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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>

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To cite this Article Xiang, Wen-Sheng , Wang, Ji-Dong , Wang, Xiang-Jing and Zhang, Ji(2008) 'Two new components from *Gnetum pendulum*', Journal of Asian Natural Products Research, 10: 11, 1081 – 1085

To link to this Article: DOI: 10.1080/10286020802318958

URL: <http://dx.doi.org/10.1080/10286020802318958>

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Two new components from *Gnetum pendulum*

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(Received 25 February 2008; final version received 3 June 2008)

Two new compounds, 3-*O*-(13-hydroxy-9*Z*,11*E*,15*E*-octadecatrienoyl) cycloeucaleanol (**1**) and 24'-hydroxy-tetracosyl ferulate (**2**), together with one known compound, tetracosyl ferulate (**3**), were isolated from the dried stems of *Gnetum pendulum*. The two new compounds were structurally elucidated by spectroscopic and chemical methods.

Keywords: *Gnetum*; *Gnetum pendulum*; 3-*O*-(13-hydroxy-9*Z*,11*E*,15*E*-octadecatrienoyl) cycloeucaleanol; 24'-hydroxy-tetracosyl ferulate

1. Introduction

Various types of compounds with biological activities have been found from three Chinese *Gnetum* species, *Gnetum parvifolium* [1–5], *Gnetum montanum* [6–8], and *Gnetum hainanense* [9,10]. *Gnetum pendulum* belongs to *Gnetum* genus.

However, bioactive substances from *G. pendulum* have been studied less [11,12]. In order to search for bioactive substances from this plant and understand its chemical composition, two new compounds, 3-*O*-(13-hydroxy-9*Z*,11*E*,15*E*-octadecatrienoyl) cycloeucaleanol (**1**) and 24'-hydroxy-tetracosyl ferulate (**2**), together with one known compound, tetracosyl ferulate (**3**), were isolated from the stems of *G. pendulum*. We report herein the isolation and structure elucidation of the two new compounds.

2. Results and discussion

The ethanolic extraction of the ground stems of *G. pendulum* was partitioned between water and ethyl acetate to yield ethyl acetate

soluble fraction, which was then subjected to silica gel and Sephadex LH-20 column chromatography to afford compounds **1–3** (Figure 1).

Compound **1** was obtained as colorless oil. The molecular formula of **1** was determined to be C₄₈H₇₈O₃ on the basis of the positive ESIMS (*m/z* 720 [M + NH₄]⁺) and HRESIMS (*m/z* 702.5953 [M]⁺). Its IR spectrum showed a broad absorption band for the hydroxyl group (3425 cm⁻¹), ester bond (1720 cm⁻¹), and double bond at 1649 cm⁻¹. The ¹H NMR spectrum of **1** showed a terminal double bond at δ 4.74 (1H, br s), 4.68 (1H, br s), and a methyl triplet at δ 0.99 (3H, t, *J* = 7.6 Hz). The two-proton signals at δ 0.42 (1H, d, *J* = 4.0 Hz) and 0.17 (1H, d, *J* = 4.0 Hz) indicated the presence of a three-member ring. The ¹³C NMR and DEPT spectra displayed eight olefinic carbon signals (Table 1) and two oxygenated methines at δ 72.1 (d) and 78.5 (d). An ester carbonyl group was presented at δ 173.7 (s). The hydrolysis of compound **1** by 10% methanolic solution of sodium methoxide gave the compounds **1a** and **1b**. The compounds **1a**

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Table 1. ^1H NMR spectral data of compounds **1**, **1a**, and **1b** (in CDCl_3).

No.	1	1a	No.	1	1a	1b
1	1.60 m	1.55 m		1.17 m	1.16 m	
	1.33 m	1.31 m	23	2.15 m	2.15 m	
2	2.00 m	1.99 m		1.92 m	1.91 m	
	1.42 m	1.44 m	25	2.26 m	2.26 m	
3	4.53 m	3.24 m	26	1.05 d (6.8)	1.05 d (6.8)	
4	1.42 m	1.16 m	27	1.05 d (6.8)	1.05 d (6.8)	
5	1.33 m	1.20 m	28	0.92 s	0.92 s	
6	1.66 m	1.70 m	29	0.85 d (6.1)	1.00 d (6.8)	
	0.60 m	0.60 m	31	4.74 br s	4.74 br s	
7	1.94 m	1.91 m		4.68 br s	4.69 br s	
	1.33 m	1.31 m	2'	2.32 t (7.6)		2.36 t (7.4)
8	1.60 m	1.58 m	3'	1.65 m		1.65 m
11	1.33 m	1.31 m	4'–7'	1.27–1.37 m		1.27–1.39 m
	1.15 m	1.08 m	8'	2.20 m		2.19 m
12	1.33 m	1.31 m	9'	5.42 m		5.45 m
15	1.64 m	1.61 m	10'	5.99 br t (11.0)		5.99 br t (11.0)
16	1.94 m	1.99 m	11'	6.53 dd (15.1, 11.0)		6.53 dd (15.2, 11.0)
	1.18 m	1.21 m	12'	5.71 dd (15.1, 6.4)		5.70 dd (15.2, 6.5)
17	1.63 m	1.61 m	13'	4.23 m		4.24 m
18	0.99 s	0.99 s	14'	2.36 m		2.36 m
19	0.42 d (4.0)	0.41 d (4.0)	15'	5.37 m		5.37 m
	0.17 d (4.0)	0.17 d (4.0)	16'	5.59 m		5.58 m
20	1.44 m	1.44 m	17'	2.09 m		2.09 m
21	0.92 d (6.0)	0.92 d (6.2)	18'	0.99 t (7.6)		0.99 t (7.5)
22	1.58 m	1.58 m				

(400 MHz for ^1H and 100 MHz for ^{13}C) spectrometer. Chemical shifts are reported on parts per million (δ), the chemical shifts being represented with TMS as an internal standard, coupling constants (J) in Hz. ^1H and ^{13}C NMR assignments were supported by ^1H - ^1H COSY, HMQC, and HMBC experiments. The ESIMS and HRESIMS spectra were taken on a Q-TOF Micro LC-MS-MS mass spectrometer. Commercial silica gel (Qing Dao Hai Yang Chemical Group Co., Qingdao, China, 100–200 and 200–300 mesh) was used for column chromatography. Precoated silica gel plates (Yan Tai Zi Fu Chemical Group Co., Yantai, China, G60 F-254) were used for analytical TLC.

3.2 Plant material

The ground stems of *G. pendulum* were collected in Xishuangbanna county of Yunnan province, China, on July 2006, and identified as *G. pendulum* C. Y. Cheng. by

Professor Bao-zhong Hu, and the voucher specimen (200689) has been deposited in the herbarium of Faculty of Science, Department of Botany, Northeast Agricultural University.

3.3 Extraction and isolation

The dried ground stems (4 kg) of *G. pendulum* were extracted with 95% EtOH extensively at room temperature to give crude extract (170 g), which was then dissolved in water (1 L) to form a suspension and partitioned with EtOAc to offer EtOAc soluble fraction (30 g). The EtOAc soluble fraction was subjected to silica gel column chromatography eluted with petroleum ether containing increasing amount of Me_2CO to afford fractions A–H on the basis of TLC. Fraction B (5 g) was applied to a silica gel column eluted with petroleum ether/ethyl ether (9:1–8:2) and the fraction with $R_f = 0.5$ (developing with petroleum ether/acetone 3:2) was then subjected to silica gel

column chromatography eluted with petroleum ether/acetone (98:2–95:5) to afford fractions B₁–B₆. Fraction B₂ was purified by Sephadex LH-20 column chromatography (100% MeOH) to afford compounds **1** (40 mg) and **3** (19 mg). Fraction F (1.7 g) was separated by silica gel column chromatography eluted with petroleum ether/ethyl ether (8:2–1:1) and the fraction with $R_f = 0.6$ (developing with petroleum ether/acetone 3:2) was subjected to Sephadex LH-20 column chromatography (100% MeOH) to yield compound **2** (36 mg).

3.3.1 Compound **1**

C₄₈H₇₈O₃, colorless oil; $[\alpha]_D^{20} + 17.6$ (*c* 0.65, CHCl₃); UV (MeOH) λ_{\max} nm (log ϵ): 206 (3.32); IR (KBr) ν_{\max} cm⁻¹: 3425 (OH), 3067, 3035, 1720, 1649, 883; ¹H NMR (CDCl₃, 400 MHz) and ¹³C NMR (CDCl₃, 100 MHz) spectral data, see Tables 1 and 2; ESIMS *m/z* 720 [M + NH₄]⁺; HRESIMS: *m/z* 702.5953 [M]⁺ (calcd for C₄₈H₇₈O₃, 702.5951).

3.3.2 Compound **1a**

C₃₀H₅₀O, white powder; ¹H NMR (CDCl₃, 400 MHz) and ¹³C NMR (CDCl₃, 100 MHz) spectral data, see Tables 1 and 2.

3.3.3 Compound **1b**

C₁₈H₃₀O₃, colorless oil; ¹H NMR (CDCl₃, 400 MHz) and ¹³C NMR (CDCl₃, 100 MHz) spectral data, see Tables 1 and 2.

3.3.4 Compound **2**

C₃₄H₅₈O₅, white amorphous powder; $[\alpha]_D^{20} - 18.2$ (*c* 0.65, CHCl₃); UV (MeOH) λ_{\max} nm (log ϵ): 324 (4.12); IR (KBr) ν_{\max} cm⁻¹: 3498 (OH), 1726, 1640, 1529, 1458, 1445, 1170. ¹H NMR (CDCl₃, 400 MHz) and ¹³C NMR (CDCl₃, 100 MHz) spectral data, see Table 3; ESIMS *m/z* 547 [M + H]⁺; HRESIMS: *m/z* 546.4285 [M]⁺ (calcd for C₃₄H₅₈O₅, 546.4284).

3.3.5 Compound **3**

C₃₄H₅₈O₄, white amorphous powder; ESIMS *m/z* 529 [M - H]⁻; ¹H NMR (CDCl₃,

Table 2. ¹³C NMR spectral data of compounds **1**, **1a**, and **1b** (in CDCl₃).

No.	1	1a	No.	1	1a	1b
1	30.5 t ^a	30.8 t	24	156.9 s	156.9 s	
2	31.0 t	34.8 t	25	33.8 d	33.8 d	
3	78.5 d	76.6 d	26	21.9 q	21.9 q	
4	41.5 d	44.6 d	27	22.0 q	22.0 q	
5	43.4 d	43.3 d	28	19.1 q	19.1 q	
6	24.7 t	24.7 t	29	14.4 q	14.4 q	
7	28.1 t	28.1 t	31	105.9 t	106.0 t	
8	46.9 d	46.8 d	1'	173.7 s		179.4 s
9	23.6 s	23.6 s	2'	34.8 t		34.0 t
10	29.4 s	29.6 s	3'	25.0 t		24.6 t
11	25.1 t	25.2 t	4'–7'	29.0–29.5 t		28.8–29.7 t
12	35.3 t	35.3 t	8'	27.7 t		27.6 t
13	45.6 s	45.5 s	9'	132.9 d		132.9 d
14	48.9 s	48.9 s	10'	127.8 d		127.8 d
15	32.8 t	32.9 t	11'	125.8 d		125.9 d
16	27.0 t	27.0 t	12'	135.1 d		134.9 d
17	52.2 d	52.2 d	13'	72.1 d		72.2 d
18	17.8 q	17.8 q	14'	35.3 t		35.2 t
19	27.2 t	27.3 t	15'	123.8 d		123.7 d
20	36.1 d	36.1 d	16'	135.2 d		35.2 d
21	18.3 q	18.3 q	17'	20.8 t		20.7 t
22	35.0 t	35.0 t	18'	14.2 q		14.2 q
23	31.3 t	31.3 t				

^aBy DEPT sequence.

Table 3. ^1H and ^{13}C NMR spectral data of compounds **2** and **3** (in CDCl_3).

No.	Proton		Carbon	
	2	3	2	3
1			167.4 s ^a	167.4 s
2	6.31 d (15.8)	6.31 d (15.9)	115.6 d	115.7 d
3	7.62 d (15.8)	7.63 d (15.9)	144.7 d	144.6 d
4			127.0 s	127.1 s
5	7.05 d (1.9)	7.05 d (1.7)	109.4 d	109.3 d
6			146.8 s	146.8 s
7			148.0 s	147.9 s
8	6.93 d (8.2)	6.93 d (8.2)	114.8 d	114.7 d
9	7.08 dd (8.2, 1.9)	7.09 dd (8.2, 1.7)	123.0 d	123.0 d
1'	4.20 t (6.8)	4.21 t (6.7)	64.6 t	64.6 t
2'	1.69 m	1.72 m	28.8 t	28.8 t
3'	1.38 m	1.42 m	26.0 t	26.0 t
4'-21'	1.27 m	1.27 m	29.3–29.7 t	29.3–29.7 t
22'	1.38 m	1.27 m	25.7 t	37.9 t
23'	1.58 m	1.32 m	32.8 t	22.7 t
24'	3.65 t (6.7)	0.90 t (7.0)	63.1 t	14.1 q
CH_3O	3.94 s	3.95 s	55.9 q	55.9 q

^aThe multiplicity of peaks was determined by DEPT sequence.

400 MHz) and ^{13}C NMR (CDCl_3 , 100 MHz) spectral data, see Table 3.

3.4 Hydrolysis of compound **1**

Compound **1** (20 mg) was dissolved in 5 ml of 10% methanolic solution of sodium methoxide. The mixture was then stirred for 12 h around at 60–70°C. The solution was then extracted with EtOAc and the ethyl acetate fraction was subjected to silica gel column chromatography, eluting with $\text{CHCl}_3/\text{MeOH}$ (95:5), to give compounds **1a** (10.5 mg) and **1b** (8.3 mg).

Acknowledgements

This research work was financially supported by National Key Project for Basic Research (2003CB114400) and National Natural Science Foundation of China (30440046).

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