

## Phenolic Constituents of *Gnetum klossii*

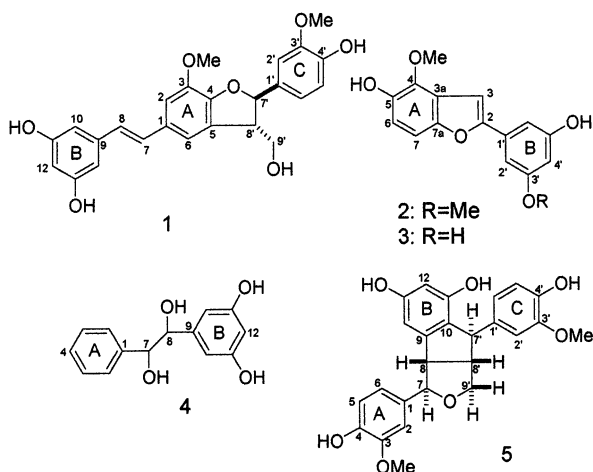
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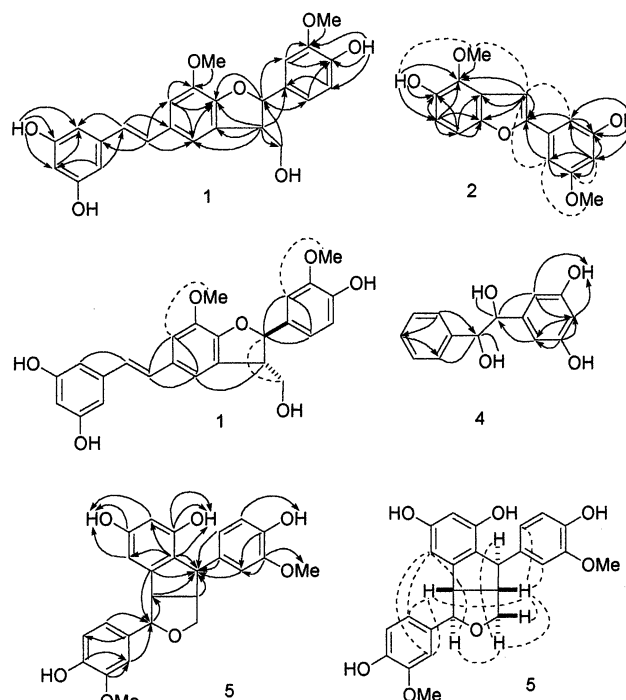
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Four new phenolic derivatives, gnetofurans A–C (**1–3**) and dihydropinosylvindiol (**4**), were isolated from a methanol-soluble extract of the stems of *Gnetum klossii*, together with nine known compounds [gnetifolin F (**5**), isorhapontigenin, gnetulin, gnetins E and C, latifolol, gnetol, (–)- $\epsilon$ -viniferin, and *trans*-resveratrol]. The structures of the new compounds were determined by spectral data analysis.

The genus *Gnetum* (Gnetaceae) consists of about 40 species distributed in South America (Amazon region), Southwest Africa, and the tropical and subtropical zones of Asia.<sup>1</sup> Various species have been used in folk medicine for the treatment of arthritis, bronchitis, and asthma.<sup>2</sup> The genus *Gnetum* is well known for its abundant polyphenolic constituents.<sup>2,3</sup> In a continuation of our phytochemical studies on *Gnetum* species,<sup>4–9</sup> we report herein the isolation and structure elucidation of four new phenolic derivatives, gnetofurans A–C (**1–3**) and dihydropinosylvindiol (**4**), along with nine known compounds from a methanol-soluble part of the stems of *G. klossii* Merr. The known constituents were gnetifolin F (**5**),<sup>10</sup> isorhapontigenin, gnetol, (–)- $\epsilon$ -viniferin,<sup>11</sup> gnetulin,<sup>4</sup> gnetins C and E,<sup>12</sup> latifolol,<sup>7</sup> and *trans*-resveratrol.<sup>13</sup>



Gnetofuran A (**1**), a white amorphous powder, showed a positive reaction to Gibbs reagent. The negative FABMS exhibited a  $[M - H]^-$  ion peak at  $m/z$  435, and the molecular formula  $C_{25}H_{24}O_7$  was deduced from the HR-FABMS at  $m/z$  435.1449  $[M - H]^-$  (calcd 435.1444). The  $^1H$  NMR,  $^1H$ - $^1H$  COSY, and  $^1H$ - $^1H$  long-range COSY spectra exhibited the presence of a set of *meta*-coupled H atoms in an AB system on a tetrasubstituted benzene ring (ring A) [ $\delta$  7.00 (1H, br s, H-6), 6.98 (1H, br s, H-2)], a set



**Figure 1.** CH long-range correlations (→) of compounds **1** and **2** from their HMBC and of compounds **4** and **5** from their COLOC spectra, HH long-range correlations (---) of **1** and **4** from their  $^1H$ - $^1H$  long-range COSY spectra, and NOE interactions (---) of compounds **1**, **2**, and **5** from their NOESY spectra.

of *meta*-coupled protons in an  $A_2B$  system on the 1,3,5-trisubstituted benzene ring (ring B) [ $\delta$  6.41 (2H, d,  $J = 2.1$  Hz, H-10(14), 6.14 (1H, t,  $J = 2.1$  Hz, H-12)], and ABX system protons for a 1,2,4-trisubstituted benzene ring (ring C) [ $\delta$  6.92 (1H, d,  $J = 2.1$  Hz, H-2'), 6.75 (1H, dd,  $J = 2.1$ , 8.1 Hz, H-6'), 6.67 (1H, d,  $J = 8.1$  Hz, H-5')]. These spectra also showed a pair of *trans*-coupled olefinic H atoms [ $\delta$  6.89 (1H, d,  $J = 16.4$  Hz, H-7), 6.78 (1H, d,  $J = 16.4$  Hz, H-8)] and a spin system of four aliphatic protons [ $\delta$  5.45 (1H, d,  $J = 5.4$  Hz, H-7'), 3.74 (2H, m, 2H-9'), 3.41 (1H, dt,  $J = 5.4$ , 12.2 Hz, H-8')]. The  $^1H$  NMR spectrum also showed two signals for methoxyl groups [ $\delta$  3.73 (3H, s,  $OCH_3$ -3), 3.69 (3H, s,  $OCH_3$ -3')], three for phenolic hydroxyl groups [ $\delta$  8.06 (2H, s, OH-11, 13), 7.47 (1H, s, OH-4')], and a signal for an aliphatic hydroxyl group [ $\delta$  4.01 (1H, br s, OH-9')]. The correlations of H-7/H-2(6), H-8/H-10(14), H-8'/H-6, and H-7'/H-2'(6') in the long-range  $^1H$ - $^1H$  COSY spectrum (Figure 1) and of H-7/C-2(6), H-8/C-10(14), H-8'/C-6, and

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H-7'/C-2'(6') in the HMBC spectrum revealed the linkages between C-7/C-1, C-8/C-9, C-8'/C-5, and C-7'/C-1', respectively. The two methoxyl groups were assigned to their respective positions by the HMBC correlations of  $\text{OCH}_3$ -3,H-2/C-3 and  $\text{OCH}_3$ -3',OH-4',H-2'/C-3' and further confirmed by the interactions observed in the NOESY spectrum between  $\text{OCH}_3$ -3/H-2 and  $\text{OCH}_3$ -3'/H-2' (Figure 1). The presence of the dihydrofuran ring was deduced by considering the degrees of unsaturation and confirmed by the correlation of H-7' ( $\delta$  5.45) with C-4 ( $\delta$  149.3) in the HMBC spectrum. In the NOESY spectrum (Figure 1), the interaction between H-7' and H-9' revealed the relative stereochemistry at dihydrofuran to be *trans*. The chemical shift values of **1** were assigned with the help of HMQC, HMBC,  $^1\text{H}$ - $^1\text{H}$  COSY,  $^1\text{H}$ - $^1\text{H}$  long-range COSY, and NOESY spectra (Figure 1). Biogenetically, compound **1** was presumed to be formed by the oxidative coupling of isorhapontigenin (*trans*-3-methoxy-4,11,13-trihydroxystilbene) with coniferyl alcohol.

Gnetofuran B (**2**), a white amorphous powder, showed a positive reaction to Gibbs reagent. The EIMS exhibited a  $[\text{M}]^+$  ion peak at  $m/z$  286. The molecular formula  $\text{C}_{16}\text{H}_{14}\text{O}_5$  was deduced from the HREIMS at  $m/z$  286.0834  $[\text{M}]^+$  (calcd 286.0841). The characteristic UV absorption bands at 321 and 303 nm showed the presence of a furan ring in the molecule. The  $^1\text{H}$  NMR spectrum showed three *meta*-coupled protons [ $\delta$  7.00 (1H, t,  $J$  = 2.0 Hz, H-6'), 6.99 (1H, t,  $J$  = 2.0 Hz, H-2'), 6.44 (1H, t,  $J$  = 2.0 Hz, H-4')], two *ortho*-coupled protons [ $\delta$  7.10 (1H, dd,  $J$  = 8.8, 0.9 Hz, H-7), 6.87 (1H, d,  $J$  = 8.8 Hz, H-6)], and one long-range coupled proton [ $\delta$  7.35 (1H, d,  $J$  = 0.9 Hz, H-3)] in the aromatic region. The signals for two methoxyl [ $\delta$  4.05 (3H, s,  $\text{OCH}_3$ -4), 3.85 (3H, s,  $\text{OCH}_3$ -3')] and two phenolic hydroxyl [ $\delta$  8.45 (1H, s, OH-5), 7.46 (1H, s, OH-5)] groups were also observed in the  $^1\text{H}$  NMR spectrum. The correlations between three *meta*-coupled protons to each other in the  $^1\text{H}$ - $^1\text{H}$  long-range COSY spectrum indicated that they are related to a 1,3,5-trisubstituted benzene ring (ring B). The correlations between H-2'(6')/C-2 and H-3/C-4(3a,7a) in the HMBC spectrum (Figure 1) revealed the linkages between C-1'/C-2, and C-3/C-3a, respectively. All chemical shifts were assigned by the combination of HMQC, HMBC, NOESY,  $^1\text{H}$ - $^1\text{H}$  COSY, and  $^1\text{H}$ - $^1\text{H}$  long-range COSY spectra (Figure 1).

Gnetofuran C (**3**), a white amorphous powder, showed a positive reaction to Gibbs reagent. The EIMS exhibited a  $[\text{M}]^+$  ion peak at  $m/z$  272. The  $[\text{M}]^+$  ion peak at  $m/z$  272.0677 (calcd 272.0685) in the HREIMS showed the molecular formula to be  $\text{C}_{15}\text{H}_{12}\text{O}_5$ . Compound **3** showed a general resemblance to **2** except for the replacement of a methoxyl by a hydroxyl group in ring B, due to which the three *meta*-coupled protons appeared as an  $\text{A}_2\text{B}$  system [ $\delta$  6.91 (2H, br s, H-2',6'), 6.04 (1H, br s, H-4')] and two phenolic hydroxyl protons appeared as a singlet with double integration [ $\delta$  8.43 (2H, s, OH-3',5')]. All chemical shift values were assigned in comparison to compound **2**.

Compounds **2** and **3** are phytoalexins with structural similarity to moracins A and B, and biogenetically these phytoalexins seem to be derived from moracin M.<sup>14</sup>

Dihydropinosylvindiol (**4**), a white amorphous powder, showed a positive reaction to Gibbs reagent. The negative FABMS exhibited a  $[\text{M} - \text{H}]^-$  ion peak at  $m/z$  245, and the molecular formula  $\text{C}_{14}\text{H}_{14}\text{O}_4$  was supported by the negative HRFABMS ( $m/z$  245.0808, calcd 245.0814). The ion peak observed at  $m/z$  228  $[\text{M} - \text{H}_2\text{O}]^+$  in the EIMS represents the loss of a water molecule. The  $^1\text{H}$  NMR spectrum showed five aromatic protons, assignable to a

1-substituted benzene ring [ $\delta$  7.28 (2H, br d,  $J$  = 8.0 Hz, H-2,6), 7.19 (3H, m, H-3,4,5)], and a set of *meta*-coupled protons in an  $\text{A}_2\text{B}$  system on a 1,3,5-trisubstituted benzene ring [ $\delta$  6.30 (2H, d,  $J$  = 2.4 Hz, H-10(14), 6.20 (1H, t,  $J$  = 2.4 Hz, H-12)]. Two mutually coupled aliphatic methines [ $\delta$  4.72 (1H, dd,  $J$  = 6.0, 4.4 Hz, H-7), 4.63 (1H, dd,  $J$  = 6.0, 4.4 Hz, H-8)] and two aliphatic hydroxyl protons [ $\delta$  4.08 (1H, d,  $J$  = 4.4 Hz, OH-7), 4.05 (1H, d,  $J$  = 4.4 Hz, OH-8)] together with two phenolic hydroxyl protons [ $\delta$  7.97 (2H, s, OH-11,13)] were also observed in this spectrum. The correlations between H-7/H-2(6), H-8/H-10(14) in the long-range  $^1\text{H}$ - $^1\text{H}$  COSY spectrum (Figure 1) and between C-2(6)/H-7, C-10(14)/H-8 in the COLOC spectrum (Figure 1) revealed the C-7/C-1 and C-8/C-9 linkages, respectively. The two aliphatic methines appeared as clear double-doublets at  $\delta$  4.60 and 4.69 ( $J$  = 6.0 Hz) when the  $^1\text{H}$  NMR spectrum of **4** was recorded in  $\text{CD}_3\text{OD}$ . Compound **4** (dihydropinosylvindiol) also belongs to phytoalexin and seems to be derived from pinosylvin<sup>11</sup> isolated from *Gnetum parvifolium*.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of gnetifolin F (**5**) and its relative stereochemistry are being reported for the first time in the native state; previously this compound was reported as the acetate form.<sup>10</sup>

## Experimental Section

**General Experimental Procedures.** Optical rotations were recorded on a JASCO P-1020 polarimeter, and UV spectra were recorded on a Shimadzu UV 2200 spectrometer. NMR spectra were recorded on a JEOL EX-400 or AL 300 spectrometer with tetramethylsilane (TMS) as an internal reference. EIMS and negative ion FABMS were measured on a JEOL JMS-DX 300 spectrometer equipped with a JMA 3500 data analysis system. Silica gel 60 (70–230 mesh, Merck) and Sephadex LH-20 (Pharmacia) were used for column chromatography. Kieselgel 60 F<sub>254</sub> (Merck) was used for analytical and preparative TLC.

**Plant Material.** *Gnetum klossii* Merr. was cultivated at Bogor Botanical Garden, Bogor, Indonesia, from where its stems were collected in April 2001 by one of the co-authors (D.D.), and a voucher specimen number GN-004 was deposited at the herbarium of Gifu Prefectural Institute of Health and Environmental Sciences.

**Extraction and Isolation.** The dried stems of *G. klossii* (550 g) were powdered and extracted with MeOH (static, 2 L  $\times$  3 days  $\times$  three times). The methanol extract (13 g) was chromatographed on silica gel eluted with a mixture of AcOEt- $\text{CHCl}_3$ -MeOH- $\text{H}_2\text{O}$  (75:75:30:5) to give 10 fractions (each 60 mL, A-J). Compound **2** (9 mg), isorhapontigenin (12 mg), and resveratrol (67 mg) were purified from fraction B after column chromatography over Sephadex LH-20 (MeOH) followed by preparative TLC [ $\text{CHCl}_3$ -MeOH, 95:5]. Fractions C and D were combined and chromatographed over Sephadex LH-20 eluted with MeOH to give 18 subfractions (each 60 mL, C-D<sub>1-18</sub>). Compound **4** (12 mg) was obtained from fraction C-D<sub>4</sub> by column chromatography over silica gel ( $\text{CHCl}_3$ -MeOH, 95:5) followed by preparative TLC [benzene-AcOEt-MeOH- $\text{H}_2\text{O}$ , 20:14:6:1], and gnetifolin F (26 mg) was purified from fraction C-D<sub>5</sub> in a fashion similar to that for compound **4**. Compounds **1** (11 mg), **3** (7 mg), and gnetulin (51 mg) were purified from fraction C-D<sub>9-10</sub> by preparative TLC [ $\text{CHCl}_3$ -MeOH- $\text{H}_2\text{O}$ , 30:10:1]. Fraction C-D<sub>11-12</sub> was treated similarly to fraction C-D<sub>9-10</sub> to afford gnetol (8 mg). Gnetin C (23 mg) and  $\epsilon$ -viniferin (89 mg) were obtained from fraction C-D<sub>12-14</sub> by column chromatography over Sephadex LH-20 eluted with MeOH. Gnetin E (17 mg) and latifolol (25 mg) were obtained from fraction E by column chromatography over Sephadex LH-20 eluted with MeOH followed by preparative TLC developed in benzene-AcOEt-MeOH- $\text{H}_2\text{O}$  (20:14:6:1).

**Gnetofuran A (1):** white amorphous powder;  $[\alpha]_{\text{D}}^{26}$  -7° (c 0.2 MeOH); UV (MeOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 308 (4.33), 288 (4.25), 220

(sh) (4.71) nm;  $^1\text{H NMR}$  ( $\text{CD}_3\text{COCD}_3$ , 300 MHz)  $\delta$  8.06 (2H, s, OH-11,13), 7.47 (1H, s, OH-4'), 7.00 (1H, br s, H-6), 6.98 (1H, br s, H-2), 6.92 (1H, d,  $J = 2.1$  Hz, H-2'), 6.89 (1H, d,  $J = 16.4$  Hz, H-7), 6.78 (1H, d,  $J = 16.4$  Hz, H-8), 6.75 (1H, dd,  $J = 8.1$ , 2.1 Hz, H-6'), 6.67 (1H, d,  $J = 8.1$  Hz, H-5'), 6.41 (2H, d,  $J = 2.1$  Hz, H-10,14), 6.14 (1H, t,  $J = 2.1$  Hz, H-12), 5.45 (1H, d,  $J = 5.4$  Hz, H-7'), 4.01 (1H, br s, OH-9'), 3.74 (2H, m, 2H-9'), 3.73 (3H, s,  $\text{OCH}_3$ -3), 3.69 (3H, s,  $\text{OCH}_3$ -3'), 3.41 (1H, dt,  $J = 5.4$ , 12.2 Hz, H-7');  $^{13}\text{C NMR}$  ( $\text{CD}_3\text{COCD}_3$ , 75 MHz)  $\delta$  159.6 (2 $\times$ s, C-11,13), 149.3 (s, C-4), 148.4 (s, C-3'), 147.3 (s, C-4'), 145.3 (s, C-3), 140.8 (s, C-9), 134.3 (s, C-1'), 132.0 (s, C-1), 130.5 (s, C-5), 129.5 (d, C-7), 127.2 (d, C-8), 119.6 (d, C-6'), 116.4 (d, C-6), 115.7 (d, C-5'), 111.9 (d, C-2), 110.5 (d, C-2'), 105.6 (2 $\times$ d, C-10,14), 102.7 (d, C-12), 88.6 (d, C-7'), 64.6 (t, C-9'), 56.4 (q,  $\text{OCH}_3$ -3), 56.2 (q,  $\text{OCH}_3$ -3'), 54.7 (d, C-8'); FABMS  $m/z$  435  $[\text{M} - \text{H}]^-$ ; HRFABMS  $m/z$  435.1449 (calcd for  $\text{C}_{25}\text{H}_{23}\text{O}_7$ , 435.1444).

**Gnetofuran B (2):** white amorphous powder; UV (MeOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 321 (4.03), 303 (4.21), 220 (4.50), 216 (sh) (4.59) nm;  $^1\text{H NMR}$  ( $\text{CD}_3\text{COCD}_3$ , 400 MHz)  $\delta$  8.45 (1H, s, OH-5'), 7.46 (1H, s, OH-5), 7.35 (1H, d,  $J = 0.9$  Hz, H-3), 7.10 (1H, dd,  $J = 8.8$ , 0.9 Hz, H-7), 7.00 (1H, t,  $J = 2.0$  Hz, H-6'), 6.99 (1H, t,  $J = 2.0$  Hz, H-2'), 6.87 (1H, d,  $J = 8.8$  Hz, H-6), 6.44 (1H, t,  $J = 2.0$  Hz, H-4'), 4.05 (3H, s,  $\text{OCH}_3$ -4), 3.85 (3H, s,  $\text{OCH}_3$ -3');  $^{13}\text{C NMR}$  ( $\text{CD}_3\text{COCD}_3$ , 100 MHz)  $\delta$  162.3 (s, C-3'), 159.8 (s, C-5'), 156.3 (s, C-2), 150.7 (s, C-7a), 144.7 (s, C-5), 140.0 (s, C-4), 133.0 (s, C-1'), 122.5 (s, C-3a), 114.4 (d, C-6), 106.3 (d, C-7), 105.2 (d, C-6'), 102.7 (d, C-4'), 102.5 (d, C-2'), 100.3 (d, C-3), 60.6 (q,  $\text{OCH}_3$ -4) 55.2 (q,  $\text{OCH}_3$ -3'); EIMS  $m/z$  286  $[\text{M}]^+$  (100), 271 (89), 243 (11), 228 (9), 149 (22), 144 (12); HREIMS  $m/z$  286.0834 (calcd for  $\text{C}_{16}\text{H}_{14}\text{O}_5$ , 286.0841).

**Gnetofuran C (3):** white amorphous powder; UV (MeOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 322 (4.28), 304 (4.43), 221 (4.63) nm;  $^1\text{H NMR}$  ( $\text{CD}_3\text{COCD}_3$ , 400 MHz)  $\delta$  8.43 (2H, s, OH-3',5'), 7.55 (1H, s, OH-5), 7.26 (1H, br s, H-3), 7.08 (1H, br d,  $J = 8.0$  Hz, H-7), 6.91 (2H, br s, H-2',6'), 6.85 (1H, d,  $J = 8.0$  Hz, H-6), 6.04 (1H, br s, H-4'), 4.05 (3H, s,  $\text{OCH}_3$ -4);  $^{13}\text{C NMR}$  ( $\text{CD}_3\text{COCD}_3$ , 100 MHz)  $\delta$  159.8 (2 $\times$ s, C-3',5'), 156.5 (s, C-2), 150.7 (s, C-7a), 144.8 (s, C-5), 140.0 (s, C-4), 133.0 (s, C-1'), 122.4 (s, C-3a), 114.4 (d, C-6), 106.3 (d, C-7), 104.3 (2 $\times$ d, C-2',6'), 104.0 (d, C-4'), 60.6 (q,  $\text{OCH}_3$ -4); EIMS  $m/z$  272  $[\text{M}]^+$  (92), 257 (100), 228 (12), 185 (15), 149 (20), 101 (10), 59 (20); HREIMS  $m/z$  272.0677 (calcd for  $\text{C}_{15}\text{H}_{12}\text{O}_5$ , 272.0685).

**Dihydropinosylvindiol (4):** white amorphous powder;  $[\alpha]_{\text{D}}^{26} -27^\circ$  (c 0.2 MeOH); UV (MeOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 283 (3.55), 279 (3.51), 228 (sh) (4.36) nm;  $^1\text{H NMR}$  ( $\text{CD}_3\text{COCD}_3$ , 400 MHz)  $\delta$  7.97 (2H, s, OH-11,13), 7.28 (2H, br d,  $J = 8.0$  Hz, H-2,6), 7.19 (3H, m, H-3,4,5), 6.30 (2H, d,  $J = 2.4$  Hz, H-10,14), 6.20 (1H, t,  $J = 2.4$  Hz, H-12), 4.72 (1H, dd,  $J = 6.0$ , 4.4 Hz, H-7), 4.63 (1H, dd,  $J = 6.0$ , 4.4 Hz, H-8), 4.08 (1H, d,  $J = 4.4$  Hz, OH-7), 4.05 (1H, d,  $J = 4.4$  Hz, OH-8);  $^{13}\text{C NMR}$  ( $\text{CD}_3\text{COCD}_3$ , 100 MHz)  $\delta$  158.7 (2 $\times$ s, C-11,13), 145.5 (s, C-9), 143.1 (s, C-1), 128.3 (2 $\times$ d, C-2,6), 128.1 (2 $\times$ d, C-3,5), 127.6 (d, C-4), 106.7 (2 $\times$ d, C-10,14), 102.2 (d, C-12), 78.6 (d, C-8), 78.5 (d, C-7);

EIMS  $m/z$  228  $[\text{M} - \text{H}_2\text{O}]^+$  (17), 212 (11), 199 (26), 181 (12), 140 (100), 111 (23), 107 (18), 77 (16); FABMS  $m/z$  245  $[\text{M} - \text{H}]^-$ ; HRFABMS  $m/z$  245.0808 (calcd for  $\text{C}_{14}\text{H}_{13}\text{O}_4$ , 245.0814).

**Gnetofolin F (5):** white amorphous powder;  $[\alpha]_{\text{D}}^{26} 0^\circ$  (c 0.5 MeOH); UV (MeOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 282 (4.24), 230 (4.62) nm;  $^1\text{H NMR}$  ( $\text{CD}_3\text{COCD}_3$ , 400 MHz)  $\delta$  8.13 (1H, s, OH-13), 7.81 (1H, s, OH-11), 7.48 (1H, s, OH-4), 7.23 (1H, s, OH-4'), 7.03 (1H, d,  $J = 2.0$  Hz, H-2), 6.89 (1H, dd,  $J = 8.0$ , 2.0 Hz, H-6), 6.82 (1H, d,  $J = 8.0$  Hz, H-5), 6.73 (1H, d,  $J = 2.0$  Hz, H-2'), 6.66 (1H, d,  $J = 8.0$  Hz, H-5'), 6.50 (1H, dd,  $J = 8.0$ , 2.0 Hz, H-6'), 6.35 (1H, d,  $J = 2.0$  Hz, H-14), 6.27 (1H, d,  $J = 2.0$  Hz, H-12), 4.71 (1H, d,  $J = 4.0$  Hz, H-7), 4.46 (1H, t,  $J = 8.8$  Hz, H-9' $\beta$ ), 4.18 (1H, s, H-7'), 3.81 (1H, dd,  $J = 8.8$ , 4.0 Hz, H-8), 3.51 (1H, t,  $J = 8.8$  Hz, H-9' $\alpha$ ), 3.03 (1H, q,  $J = 8.8$  Hz, H-8), 3.86 (3H, s,  $\text{OCH}_3$ -3), 3.74 (3H, s,  $\text{OCH}_3$ -3');  $^{13}\text{C NMR}$  ( $\text{CD}_3\text{COCD}_3$ , 100 MHz)  $\delta$  159.8 (s, C-13), 155.8 (s, C-11), 148.3 (2 $\times$ s, C-3,9), 148.0 (s, C-3'), 146.7 (s, C-4), 145.5 (s, C-4'), 138.0 (s, C-1'), 135.5 (s, C-1), 122.8 (s, C-10), 120.3 (d, C-6'), 119.6 (d, C-6), 115.5 (d, C-5), 115.4 (d, C-5'), 111.9 (d, C-2'), 110.5 (d, C-2), 103.3 (d, C-14), 102.7 (d, C-12), 88.3 (d, C-7), 74.5 (t, C-9'), 59.7 (d, C-8), 56.2 (q,  $\text{OCH}_3$ -3), 56.1 (q,  $\text{OCH}_3$ -3'), 55.9 (d, C-8'), 51.0 (d, C-7'); FABMS  $m/z$  435  $[\text{M} - \text{H}]^-$ ; HRFABMS  $m/z$  435.1448 (calcd for  $\text{C}_{25}\text{H}_{23}\text{O}_7$ , 435.1444).

## References and Notes

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