PERGAMON

Phytochemistry 54 (2000) 875–881

PHYTOCHEMISTRY

www.elsevier.com/locate/phytochem

Stilbene dimers from the lianas of *Gnetum hainanense*

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Received 14 December 1999; received in revised form 8 March 2000

Abstract

Five stilbene dimers, gnetuhainins F–J, were isolated together with gnetulin, rhapontigenin, isorhapontigenin and gnetol from the lianas of *Gnetum hainanense* C. Y. Cheng. Their structures and stereochemistry have been established on the basis of spectral evidence, especially 2D NMR spectroscopic techniques.

Keywords: *Gnetum hainanense*; Gnetaceae; Oligostilbenes; Gnetuhainins F–J; Structural elucidation

1. Introduction

Gnetum species are known to contain oligomers of isorhapontigenin (3′,4,5′-trihydroxy-3-methoxystilbene) in addition to resveratrol oligomers (Lin et al., 1991; Lin, 1992; Siddiqui et al., 1993; Sotheeswaran and Pasupathy, 1993; Chen and Lin, 1998, 1999). Continuous investigation on the constituents of *Gnetum hainanense* resulted in the isolation of five new stilbene dimers named gnetuhainins F–J (**1**–**5**) together with gnetulin (**6**) (Siddiqui et al., 1993), rhapontigenin (Kashiwata et al., 1984), isorhapontigenin (Li et al., 1991) and gnetol (Zaman et al., 1983), and gnetuhainins A–E, dimers of resveratrol and oxyresveratrol which were previously reported (Huang et al., 2000). Compounds **1**–**4** are dimers of isorhapontigenin, whereas compound **5** is the first dimer of an isorhapontigenin unit and an oxyresveratrol unit.

2. Results and discussion

Gnetuhainin F (**1**) was obtained as a greenish amorphous powder, exhibiting strong blue violet fluorescence under UV light at 254 nm. The high resolution EIMS *m*/*z* 512.1482 agreed with a molecular formula of $C_{30}H_{24}O_8$ (requires 512.1471), with 19 degrees of unsaturation. The UV spectrum (λ_{max}: 316 nm) revealed the presence of a strong conjugated system in the structure. The ^{1}H NMR spectrum of **1** showed signals as follows: a doublet at δ 7.20 (1H, *d*, $J = 2.1$ Hz), a doublet at δ 6.80 (1H, *d*, $J = 8.7$ Hz) and a doublet of doublets at δ 7.19 (1H, *dd*, $J = 8.7$ and 2.1 Hz) of an ABX system for ring A_1; two sets of AB_2 system signals at δ 6.43 (2H, *d*, $J = 2.1$ Hz) and 6.38 (1H, *t*, $J = 2.1$ Hz), 6.52 (2H, *d*, $J = 2.1$ Hz) and 6.21 (1H, *t*, $J = 2.1$ Hz) for rings A_2 and B_2; two *meta*-coupled signals at δ 7.17 (1H, *br s*) and 7.10 (1H, *br s*) for ring B_1; two doublets for two *trans* olefinic protons at δ 7.12 (1H, *d*, $J = 16.5$ Hz) and 6.98 (1H, *d*, $J = 16.5$ Hz), and two singlets of methoxy groups at δ 3.64 and 4.04 (each 3H, *s*). The ^{13}C NMR spectrum of **1** exhibited two carbon signals for two methoxy groups at δ 55.2 and 55.7 besides 28 aromatic and olefinic carbons at δ 102.1–159.2, and all protonated carbons were confirmed by analysis of the HMQC spectrum. These ^{1}H and ^{13}C NMR spectral assignments, combined with a molecular formula of $C_{30}H_{24}O_8$ and NOEs between Me/H-2a and Me/H-2b in the NOESY spectrum, indicated that **1** was an isorhapontigenin

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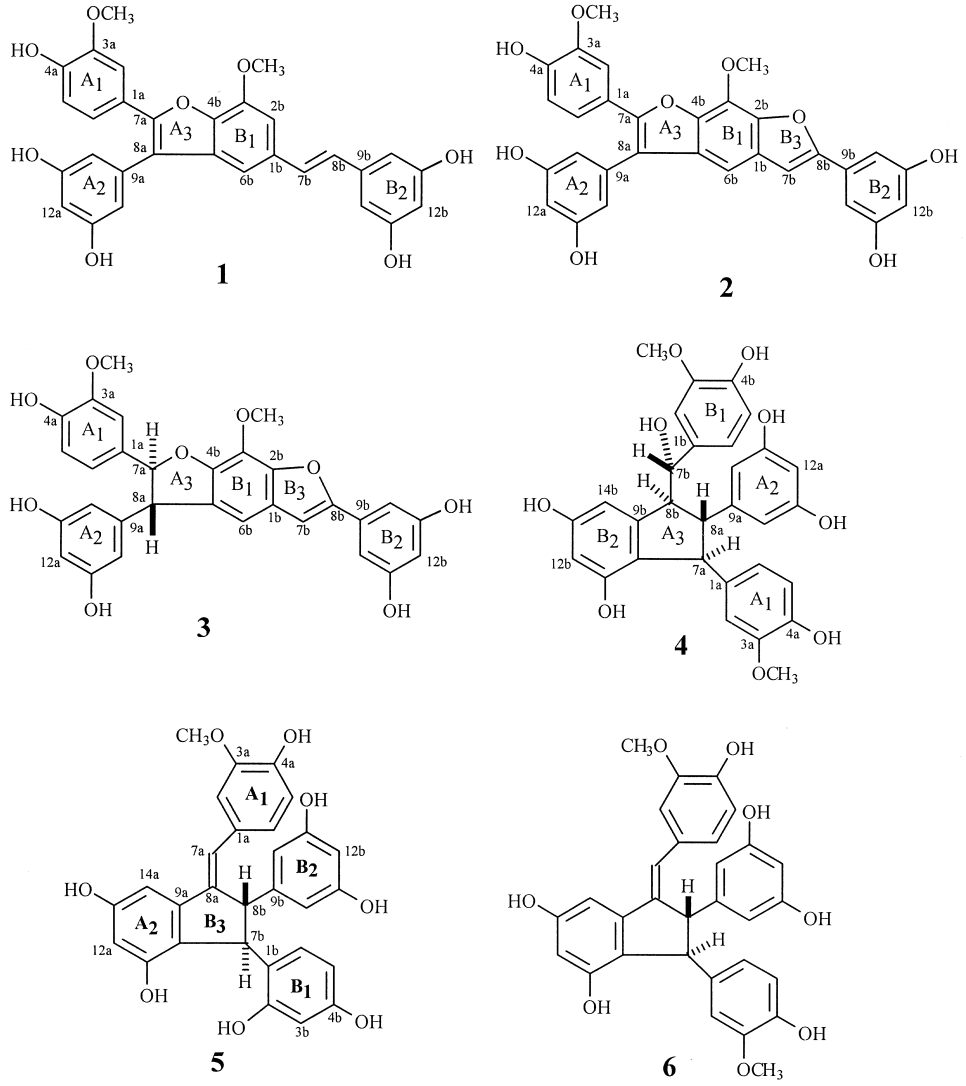
0031-9422/00/$ - see front matter
PII: S0031-9422(00)00151-5

dimer. Seventeen degrees of unsaturation were accounted for by four aromatic rings (A_1, A_2, B_1, B_2) and a double bond, leaving two additional degrees of unsaturation (Scheme 1). Thus, we proposed that two isorhapontigenin units should be connected with a benzofuran group (ring A_3), and the long-range correlations in the HMBC spectrum (Fig. 1) supported the structure as shown in **1**.

Gnetuhainin G (**2**) was obtained as a greenish amorphous powder, exhibiting a strong blue violet fluorescence under UV light at 254 nm. The high resolution EIMS *m/z* 526.1259 $[M]^+$ gave a molecular formula of $C_{30}H_{22}O_9$ (requires 526.1264). Its UV and IR spectra were similar to those of **1**, indicating a similar structure. The ^1H NMR spectrum of **2** displayed similar patterns to that of **1**, with the obvious difference between them being the absence of *trans* olefinic proton signals in the spectrum of **2**. It was suggested that another benzofuran ring (ring B_3) could be formed, considering that there was an extra oxygen atom and an additional degree of unsaturation in compound **2** as compared to **1**. Thus, the structure of **2** was determined as shown, with the aid of long-range correlations in HMBC spectrum (Fig. 1).

Gnetuhainin H (**3**) was obtained as a yellowish amorphous powder, $[\alpha]_D^{25}$ $+16.0^\circ$ (*c* 0.072, MeOH), exhibiting a strong white fluorescence under UV light at 254 nm. Its molecular formula, $C_{30}H_{24}O_9$, was determined by a high resolution EIMS *m/z* 528.1436 $[M]^+$ (requires 528.1420). The ^1H NMR spectrum of **3** was similar to that of **2**, except for the presence of two doublets due to aliphatic protons of a dihydrobenzofuran moiety in **3**. It was, therefore, suggested that **3** contained a dihydrobenzofuran ring, which could be formed by dehydrogenation of benzofuran ring A_3 of **2**. This structure was confirmed by long-range corre-



Scheme 1.

lations between H-7a/C-2a, 6a, and H-8a/C-10(14)a in the HMBC spectrum (Fig. 1). The configuration of H-7a and H-8a was established based on a NOESY spectrum, wherein NOE interactions between H-7a/H-10(14)a and H-8a/H-2a indicated that H-7a and H-8a were in *trans* relationship, resulting in a relative configuration of *rel*-(7a*S*,8a*S*) for **3**.

Gnetuhainin I (**4**) was isolated as an off-white amorphous powder; HR-FABMS *m/z* 533.1808 $[MH]^+$ suggested a molecular formula of $C_{30}H_{28}O_9$ (533.1812 calcd. for $C_{30}H_{29}O_9$), corresponding to 17 degrees of unsaturation. The ^1H NMR spectrum of **4** presented signals for two sets of ABX systems for rings A_1 and B_1 at δ 6.60 (1H, *d*, $J = 2.1$ Hz), 6.67 (1H, *d*, $J = 8.4$ Hz), 6.41 (1H, *dd*, $J = 8.4$ and 2.1 Hz) and δ 6.52 (1H, *d*, $J = 2.1$ Hz), 6.64 (1H, *d*, $J = 8.4$ Hz), 6.48 (1H, *dd*, $J = 8.4$, 2.1 Hz); a set of AB_2 system signals for ring A_2 at δ 5.88 (2H, *d*, $J = 2.1$ Hz) and 6.09 (1H, *t*, $J = 2.1$ Hz); two *meta*-coupled doublets for ring B_2 at δ 6.28 (1H, *d*, $J = 2.1$ Hz) and 6.57 (1H, *d*, $J = 2.1$ Hz); signals for four multi-coupled aliphatic protons at δ 4.16 (1H, *d*, $J = 5.7$ Hz), 2.91 (1H, *dd*, $J = 5.7$ and 8.1 Hz), 3.32 (1H, *dd*, overlapped with H_2O signal) and 4.48 (1H, *d*, $J = 8.1$ Hz) and two singlets for two methoxy groups at δ 3.69 and 3.62 (each 3H, *s*). The ^{13}C NMR spectrum revealed the presence of four aliphatic carbons as well as 24 aromatic carbons and two methoxy carbons. The aliphatic carbon signal at δ 77.0 was due to an alcoholic carbon. Another ring was postulated in addition to the four aromatic rings (A_1, A_2, B_1, B_2) in order to satisfy the 17 degrees of unsaturation. In the HMBC spectrum of **4** (Fig. 1), a cross-peak between H-2(6)b and C-7b, which attached to a hydroxyl group, indicated that C-7b was excluded from the additional ring. Thus, the other three aliphatic carbons probably formed a five-membered ring with two aromatic carbons as shown in **4**, which was confirmed by the cross-peaks in the HMBC spectrum, and was supported by analysis of the spectral data of the structurally analogous compounds, lehmbachols A–C (Kawazoe et al., 1997). The stereochemistry of **4** was determined by analysis of the NOESY spectrum (Fig. 2), wherein strong NOEs between H-10(14)a/H-7a and 8b suggested a *trans* orientation between H-8a and H-7a as well as between H-8a and H-8b. The NOE interactions between H-8a and H-7b revealed a *cis* relationship of H-8a and H-7b. Accordingly, the relative configuration of **4** was determined to be *rel*-(7a*S*,8a*S*,7b*S*,8b*R*) as shown.

Gnetuhainin J (**5**) was isolated as an off-white amorphous powder, $[\alpha]_D^{25}$ $+29.3^\circ$ (*c* 0.084, MeOH). Its high resolution EIMS *m/z* 500.1418 agreed with a molecular formula of $C_{29}H_{24}O_8$ (requires 500.1471). The ^1H NMR spectrum of **5** showed signals for two ABX systems for rings A_1 and B_1 at δ 6.85 (1H, *d*, $J = 2.1$ Hz), 6.64 (1H, *d*, $J = 8.4$ Hz), 6.76 (1H, *dd*, $J = 8.4$ and 2.1 Hz) and δ 6.36 (1H, *d*, $J = 2.1$ Hz), 6.06 (1H, *dd*, $J = 8.4$ and 2.1 Hz), 6.34 (1H, *d*, $J = 8.4$ Hz); a set of AB_2 systematic signals for ring B_2 at δ 6.37 (2H, *d*, $J = 2.1$ Hz) and 6.12 (1H, *t*, $J = 2.1$ Hz); two *meta*-coupled doublets for ring A_2 at δ 6.19 (1H, *d*, $J = 2.1$ Hz) and 6.69 (1H, *d*, $J = 2.1$ Hz); three multi-coupled singlets at δ 6.94, 4.51 and 4.21 (each 1H) and a singlet for methoxy group at δ 3.52 (3H). The ^{13}C NMR spectrum of **5** revealed the presence of three aliphatic carbons in addition to 26 aromatic and olefinic carbons;

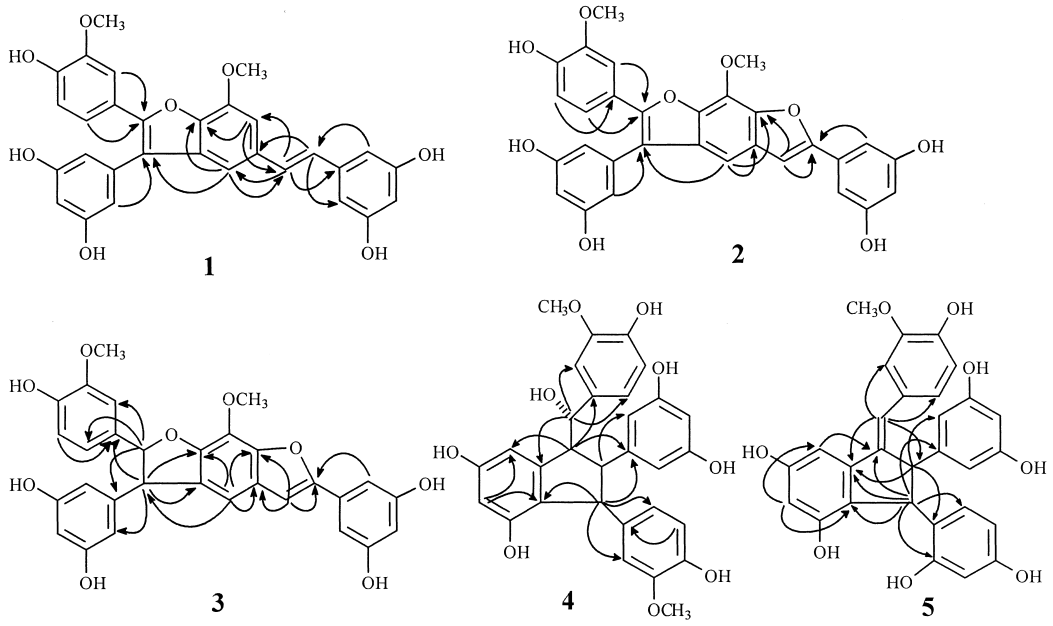


Fig. 1. Important ^{13}C–^1H long-range correlations for compounds **1**–**5**.

all protonated carbons were confirmed by HMQC spectrum. The ^{1}H and ^{13}C NMR spectroscopic evidence, together with a molecular formula of $C_{29}H_{24}O_8$, indicated that **5** was a dimer of an isorhapotigenin unit and an oxyresveratrol unit. The three multi-coupled singlets at δ 6.94, 4.51 and 4.21 in the ^{1}H NMR spectrum and their related carbon signals at δ 122.0, 49.3 and 59.6 in the ^{13}C NMR spectrum were very similar to those of H-7a, 7b and 8b in ampelopsin D (Oshima and Ueno, 1993) and gnetulin (**6**), so we proposed that compound **5** shared the same skeleton. In the HMBC spectrum (Fig. 1), long-range cross-peaks between H-7a/C-2a,6a,9a,8b, H-7b/C-2b,6b,9b,8a,10a, and H-8b/C-1b,10(14)b,9a confirmed the structure of **5** as shown. The stereochemistry of **5** was determined on the basis of NOESY interactions (Fig. 2), where enhancement between H-7a and H-14a suggested that rings A_1 and A_2 were in *trans* position. The coupling constant between H-7b and H-8b was zero and both protons appeared as singlets, indicating the angles between H-7b and H-8b was almost 90°. Therefore, we proposed that H-7b and H-8b were in a *trans* orientation. The NOE enhancements between H-8b and H-6b,10(14)b supported the relative configurations of *rel*-(7b*S*,8b*S*) for **5**. Compound **5** was the first dimer of an isorhapontigenin unit and an oxyresveratrol unit.

3. Experimental

3.1. General experimental procedures

Melting points were measured on a micromelting apparatus and are uncorrected. Optical rotations were determined on a Perkin-Elmer digital polarimeter. UV spectra were recorded on a Shimadzu UV-300 spectrophotometer. IR spectra were recorded on a Perkin-Elmer 683 infrared spectrometer as KBr pellets. NMR spectra were recorded on a Varian Mercury-300 NMR spectrometer using TMS as internal standard. EIMS and FABMS were obtained using an Autospec-Ulma-Tof mass spectrometer. HPLC was performed on a Waters 411 instrument equipped with a UV detector.

3.2. Plant material

The lianas of *G. hainanense* C. Y. Cheng (Gnetaceae) were collected at Jianfengling in Ledong County of Hainan Province, People's Republic of China in September 1991, and were identified by Prof. W. Z. Song, Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College. A voucher specimen (No. 910,920) has been deposited in the herbarium of this institute.

3.3. Extraction and isolation

The dried and powdered lianas of *G. hainanense* (22 kg) were extracted with 95% EtOH under conditions of refluxing, and the crude extract (1.9 kg) obtained after removing solvent in vacuo was further extracted with EtOAc to provide after evaporating to dryness a residue (500 g). The residue was next subjected to silica gel column chromatography (100–200 mesh, 10×150 cm) eluted with a $CHCl_3$–MeOH gradient of increasing MeOH to provide seven fractions (A–G). Isorhapontigenin (1.32 g, 0.006%) and rhapontigenin (684 mg, 0.0031%) were obtained from fraction B (28.2 g) by additional silica gel column chromatography (100–200 mesh, 10×150 cm) eluted with cyclohexane–acetone (3:2). Fraction D (21.8 g) was also subjected to silica gel chromatography (100–200 mesh, 5×100 cm), eluted with cyclohexane–acetone (3:2) to afford gnetol (2.04 g, 0.0091%) and fractions D_1–D_3. Fraction D_3 was subjected to medium-pressure liquid chromatography (Lobar column, RP-18, 43–63 μm, 2.5×31 cm, MeOH–H_2O of 6:4) to afford **1** (10 mg, 0.000045%), **2** (8 mg, 0.000036), and **3** (12 mg, 0.000055%). Fraction E (81.7 g) was subjected to silica

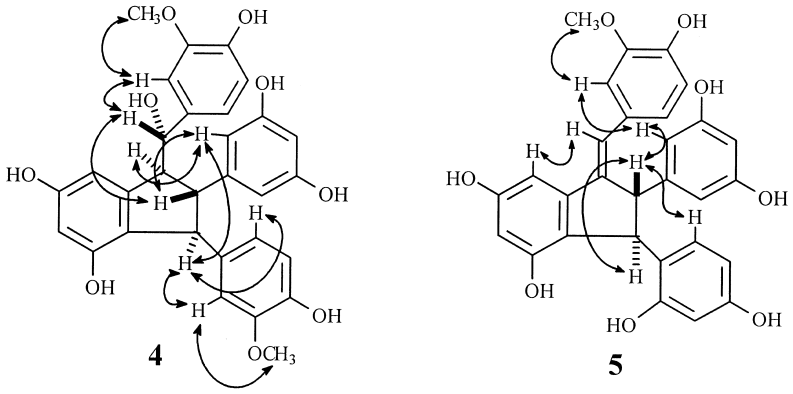


Fig. 2. NOE interactions for compounds **4** and **5**.

gel chromatography (100–200 mesh, 5×100 cm) eluted with cyclohexane–acetone (3:2) to afford fractions E_1–E_5. Fraction E_5 was subjected to medium-pressure liquid chromatography (Lobar column, RP-18, 43–63 μm, 2.5×31 cm, MeOH–H_2O of 3:7) to afford **4** (280 mg, 0.0013%). Identical treatment of fraction E_1 yielded **5** (30 mg, 0.00014%), and **6** (3.43 g, 0.016%).

3.4. Gnetuhainin F (*1*)

Greenish amorphous powder; $[\alpha]_D^{25}$ 0° (*c* 0.12, MeOH); UV (MeOH) λ_{max} (log ε): 316 (4.6) nm; IR (KBr) ν_{max}: 3330, 2915, 2850, 1608, 1516, 1464, 1263, 1151, 1003 and 847 cm^{-1}; ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectral data: see Table 1; LR-EIMS *m/z* (%): 513 $[M + 1]^+$ (13), 512 $[M]^+$ (68), 482 (2), 389 (1), 336 (0.9), 238 (0.9), 125 (10), 111 (20), 97 (34), 85 (45), 57 (100); HR-EIMS *m/z*: 512.1482 $[M]^+$ (calcd. for $C_{30}H_{24}O_8$, 512.1471).

Table 1
^1H and ^{13}C NMR spectral data for compounds **1** and **2**[a]

Position	**1**		**2**	
	^1H	^{13}C	^1H	^{13}C
1a		122.0		122.1
2a	7.20 *d* (2.1)	110.4	7.26 *d* (2.1)	110.3
3a		147.4		147.4
4a		147.4		147.2
5a	6.80 *d* (8.7)	115.2	6.85 *d* (8.4)	115.3
6a	7.19 *dd* (8.7, 2.1)	120.1	7.25 *dd* (8.4, 2.1)	119.8
7a		151.1		150.5
8a		116.4		117.5
9a		134.6		134.7
10a	6.43 *d* (2.1)	108.0	6.50 *d* (2.1)	108.0
11a		159.2		159.3
12a	6.38 *t* (2.1)	102.1	6.42 *t* (2.1)	102.2
13a		159.2		159.3
14a	6.43 *d* (2.1)	108.0	6.50 *d* (2.1)	108.0
1b		134.0		118.5
2b	7.17 *br s*	104.9		139.6
3b		145.4		150.1
4b		142.5		140.0
5b		132.3		132.0[b]
6b	7.10 *br s*	110.8	6.76 *s*	94.2
7b	7.12 *d* (16.5)	128.8	7.26 *s*	100.3
8b	6.98 *d* (16.5)	128.0		154.8
9b		139.5		131.8[b]
10b	6.52 *d* (2.1)	104.8	6.85 *d* (2.1)	103.0
11b		158.8		159.1
12b	6.21 *t* (2.1)	102.1	6.38 *t* (2.1)	103.1
13b		158.8		159.1
14b	6.52 *d* (2.1)	104.8	6.85 *d* (2.1)	103.0
OMe				
−3a	3.64 *s*	55.2	3.75 *s*	55.2
−3b	4.04 *s*	55.7	3.96 *s*	55.5

[a] Measured in CD_3COCD_3 at 300 MHz for ^1H and 75 MHz for ^{13}C, respectively, with assignments confirmed by ^1H–^1H COSY, HMQC, HMBC and NOESY spectra.
[b] May be interchanged within the same column.

3.5. Gnetuhainin G (*2*)

Greenish amorphous powder; $[\alpha]_D^{25}$ 0° (*c* 0.084, MeOH); UV (MeOH) λ_{max} (log ε): 284 (4.4), 335 (4.6) nm; IR (KBr) ν_{max}: 3305, 1606, 1471, 1282, 1203, 1155, 1001 and 843 cm^{-1}; ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectral data: see Table 1; LR-EIMS *m/z* (%): 527 $[M + 1]^+$ (100) 526 $[M]^+$ (80), 483 (15), 453 (15), 391 (4), 258 (14), 228 (8), 137 (10), 91 (5), 69 (10); HR-EIMS *m/z*: 526.1259 $[M]^+$ (calcd. for $C_{30}H_{22}O_9$, 526.1264).

3.6. Gnetuhainin H (*3*)

Yellowish amorphous powder; $[\alpha]_D^{25} + 16.0°$ (*c* 0.072, MeOH); UV (MeOH) λ_{max} (log ε): 274 (4.3), 302 (4.4), 318 (4.3) nm; IR (KBr) ν_{max}: 3332, 2925, 2850, 1604, 1518, 1493, 1464, 1342, 1275, 1205, 1157, 1001 and 841 cm^{-1}; ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectral data: see Table 2; LR-EIMS *m/z* (%): 529 $[M + 1]^+$ (23), 528 $[M]^+$ (80) 515 (30), 514 (12), 484 (5), 390 (20), 272 (4), 258 (100), 244 (50), 225 (10), 197 (24); HR-EIMS *m/z*: 528.1436 $[M]^+$ (calcd. for $C_{30}H_{24}O_9$, 528.1420).

3.7. Gnetuhainin I (*4*)

Off-white amorphous powder; $[\alpha]_D^{25} + 18.5°$ (*c* 0.13, MeOH); UV (MeOH) λ_{max} (log ε): 284 (4.4) nm; IR (KBr) ν_{max}: 3386, 1604, 1514, 1464, 1338, 1151, 1126, 1032, 997 and 839 cm^{-1}; ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectral data: see Table 2; LR-EIMS m/z (%): 515 $[M + 1 - H_2O]^+$ (20) 514 $[M - H_2O]^+$ (87), 473 (2), 436 (1), 392 (10), 259 (4), 137 (8), 108 (4), 64 (30), 46 (100); HR-FABMS *m/z*: 533.1808 $[MH]^+$ (calcd. for $C_{30}H_{29}O_9$, 533.1812).

3.8. Gnetuhainin J (*5*)

Off-white amorphous powder; $[\alpha]_D^{25} + 29.3°$ (*c* 0.084, MeOH); UV (MeOH) λ_{max} (log ε): 284 (4.4), 304 sh (4.4), 328 (4.5) nm; IR (KBr) ν_{max}: 3302, 1603, 1514, 1462, 1340, 1279, 1155, 1005, 837 cm^{-1}; ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectral data: see Table 2; LR-EIMS *m/z* (%): 501 $[M + 1]^+$ (24), 500 $[M]^+$ (100), 470 (32), 350 (14), 274 (28); HR-EIMS *m/z*: 500.1418 $[M]^+$ (calcd. for $C_{29}H_{24}O_8$, 500.1471).

3.9. Gnetulin (*6*)

Pale yellow amorphous powder; $[\alpha]_D^{25}$0° (*c* 0.12, MeOH); UV (MeOH) λ_{max} (log ε): 283 (3.98), 3.03 (4.15), 323 (4.17), 336 (4.06); IR (KBr) λ_{max}: 3380,

Table 2
^{1}H and ^{13}C NMR spectral data for compounds **3**–**5**[a]

Position	**3**		**4**		**5**	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1a		131.7		138.0		129.5
2a	7.00 *d* (2.1)	110.1	6.60 *d* (2.1)	112.1	6.85 *d* (2.1)	111.5
3a		147.7[b]		147.6		147.3
4a		146.8		145.3		145.7
5a	6.77 *d* (8.4)	114.9	6.67 *d* (8.4)	115.0[b]	6.64 *d* (8.4)	114.8
6a	6.83 *dd* (8.4, 2.1)	119.4	6.41 *dd* (8.4, 2.1)	120.6	6.76 *dd* (8.4, 2.1)	122.7
7a	5.53 *d* (8.4)	94.5	4.16 *d* (5.7)	55.8	6.94 *br s*	122.0
8a	4.53 *d* (8.4)	58.1	2.91 *dd* (5.7, 8.1)	59.2		142.6
9a		144.2		150.4		146.3
10a	6.18 *d* (2.1)	106.6	5.88 *d* (2.1)	105.8		123.3[b]
11a		158.8		158.8		154.8
12a	6.23 *t* (2.1)	101.5	6.09 *t* (2.1)	100.9	6.19 *d* (2.1)	102.6
13a		158.8		158.8		158.6
14a	6.18 *d* (2.1)	106.6	5.88 *d* (2.1)	105.8	6.69 *d* (2.1)	97.8
1b		121.0		136.4		123.2[b]
2b		139.0	6.52 *d* (2.1)	111.4		154.3
3b		147.8[b]		147.9	6.36 *d* (2.1)	102.4
4b		137.5		146.0		156.6
5b		126.9	6.64 *d* (8.4)	115.1[b]	6.06 *dd* (8.4,2.1)	106.8
6b	6.37 *s*	100.7	6.48 *dd* (8.4, 2.1)	120.2	6.34 *d* (8.4)	127.4
7b	7.09 *s*	99.7	4.48 *d* (8.1)	77.0	4.51 *br s*	49.3
8b		155.2	3.32 overlap	61.5	4.21 *br s*	59.6
9b		131.7		148.6		148.1
10b	6.86 *d* (2.1)	103.0		122.1	6.37 *d* (2.1)	196.0
11b		159.1		154.9		158.5
12b	6.33 *t* (2.1)	103.2	6.28 *d* (2.1)	102.1	6.12 *t* (2.1)	100.5
13b		159.1		158.6		158.5
14b	6.86 *d* (2.1)	103.0	6.57 *d* (2.1)	105.7	6.37 *d* (2.1)	106.0
OMe						
−3a	3.77 *s*	55.5	3.69 *s*	56.1	3.52 *s*	55.3
−3b	3.78 *s*	55.5	3.62 *s*	55.9		

[a] Measured in CD_3COCD_3 at 300 MHz for ^{1}H and 75 MHz for ^{13}C, respectively, with assignments confirmed by ^{1}H–^{1}H COSY, HMQC, HMBC and NOESY spectra.
[b] May be interchanged within the same column.

1600, 1510, 1450, 1280, 1157, 833 cm^{-1}; ^{1}H NMR spectral data (300 MHz, in CD_3COCD_3): δ 6.81 (1H, *d*, $J = 2.1$ Hz, H-2a), 6.63 (1H, *d*, $J = 8.4$ Hz, H-5a), 6.76 (1H, *dd*, $J = 8.4$ and 2.1 Hz, H-6a), 6.97 (1H, *br d*, $J = 0.9$ Hz, H-7a), 6.23 (1H, *d*, $J = 2.1$ Hz, H-12a), 6.74 (1H, *d*, $J = 2.1$ Hz, H-14a), 6.71 (1H, *d*, $J = 2.1$ Hz, H-2b), 6.58 (1H, *d*, $J = 8.4$ Hz, H-5b), 6.41 (1H, *dd*, $J = 8.4$ and 2.1 Hz, H-6b), 4.18 (1H, *br s*, H-7b), 4.10 (1H, *br s*, H-8b), 6.26 (2H, *d*, $J = 2.1$ Hz, H-10b, H-14b), 6.14 (1H, *t*, $J = 2.1$ Hz, H-12b), 3.51 and 3.66 (each 3H, *s*, OCH_3).

Acknowledgements

This research program was supported by the National Natural Science Foundation of the People's Republic of China (No. 39,570,836). The authors thank the Department of Instrumental Analysis, Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, for the measurement of UV, IR, NMR, and MS spectra.

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