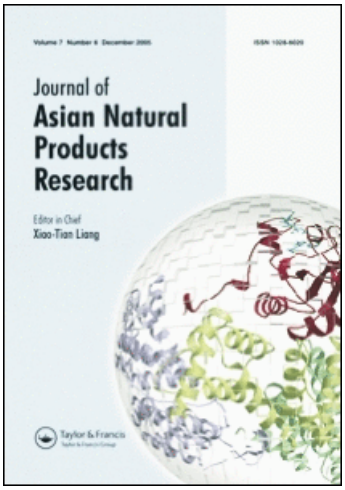

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Two new compounds from *Cynanchum amplexicaule*

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A new phenolic glycoside, sinapic acid 4-*O*-β-D-(6′-sinapoyl)glucopyranoside (**1**) and a new sucrose ester, 6,6′-di-*O*-sinapoylsurcose (**3**), were isolated from the roots of *Cynanchum amplexicaule* (Sieb. et Zucc.), along with two known compounds, 6-*O*-[*E*]-sinapoyl-D-glucopyranoside (**2**) and sibricose A_1 (**4**). Their structures were elucidated on the basis of both chemical and spectroscopic methods.

Keywords: *Cynanchum amplexicaule* (Sieb. et Zucc.); 6,6′-Di-*O*-sinapoylsurcose; sinapic acid 4-*O*-β-D-(6′-sinapoyl)glucopyranoside; 6-*O*-[*E*]-sinapoyl-D-glucopyranoside; sibricose A_1

1. Introduction

Cynanchum amplexicaule (Sieb. et Zucc.) is widely distributed in China and used as a Chinese folk medicine for the treatment of rheumatoid arthritis, hectic fevers and abscesses. Earlier phytochemical investigation of this plant had led to the isolation of two C-21 steroids.[1] In this paper, we report the isolation and structure elucidation of two new compounds and two known compounds from this plant.

2. Results and discussion

Compound **1** was obtained as a white amorphous powder. Its molecular formula was determined to be $C_{28}H_{32}O_{14}$ by the $[M + Na]^+$ ion peak at *m/z* 615.1673 in the HRESI-MS. The ^{1}H NMR spectrum of **1** showed four vinyl proton signals at δ 7.48 (1H, d, $J = 15.4$ Hz), 7.45 (1H, d, $J = 15.4$ Hz), 6.48 (1H, d, $J = 15.4$ Hz) and 6.45 (1H, d, $J = 15.4$ Hz), four aromatic proton signals at δ 6.98 (2H, s) and 6.97 (2H, s) and four methoxy group signals at δ 3.78 (6H, s) and 3.76 (6H, s), which were typical signals for two sinapoyl moieties.[2] The ^{13}C NMR spectrum showed the presence of two carbonyl carbons (δ 167.8, 166.6), 16 olefinic carbons (δ 152.9–106.3), and characteristic signals of a 1,6-disubstituted glucose (δ 102.7, 76.4, 74.1 × 2, 69.8, 63.3).[3] The relatively large *J* value (6.9 Hz) of the anomeric proton (δ 4.94) of glucose indicated that the anomeric configuration was β. The point of linkage of two sinapoyl moieties with the glucose was solved by analysis of the HMBC experiment, in which the cross peaks between H-1′ (δ 4.94) and C-4 (δ 136.0), H-6′ (δ 4.25 and 4.17) and C-9″ (δ 166.6) were observed. The structure of **1** was therefore elucidated as sinapic acid 4-*O*-β-D-(6′-sinapoyl)glucopyranoside (Figure 1).

Compound **3** was obtained as a white amorphous powder. Its molecular formula was determined to be $C_{34}H_{42}O_{19}$ by the $[M + Na]^+$ ion peak at *m/z* 777.2245 in the HRESI-MS. In the ^{1}H NMR spectrum of **3**, the low field region contained signals attributed to two sinapoyl moieties, including four vinyl proton signals at δ 7.58 (1H, d, $J = 15.4$ Hz), 7.50 (1H, d, $J = 15.4$ Hz), 6.57 (1H, d, $J = 15.4$ Hz) and 6.53 (1H, d, $J = 15.4$ Hz), four aromatic proton signals at δ 7.05 (2H, s) and 7.00 (2H, s) and four methoxy group signals at δ 3.78 (12H, s). The presence of two sinapoyl moieties was also supported by the ^{13}C NMR spectrum, which in the low field region had signals for two sinapoyl moieties at δ 166.8, 166.7, 148.1 × 4, 145.7 × 2, 138.4 × 2, 124.5 × 2, 114.7 × 2, and 106.3 × 4. Furthermore, the ^{13}C NMR spectrum showed 12 carbon signals arising from a disaccharide moiety. The two anomeric carbon signals at δ 104.2 and 91.6, and three methylene groups at δ 65.9, 64.4, 62.1 suggested that the disaccharide is sucrose,[4] which was finally confirmed by comparison with authentic sample using PC after alkaline hydrolysis (Figure 1). In the HMBC spectrum, the cross peaks between H-6 (δ 4.44 and 4.07) and C-9″ (δ 166.7), H-6″ (δ 4.44 and 4.30) and C-9‴ (δ 166.8) were observed. Thus, the structure of compound **3** was elucidated as 6,6′-di-*O*-sinapoylsurcose (Figure 2).

Spectral data for 6-*O*-[*E*]-sinapoyl-D-glucopyranoside (**2**) and sibricose A_1 (**4**) were in complete agreement with published data,[2,5] and **2** existed as an α,β-anomeric mixture (1:1) in solution.

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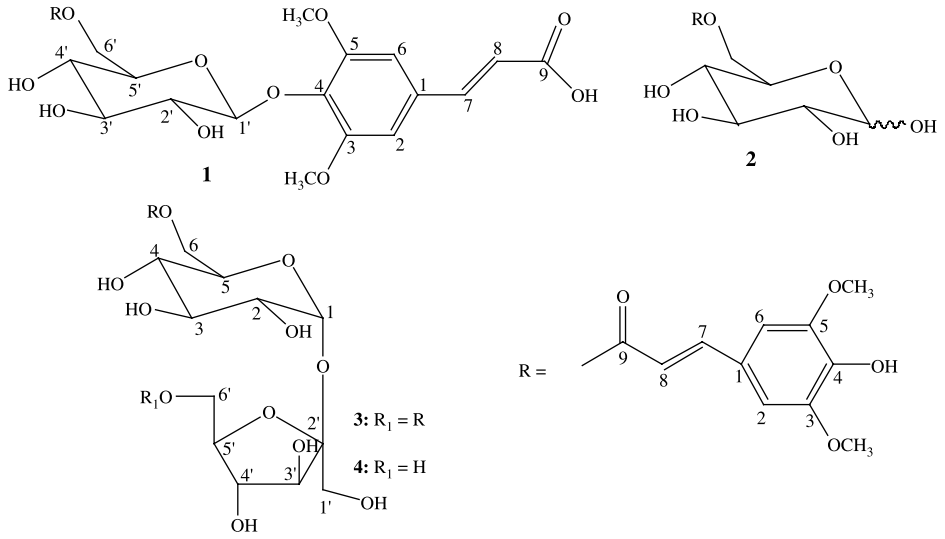

Figure 1. Structures of compounds **1**–**4**.

3. Experimental

3.1 General experimental procedures

Optical rotations were obtained in CH_3OH at 25°C, using a P-E 241 MC. Melting points were obtained by using a Yanaco MP-S3 micro melting point apparatus and are uncorrected. IR spectra were recorded on a NEXUS-470 spectrophotometer. UV spectra were obtained on a Hitachi 200-10 spectrophotometer. The NMR spectral data were recorded on Bruker AV-600 (600 MHz for ^1H and 150 MHz for ^{13}C) in DMSO-d6 with TMS as internal standard. The HRESI-MS data were obtained on a Micross Mass Autospec-Ultima ETOF spectrometer. Chromatography was performed on silica gel (200–300 mesh, Qingdao Haiyang Chemical Factory), Sephadex LH-20, and reversed-phase HPLC (Shimadzu LC-8A vp).

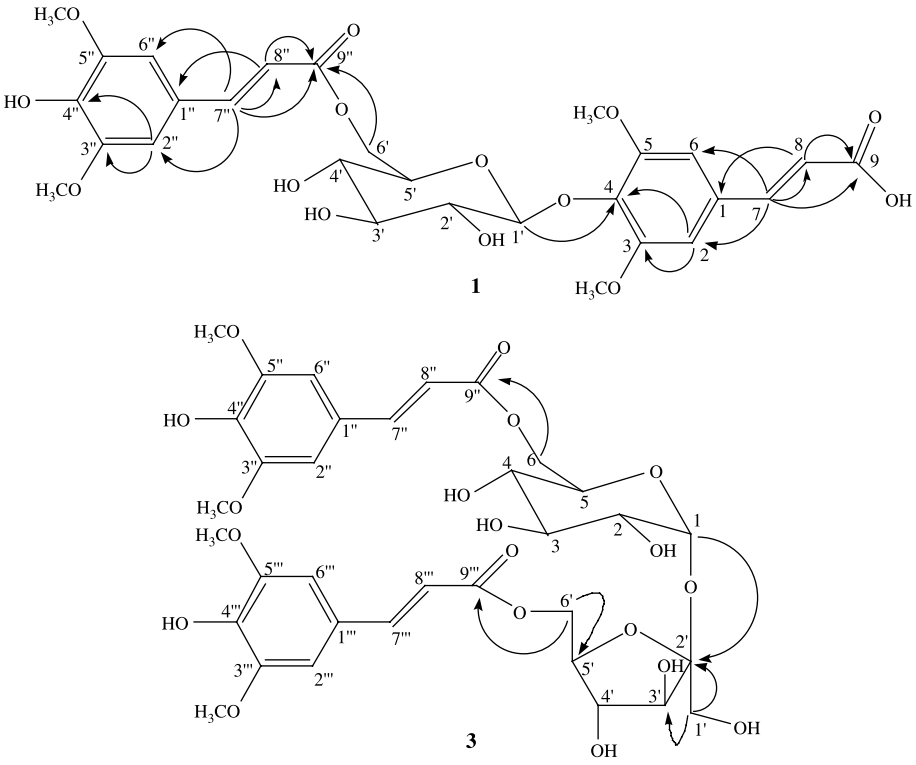

Figure 2. Key HMBC correlations of compounds **1** and **3**.

Table 1. NMR data of compounds **1** and **3** (600 MHz for ^{1}H, 150 MHz for ^{13}C)[a,b].

1			**2**		
Position	H (J, Hz)	C	Position	H (J, Hz)	C
1		130.1	1	5.18 (d, 3.3)	91.6
2	6.98 (s)	106.5	2	3.25 m	71.6
3		152.9	3	3.52 (t, 9.5)	72.8
4		136.0	4	3.08 (t, 9.5)	70.4
5		152.9	5	4.04[d]	70.6
6	6.98 (s)	106.5	6	4.44[e]	64.4
	7.45 (d, 15.4)	144.0		4.07[d]	
1′	6.48 (d, 15.4)	118.7	1′	3.40 (br. s)	62.1
2′		167.8	2′		104.2
3′	3.78 (s)	56.2	3′	3.94[f]	76.4
4′	4.95 (d, 6.9)	102.7	4′	3.93[f]	74.8
5′	3.27[c]	74.1	5′	3.83 (t, 9.5)	79.3
6′	3.26[c]	76.4	6′	4.44[e]	65.9
	3.25[c]	69.8		4.30 (dd, 9.5, 12.0)	
1″	3.36[c]	74.1	1″		124.5
2″	4.25 (d, 10.5)	63.3	2″	7.05 (s)[g]	106.3
3″	4.17 (dd, 6.0, 10.5)		3″		148.1
4″		124.4	4″		138.4
5″	6.97 (s)	106.3	5″		148.1
6″		148.1	6″	7.05 (s)[g]	106.3
7″		138.4	7″	7.58 (d, 15.4)[h]	145.7
8″		148.1	8″	6.57 (d, 15.4)[i]	114.7
9″	6.97 (s)	106.3	9″		166.7
1‴	7.48 (d, 15.4)	145.6	1‴		124.5
2‴	6.45 (d, 15.4)	114.7	2‴	7.00 (s)[g]	106.3
3‴		166.6	3‴		148.1
4‴	3.76 (s)	56.5	4‴		138.4
5‴			5‴		148.1
6‴			6‴	7.00 (s)[g]	106.3
7‴			7‴	7.50 (d, 15.4)[h]	145.7
8‴			8‴	6.53 (d, 15.4)[i]	114.7
9‴			9‴		166.8
—OMe × 4			—OMe × 4	3.78 (s)	56.1

[a] ppm from TMS, in DMSO-d6, room temperature.
[b] Assignments were confirmed by HSQC and HMBC experiments.
[c–f] Overlapping signals.
[g–i] The assignments were interchangeable for the shifts having the same superscript.

3.2 Plant material

The roots of *Cynanchum amplexicaule* were collected in August 2005 at Xinxiang, Henan province, China. A voucher specimen was identified by Professor Qishi Sun and has been deposited in the School of Traditional Chinese Materia Medica of Shenyang Pharmaceutical University (No. 6039).

3.3 Extraction and isolation

The roots (10 kg) of *C. amplexicaule* were extracted three times with hot 95% EtOH for 2 h, and the combined solution was concentrated *in vacuo* to give a syrup (1100 g), followed by suspension in water. The suspension was then extracted with petroleum ether, ethyl acetate, and *n*-butanol successively. The *n*-butanol fraction (252 g) was further fractionated by silica gel column chromatography (eluted with $CHCl_3$ and MeOH in increasing polarity) to obtain nine fractions (I–IX). Fraction III was purified by Sephadex LH-20 column chromatography eluted with MeOH to give compound **1** (20 mg). Fraction IV was chromatographed over silica gel eluted with $CHCl_3$/MeOH (10:1) to afford compound **2** (250 mg). Fraction VI was chromatographed over silica gel and further separated by preparative HPLC eluted with 42% aqueous MeOH to give compounds **3** (39 mg) and **4** (33 mg).

*3.3.1 Sinapic acid 4-O-β-D-(6′-sinapoyl)gluco-pyranoside (**1**)*

White amorphous powder, mp 159–161°C; $[\alpha]_D^{25}$ +75.9 (*c* 0.01, MeOH); UV (MeOH) λ_{max}: 234, 321 nm; IR (KBr) cm^{-1}: 3480, 2970, 1690, 1600, 1505, 1110, 970;

^{1}H NMR and ^{13}C NMR spectral data, see Table 1; HRESI-MS *m/z*: 615.1673 $[M + Na]^+$ (calcd for $C_{28}H_{32}O_{14}Na$, 615.1690).

3.3.2 6,6′-di-O-sinapoylsurcose (*3*)

White amorphous powder, mp 110–113°C; $[\alpha]_D^{25}$ −45.6 (*c* 0.01, MeOH); UV (MeOH) λ_{max}: 219, 280 nm; IR (KBr) cm^{-1}: 3520, 1710, 1605, 1510, 1150, 970; ^{1}H NMR and ^{13}C NMR spectral data, see Table 1; HRESI-MS *m/z*: 777.2245 $[M + Na]^+$ (calcd for $C_{34}H_{42}O_{19}Na$, 777.2218).

3.3.3 Alkaline hydrolysis of *3*

Compound **3** (10 mg) was dissolved in 0.5 M NH_4OH (5 ml) and the mixture was stirred at room temperature for 4 h. The solution was neutralised with 0.1 M HCl, and then partitioned between EtOAc and H_2O. Sinapic acid was detected from the EtOAc extract on TLC and sucrose was detected from the aqueous layer on PC, by direct comparison with authentic samples.

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