytochemical investigations on the crude drug revealed phenylpropanoid glycosides.<sup>2,3</sup> During our search for bioactive compounds from Chinese herbal medicine, we investigated the constituents of the rhizomes of *S. stoloniferum* with the isolation of two new sucrose esters,  $\beta$ -D-(1-*O*-acetyl-3-*O*-*trans*-feruloyl)fructofuranosyl- $\alpha$ -D-2',4',6'-*O*-triacylglucopyranoside (**1**) and  $\beta$ -D-(1-*O*-acetyl-3-*O*-*trans*-feruloyl)fructofuranosyl- $\alpha$ -D-2',3',6'-*O*-triacylglucopyranoside (**2**), and two known sucrose esters,  $\beta$ -D-(1-*O*-acetyl-3,6-*O*-*trans*-diferuloyl)fructofuranosyl- $\alpha$ -D-2',4',6'-*O*-triacylglucopyranoside (**3**) and  $\beta$ -D-(1-*O*-acetyl-3,6-*O*-*trans*-diferuloyl)fructofuranosyl- $\alpha$ -D-2',3',6'-*O*-triacylglucopyranoside (**4**). Herein, we report the isolation and structural elucidation of the new compounds.

### 2. Results and discussion

Compound **1** was obtained as a colourless amorphous solid,  $[\alpha]_D^{25} + 50.0$  (*c* 0.1, CHCl<sub>3</sub>). Its HR-ESI-MS showed  $[M + Na]^+$  at *m/z* 709.1941, corresponding to the molecular formula C<sub>30</sub>H<sub>38</sub>O<sub>18</sub>. The IR spectrum showed absorption bands of hydroxyl (3459 cm<sup>-1</sup>), ester carbonyl (1745 cm<sup>-1</sup>), and aromatic rings (1631, 1595, and 1515 cm<sup>-1</sup>). The <sup>1</sup>H and <sup>13</sup>C NMR spectra (Table 1), extensively analyzed with the aid of <sup>1</sup>H–<sup>1</sup>H COSY and HSQC experiments, exhibited proton signals characteristic of an *E*-feruloyl moiety [three aromatic proton signals at  $\delta_H$  7.11 (1H, dd, *J* = 1.6, 8.4 Hz), 7.09 (1H, d, *J* = 1.6 Hz), and 6.91 (1H, d, *J* = 8.4 Hz) as an ABX-type system, one methoxy group signal at  $\delta_H$  3.94 (3H, s) and one *trans*-double bond signals at  $\delta_H$  7.70 and 6.34 (each 1H, d, *J* = 16.0 Hz)]. Additionally, 12 carbon signals ( $\delta_C$  60.5–102.9) were assumed to be D-sucrose by <sup>1</sup>H NMR and TOCSY spectra. The sugar was further identified by acid hydrolysis and compared with the authentic samples (Sigma,

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Table 1.  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  (100 MHz) NMR spectral data of compounds **1** and **2** ( $\text{CDCl}_3$ ,  $\delta$  ppm,  $J$  Hz).

No.	<b>1</b>		<b>2</b>	
	$\delta_{\text{H}}$	$\delta_{\text{C}}$	$\delta_{\text{H}}$	$\delta_{\text{C}}$
1	4.10, 4.21 (2H, d, 11.6)	64.7	4.08, 4.15 (2H, d, 11.6)	64.3
2		102.9		102.8
3	5.31 (1H, d, 7.6)	79.6	5.34 (1H, d, 8.0)	79.3
4	4.55 (1H, t, 7.6)	71.8	4.56 (1H, t, 8.0)	71.6
5	3.96 (1H, m)	83.0	3.90 (1H, m)	82.9
6	3.73, 3.89 (2H, dd, 12.4, 2.8)	60.5	3.73, 3.86 (2H, d, 12.4)	60.4
1-OAc	1.99 (3H, s)	170.2, 20.6	2.05 (3H, s)	170.3, 20.6
1'	5.64 (1H, d, 3.6)	89.8	5.62 (1H, d, 3.6)	89.8
2'	4.76 (1H, dd, 10.0, 3.6)	72.9	4.83 (1H, dd, 3.6, 10.4)	70.2
3'	4.00 (1H, t, 9.6)	69.6	5.29 (1H, t, 9.6)	71.9
4'	4.93 (1H, t, 9.6)	70.4	3.55 (1H, t, 9.6)	68.7
5'	Overlap	68.7	Overlap	71.2
6'	4.13, 4.17 (2H, d, 12.4)	61.7	4.30, 4.46 (2H, dd, 12.4, 3.6)	62.3
2'-OAc	2.14 (3H, s)	171.5, 21.0	2.08 (3H, s)	170.9, 20.7
3'-OAc			2.08 (3H, s)	171.2, 20.7
4'-OAc	2.05 (3H, s)	170.7, 20.7		
6'-OAc	2.12 (3H, s)	170.8, 20.7	2.10 (3H, s)	171.8, 20.8
1''		126.4		126.5
2''	7.09 (1H, d, 1.6)	109.6	7.13 (1H, br s)	110.0
3''		147.3		146.9
4''		148.7		148.5
5''	6.91 (1H, d, 8.4)	114.9	6.90 (1H, d, 8.4)	114.8
6''	7.11 (1H, dd, 8.4, 1.6)	123.7	7.12 (1H, dd, 8.4, 2.0)	123.6
7''	7.70 (1H, d, 16.0)	147.0	7.69 (1H, d, 16.0)	147.3
8''	6.34 (1H, d, 16.0)	113.4	6.37 (1H, d, 16.0)	113.5
9''		167.3		167.6
OCH <sub>3</sub>	3.94 (3H, s)	56.0	3.92 (3H, s)	56.0

St. Louis, USA 99%) on TLC. Furthermore,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra revealed the presence of four acetyl groups [ $\delta_{\text{H}}$  1.99 (3H, s), 2.05 (3H, s), 2.12 (3H, s), 2.14 (3H, s);  $\delta_{\text{C}}$  20.6, 20.7, 20.7, 21.0, 170.2, 170.7, 170.8, 171.5] located in the sucrose moiety. In the HMBC spectrum (Figure 1) of **1**, the cross-peak between the signal of H-3 of fructosyl group at  $\delta_{\text{H}}$  5.31 and the carbon signal at  $\delta_{\text{C}}$  167.3 assigned to C-9 of *trans*-feruloyl group indicated that the *trans*-feruloyl group was linked to C-3 of the fructosyl group. Also, the cross-peaks between the signals of H-2' ( $\delta_{\text{H}}$  4.76), H-4' ( $\delta_{\text{H}}$  4.93), and H-6' ( $\delta_{\text{H}}$  4.13 and 4.17) of the glucosyl group and the three acetyl carbonyl carbon signals at  $\delta_{\text{C}}$  171.5, 170.7, and 170.8, respectively, and the signal of H-1 ( $\delta_{\text{H}}$  4.10 and 4.21) and one acetyl carbonyl carbon signal at  $\delta_{\text{C}}$  170.2, indicated

that four acetyl groups were located at C-2', C-4', and C-6' of the glucosyl group, and C-1 of the fructosyl group, respectively. These data confirmed the structure of compound **1** as  $\beta$ -D-(1-*O*-acetyl-3-*O*-*trans*-feruloyl)fructofuranosyl- $\alpha$ -D-2',4',6'-*O*-triacylglucopyranoside.

Compound **2** was also isolated as a colourless amorphous solid,  $[\alpha]_{\text{D}}^{25} + 57.1$  ( $c$  0.07,  $\text{CHCl}_3$ ). Its molecular formula was determined as  $\text{C}_{30}\text{H}_{38}\text{O}_{18}$  by HR-ESI-MS at  $m/z$  709.1952  $[\text{M} + \text{Na}]^+$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Table 1) of compound **2** showed that its structure was similar to that of **1**, except for the position of the acetyl groups. In the HMBC spectrum (Figure 1) of **2**, the correlated signals of H-1 ( $\delta_{\text{H}}$  4.08 and 4.15)/C=O (170.3), H-2' ( $\delta_{\text{H}}$  4.83)/C=O (170.9), H-3' ( $\delta_{\text{H}}$  5.29)/C=O (171.2), and

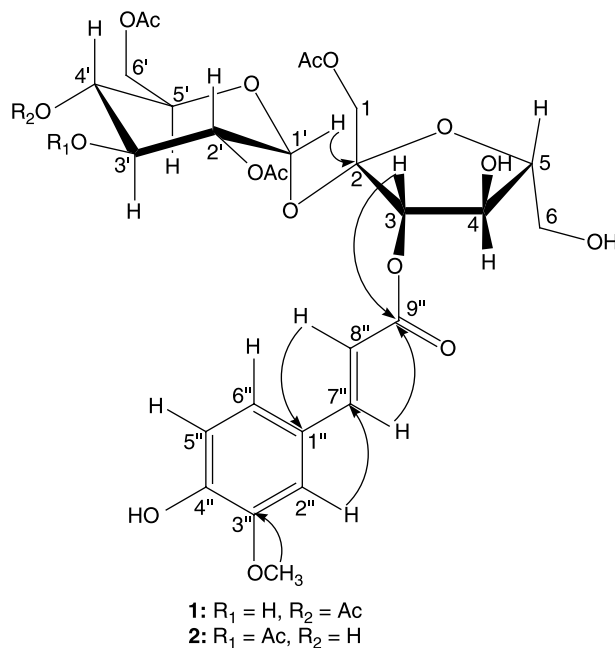


Figure 1. Structures and key HMBC (H → C) correlations of compounds **1** and **2**.

H-6' ( $\delta_{\text{H}}$  4.30 and 4.46)/C=O (171.8) indicated that the four acetyl groups were located at C-1 of the fructosyl group, and C-2', C-3', and C-6' of the glucosyl group, respectively. Consequently, the structure of compound **2** was elucidated to be  $\beta$ -D-(1-*O*-acetyl-3-*O*-*trans*-feruloyl)fructofuranosyl- $\alpha$ -D-2',3',6'-*O*-triacylglucopyranoside.

Compounds **3** and **4** were obtained as colourless amorphous solids and identified by the comparison of their spectral and physical data with those described in the literature.<sup>3</sup>

### 3. Experimental

#### 3.1 General experimental procedures

Optical rotations were measured on a WZZ-3 automatic polarimeter. IR spectra were obtained using a Bio-Rad FTS 6000 infrared spectrometer. HR-ESI-MS spectra were obtained using an Ionspec 7.0 T FTICR MS. 1D and 2D NMR spectra were recorded on a Bruker AVANCE-400 (400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C) NMR spectrometer using TMS as the internal standard. Preparative

HPLC was carried out on an ODS column (25 × 2 cm i.d., YMC) with a JASCO RI-1530 intelligent refractive index detector. For column chromatography, silica gel (200–300 mesh, Qingdao Ocean Chemical Group Co., Qingdao, China) and Sephadex LH-20 (Merck Co., Dr Whitehouse Station, NJ, USA) were used; for TLC, silica gel GF254 (Qingdao Ocean Chemical Group Co.) was used.

#### 3.2 Plant material

The rhizome of *S. stoloniferum* was purchased from Chinese Materia Medica Market in the Anguo city of Hebei Province, China and was identified by Professor Wen-Yuan Gao (Tianjin University, China). A voucher specimen (No. 200518) has been deposited with the School of Pharmaceutical Science and Technology, Tianjin University, China.

#### 3.3 Extraction and isolation

The rhizomes of *S. stoloniferum* (20 kg) were powdered and subsequently extracted with 95

and 65% EtOH under reflux and filtered. After removal of the solvent under reduced pressure, the residue (850 g) was suspended in water and partitioned with light petroleum ether and  $\text{CHCl}_3$  successively. The  $\text{CHCl}_3$  extract (70 g) was chromatographed on a silica gel column and eluted with a gradient of  $\text{CHCl}_3/\text{MeOH}$  (1:0  $\rightarrow$  0:1, V/V) to give 16 fractions. Fraction 10 (3 g) was separated by preparative HPLC on an ODS column with  $\text{MeOH}/\text{H}_2\text{O}$  (5:5) as mobile phase and purified on a Sephadex LH-20 column eluted with  $\text{CHCl}_3/\text{MeOH}$  (1:1, V/V) to yield compounds **1** (35 mg) and **2** (19 mg). Similarly, fraction 9 (5 g) was separated by preparative HPLC on an ODS column with  $\text{MeOH}/\text{H}_2\text{O}$  (6:4) as the mobile phase and purified on a Sephadex LH-20 column eluted with  $\text{CHCl}_3/\text{MeOH}$  (1:1, V/V) to yield compounds **3** (100 mg) and **4** (28 mg).

### 3.3.1 $\beta$ -D-(1-O-Acetyl-3-O-trans-feruloyl)fructofuranosyl- $\alpha$ -D-2',4',6'-O-triacetylglucopyranoside (**1**)

Colourless amorphous solid;  $[\alpha]_{\text{D}}^{25} + 50.0$  (c 0.1,  $\text{CHCl}_3$ ); IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 3459, 1745, 1631, 1595, 1515, 1431, 1372, 1238, 1160, 1042;  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectral data are shown in Table 1; positive HR-ESI-MS  $m/z$  709.1941  $[\text{M} + \text{Na}]^+$  (calcd for  $\text{C}_{30}\text{H}_{38}\text{O}_{18}\text{Na}$ , 709.1956).

### 3.3.2 $\beta$ -D-(1-O-Acetyl-3-O-trans-feruloyl)fructofuranosyl- $\alpha$ -D-2',3',6'-O-triacetylglucopyranoside (**2**)

Colorless amorphous solid;  $[\alpha]_{\text{D}}^{25} + 51.7$  (c 0.07,  $\text{CHCl}_3$ ); IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 3454, 1743, 1631, 1595, 1516, 1431, 1371, 1241, 1160, 1048;  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectral data are shown in Table 1; positive HR-ESI-MS  $m/z$  709.1952  $[\text{M} + \text{Na}]^+$  (calcd for  $\text{C}_{30}\text{H}_{38}\text{O}_{18}\text{Na}$ , 709.1956).

### 3.3.3 Acid hydrolysis of **1** and **2**

Each sucrose ester sample (5 mg) was refluxed with 5% HCl (5 ml) in methanol for 2 h. The reaction mixture was neutralized with 3% KOH/MeOH and was subjected to a Sephadex LH-20 column using MeOH as eluant. The fractions containing sugars were examined with authentic samples using silica gel TLC successively developed with  $\text{CHCl}_3/\text{MeOH}/\text{H}_2\text{O}$  (7:3:0.6) and EtOAc/MeOH/ $\text{H}_2\text{O}$ /acetic acid (6:2:1:1) and detected with aniline–diphenylamine–phosphoric acid reagent at 85°C.

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