# Stilbene Derivatives from *Gnetum montanum* MARKGR. f. *megalocarpum* MARKGR.

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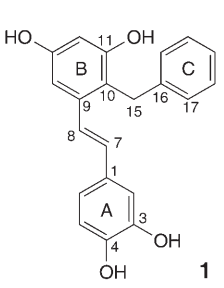
Three new stilbene derivatives, gnetumelin A (**1**), gnetumelin B (**2**), and gnetumelin C (**3**), along with the nine known stilbene derivatives **4**–**12** were isolated from *Gnetum montanum* MARKGR. f. *megalocarpum* MARKGR. Their structures were determined by spectroscopic analysis and comparison of the data with reported ones.

**Introduction.** – The plants of *Gnetum* (Gnetatae, member of Gnetales) are a special group of gymnospermous plants that share several angiospermous morphological features [1][2]. In the world, there are more than thirty species, among which nine species are distributed in China. The Gnetales and angiosperms were regarded as closely related [2]. The question whether this view can be interpreted by the secondary metabolites of the plants or not prompted us to investigate the chemical components of the plants of the *Gnetum* genus. In this paper, we present the isolation and structure elucidation of twelve stilbene derivatives **1**–**12**[1]) from the EtOH extracts of *Gnetum montanum* MARKGR. f. *megalocarpum* MARKGR., among which **1**–**3** were new compounds.

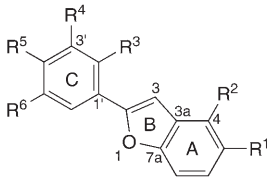
**Results and Discussion.** – Compound **1** was isolated as a yellow solid. Its molecular formula $C_{21}H_{18}O_4$ was established by $^{13}$C-NMR (*Table 1*) and HR-ESI-MS data ($[M+Na]^+$ at *m/z* 357.1098), corresponding to an unsaturation degree of 13. The $^1$H- and $^{13}$C-NMR data of **1** (*Table 1*) indicated that its skeleton consists of a demethylisorhapontigenin and a benzyl group, *i.e.*, **1** was similar to gnetupendin A (= 5-[(1*E*)-2-(4-hydroxy-3-methoxyphenyl)ethenyl]-4-[(4-hydroxyphenyl)methyl]benzene-1,3-diol [3]. The location of the benzyl group was determined by a HMBC experiment (*Table 1*), but the group was not the same as that of gnetupendin A. Thus, the structure of **1** was characterized as 10-benzyl-3-*O*-demethylisorhapontigenin[1]) and named gnetumelin A.

The $^1$H-NMR of **1** showed the presence of ten aromatic and olefinic protons, and the presence of an *ABX*, *AX*, and $A_2M_2X$ system. Its 2D NMR spectra showed signals as follows: an *ABX* system for ring A at $\delta$ 6.69 (br. *s*, H–C(2)), 6.66 (*d*, $J$ = 7.7 Hz, H–C(5)), and 6.61 (*d*, $J$ = 7.7 Hz, H–C(6)); an *AX* system for ring B at $\delta$ 6.45 (br. *s*, H–C(12)) and 6.73 (br. *s*, H–C(14)); an $A_2M_2X$ system for ring C at $\delta$ 7.47 (*d*, $J$ = 7.7 Hz, H–C(17), H–C(21)), 7.31 (*t*, $J$ = 7.7 Hz, H–C(18), H–C(20)), and 7.21 (*t*, $J$ = 7.7 Hz,

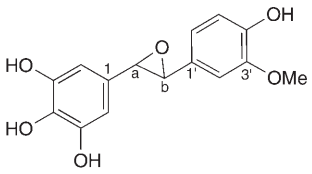
[1]) Trivial atom numbering; for systematic names, see *Exper. Part*.



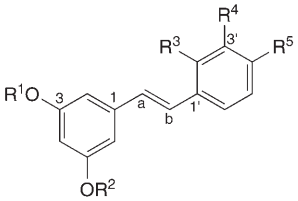
**1**



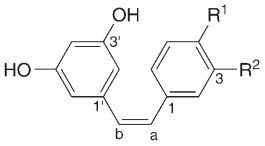
**2** $R^1 = R^6 = OH$, $R^2 = R^3 = R^5 = MeO$, $R^4 = H$
**11** $R^1 = R^4 = OH$, $R^2 = R^6 = MeO$, $R^3 = R^5 = H$
**12** $R^1 = R^3 = R^5 = H$, $R^2 = R^4 = OH$, $R^6 = MeO$



**3**



**4** $R^1 = R^2 = R^4 = H$, $R^3 = R^5 = OH$
**6** $R^1 = R^2 = R^3 = R^4 = H$, $R^5 = OH$
**7** $R^1 = R^3 = H$, $R^2 = Glc$, $R^4 = MeO$, $R^5 = OH$
**8** $R^1 = R^2 = R^3 = H$, $R^5 = GlcO$, $R^4 = MeO$
**9** $R^1 = R^3 = H$, $R^2 = R^5 = GlcO$, $R^4 = MeO$



**5** $R^1 = MeO$, $R^2 = OH$
**10** $R^1 = R^2 = H$

Table 1. *$^{13}C$- and $^{1}H$-NMR Data* (125 and 500 MHz, resp., $(CD_3)_2CO$) *of Compound* **1**[1]). $\delta$ in ppm, $J$ in Hz.

| | $\delta$(C) | $\delta$(H) | HMBC (H → C) |
|---|---|---|---|
| C(1) | 134.6 (*s*) | | |
| H–C(2) | 116.2 (*d*) | 6.69 (br. *s*) | C(3), C(6) |
| C(3) | 143.6 (*s*) | | |
| C(4) | 145.6 (*s*) | | |
| H–C(5) | 115.7 (*d*) | 6.66 (*d*, $J = 7.7$) | C(1), C(4) |
| H–C(6) | 120.3 (*d*) | 6.61 (*d*, $J = 7.7$) | C(2) |
| H–C(7) | 130.2 (*d*) | 6.96 (*d*, $J = 16.5$) | C(9), C(8) |
| H–C(8) | 127.8 (*d*) | 7.43 (*d*, $J = 16.5$) | C(14), C(10), C(9) |
| C(9) | 139.2 (*s*) | | |
| C(10) | 118.6 (*s*) | | |
| C(11) | 157.2 (*s*) | | |
| H–C(12) | 103.2 (*d*) | 6.45 (br. *s*) | C(13), C(10), C(14) |
| C(13) | 157.2 (*s*) | | |
| H–C(14) | 104.5 (*d*) | 6.73 (br. *s*) | C(10), C(12), C(13), C(8) |
| $CH_2$(15) | 30.6 (*t*) | 4.01 (*s*) | C(9), C(10), C(11), C(16), C(17), C(21) |
| C(16) | 138.6 (*s*) | | |
| H–C(17), H–C(21) | 127.3 (*d*) | 7.47 (*t*, $J = 7.7$) | C(16), C(18), C(20) |
| H–C(18), H–C(20) | 129.4 (*d*) | 7.31 (*t*, $J = 7.7$) | C(19), C(16) |
| H–C(19) | 128.2 (*d*) | 7.21 (*t*, $J = 7.7$) | C(17), C(21) |

H–C(19)); two *trans*-positioned olefinic protons at $\delta$ 6.96 (*d*, $J = 16.5$ Hz, H–C(7)) and 7.43 (*d*, $J = 16.5$ Hz, H–C(8)); one benzylic $CH_2$ *s* at 4.01 ($CH_2$(15)). The $^{13}$C-NMR and DEPT spectra exhibited one benzylic $CH_2$ group at $\delta$ 30.6, and twenty aromatic and olefinic C-atoms at $\delta$ 103.2–157.2 (*Table 1*).

Compound **2** was isolated as a brown solid. Its molecular formula $C_{17}H_{16}O_6$ was established by $^{13}$C-NMR (*Table 2*) and HR-ESI-MS data ($[M+1]^+$ at *m/z* 317.1023), corresponding to an unsaturation degree of 10. Further NMR data (*Table 2*) indicate that the skeleton of **2** was very similar to that of gnetofuran B (=2-(3-hydroxy-5-methoxyphenyl)-4-methoxybenzofuran-5-ol) [4]. However, the correlations from the HMBC experiment (*Table 2*) suggested that the substituting groups at ring C were not the same as those of gnetofuran B. Compound **2** was assigned as 2-(5-hydroxy-2,4-dimethoxylphenyl)-4-methoxylbenzofuran-5-ol and named gnetumelin B.

The $^1$H-NMR of **2** indicated the presence of three MeO groups, two OH groups, one benzofuran proton at $\delta$ 7.33 (*s*), and four aromatic protons, among which two protons were *ortho*-coupled with each other (*Table 2*). The $^{13}$C-NMR and DEPT showed the presence of three MeO groups, twelve aromatic C-atoms and two benzofuran C-atoms. From the correlations $\delta$ 4.08 (MeO–C(4))/7.33 (H–C(3)), $\delta$ 7.69 (OH–C(5))/6.87 (H–C(6)), $\delta$ 7.11 (H–C(6′))/8.12 (OH–C(5′)), $\delta$ 3.95 (MeO–C(2′))/7.11 (H–C(3′)), and $\delta$ 3.82 (MeO–C(4′))/8.12 (OH–C(5′)) in the NOESY experiment, the position of the OH and MeO groups were established.

Table 2. *$^{13}$C- and $^1$H-NMR Data* (125 and 500 MHz, resp., $(CD_3)_2CO$) *of Compound* **2**[1]). $\delta$ in ppm, *J* in Hz.

| | $\delta$(C) | $\delta$(H) | HMBC (H → C) |
|---|---|---|---|
| C(2) | 156.4 (*s*) | | |
| H–C(3) | 99.6 (*d*) | 7.33 (*s*) | C(3a), C(7a), C(2), C(1′), C(4) |
| C(3a) | 122.7 (*s*) | | |
| C(4) | 140.1 (*s*) | | |
| C(5) | 144.9 (*s*) | | |
| H–C(6) | 114.3 (*d*) | 6.87 (*d*, $J = 8.8$) | C(4), C(5) |
| H–C(7) | 106.5 (*d*) | 7.11 (overlap) | |
| C(7a) | 150.8 (*s*) | | |
| *Me*O–C(4) | 60.6 (*q*) | 4.08 (*s*) | C(4) |
| OH–C(5) | | 7.69 (*s*) | C(4), C(5), C(6) |
| C(1′) | 126.9 (*s*) | | |
| C(2′) | 154.6 (*s*) | | |
| H–C(3′) | 101.7 (*d*) | 7.11 (overlap) | |
| C(4′) | 138.1 (*s*) | | |
| C(5′) | 151.7 (*s*) | | |
| H–C(6′) | 106.3 (*d*) | 7.11 (overlap) | |
| *Me*O–C(2′) | 56.4 (*q*) | 3.95 (s) | C(2′) |
| *Me*O–C(4′) | 60.9 (*q*) | 3.82 (*s*) | C(4′) |
| OH–C(5′) | | 8.12 (*s*) | C(6′), C(4′), C(5′) |

Compound **3** was obtained as a brown solid. Its molecular formula $C_{15}H_{14}O_6$ was established by $^{13}$C-NMR (*Table 3*) and HR-ESI-MS data ($[M+1]^+$ at *m/z* 291.0875), corresponding to an unsaturation degree of 9. The $^1$H-NMR data (*Table 3*) and the HMBC experiment indicated that the structure of **3** was 5-[3-(4-hydroxy-3-methoxyphenyloxiran-2-yl]benzene-1,2,3-triol, which was named gnetumelin C.

Table 3. *$^{13}$C- and $^{1}$H-NMR* (125 and 500 MHz, $(CD_3)_2CO$) *Data of Compound* **3**[1]). $\delta$ in ppm, $J$ in Hz.

| | $\delta$(C) | $\delta$(H) | HMBC (H → C) |
|---|---|---|---|
| C(1) | 123.7 (*s*) | | |
| H–C(2) | 102.6 (*d*) | 6.12 (*d*, $J$ = 1.8) | C(6), C(1), C(3), C(4) |
| C(3) | 155.5 (*s*) | | |
| C(4) | 159.3 (*s*) | | |
| C(5) | 150.8 (*s*) | | |
| H–C(6) | 103.4 (*d*) | 6.53 (*d*, $J$ = 1.8) | C(a), C(1), C(2), C(4) |
| H–C(a) | 60.9 (*d*) | 3.73 (*s*) | C(b), C(1), C(2), C(1′) |
| H–C(b) | 55.1 (*d*) | 4.46 (*s*) | C(a), C(1′), C(2′) |
| C(1′) | 139.1 (*s*) | | |
| C(2′) | 112.1 (*d*) | 6.65 (*d*, $J$ = 1.6) | C(b), C(1′), C(3′), C(4′) |
| C(3′) | 148.7 (*s*) | | |
| C(4′) | 145.4 (*s*) | | |
| H–C(5′) | 120.6 (*d*) | 6.67 (*d*, $J$ = 8.2) | C(b), C(1′), C(3′), C(4′) |
| H–C(6′) | 116.1 (*d*) | 6.55 (*dd*, $J$ = 1.6, 8.2) | C(b), C(2′), C(4′) |
| *Me*O–C(3) | 56.3 (*q*) | 3.73 (*s*) | C(3′) |

The $^{1}$H-NMR of **3** showed the presence of five aromatic protons and displayed the presence of an *ABX* and an *AX* system. Its 2D NMR spectra showed signals as follows: an *AX* system for ring A at $\delta$ 6.12 (*d*, $J$ = 1.8 Hz, H–C(2)) and 6.53 (*d*, $J$ = 1.8 Hz, H–C(6)), and an *ABX* system for ring B at $\delta$ 6.65 (*d*, $J$ = 1.6 Hz, H–C(2′)), 6.67(*d*, $J$ = 8.2 Hz, H–C(5′)), and 6.55 (*dd*, $J$ = 1.6, 8.2 Hz, H–C(6′)). The $^{13}$C-NMR and DEPT showed the presence of one MeO group, two oxygenated CH groups ($\delta$ 60.1 and 56.3), five aromatic CH groups, and seven aromatic quaternary C-atoms, among which five C-atoms ($\delta >$ 140 ppm) were linked to MeO or OH groups.

The nine known stilbene derivatives were determined to be oxyresveratrol[1]) (**4**), rhapontigenin[1]) (**5**), resveratrol (**6**), isorhapontigenin 3-($\beta$-D-glucopranoside)[1]) (**7**), gnetifolin E[1]) (**8**), gnetifolin K[1]) (**9**), pinosylvine[1]) (**10**), gnetofuran B[1]) (**11**), and gnetifolin M[1]) (**12**), as inferred from the comparison of their NMR data with those reported in [5–10].

To answer the question whether the secondary metabolites of the *Gentum* plants can establish that Gnetales and angiosperms are closely related or not needs further investigations.

## Experimental Part

*General*. NMR Spectra: *Bruker AV-400* and *DRX-500* spectrometers; $\delta$ in ppm rel. to $SiMe_4$ as internal standard, $J$ in Hz; multiplicity of $^{13}$C-NMR by DEPT. MS: *VG Autospec-3000* spectrometer; *m*/*z* (rel. %).

*Plant Material.* The materials were collected in 2003 from Xishuangbanna in Yunnan province in China and identified by *Cui Jingyun* in Xishuangbanna botanical garden.

*Extraction and Isolation*. The air-dried and powdered linans of *Gnetum montanum* MARKGR. f. *megalocarpum* MARKGR. (11 kg) were extracted with EtOH (3 ×) under reflux. After concentration of the combined crude extracts, the resulting gummy material was suspended in $H_2O$ and then partitioned with $CHCl_3$ to afford a $CHCl_3$ and an $H_2O$ extract (160 g and 370 g, resp.). The $CHCl_3$ extract (130 g) was subjected to CC (silica gel, $CHCl_3$/MeOH 9 :1): *Fractions 1–3*. Each fraction was repeatedly subjected to CC (silica gel, *Sephadex LH-20*, and *RP-18*) to afford **1** (22mg), **5** (491 mg) and **6** (48 mg) from *Fr. 2*, and

**2** (25 mg), **10** (40 mg), **11** (28 mg), and **12** (12 mg) from *Fr. 3*. The $H_2O$ extract (170 g) was subjected to CC (silica gel, $CHCl_3$/MeOH/$H_2O$ 7:3:0.5): *Fractions 4–7*. Each fraction was repeatedly subjected to CC (silica gel, *Sephadex LH-20*, and *RP-18*) to afford **3** (6 mg) and **4** (128 mg) from *Fr. 5*, **7** (846 mg) and **8** (161 mg) from *Fr. 6*, and **9** (29 mg) from *Fr. 7*.

*Gnetumelin A* (=*4-[(1*E*)-2-[3,5-Dihydroxy-2-(phenylmethyl)phenyl]ethenyl]benzene-1,2-diol*; **1**): Yellow solid. M.p. 181–183° (MeOH/$CHCl_3$). $^1$H- and $^{13}$C-NMR: *Table 1*. FAB-MS (neg.): 333 (100, $[M-1]^-$), 223 (49). HR-ESI-MS: 357.1098 ($[M+Na]^+$, $C_{21}H_{18}NaO_4^+$; calc. 357.1102).

*Gnetumelin B* (=*2-(5-Hydroxy-2,4-dimethoxyphenyl)-4-methoxybenzofuran-5-ol*; **2**). Brown solid. M.p. 139–141° (MeOH/$CHCl_3$). $^1$H- and $^{13}$C-NMR: *Table 2*. EI-MS: 316 (100, $M^+$), 302 (29), 301 (94), 287 (12), 286 (25), 273 (30), 258 (27), 240 (21), 158 (21), 151 (22). HR-ESI-MS: 317.1023 ($[M+1]^+$, $C_{17}H_{17}O_6^+$; calc. 317.1025).

*Gnetumelin C* (=*5-[3-(4-Hydroxy-3-methoxyphenyl]oxiran-2-yl)benzene-1,2,3-triol*; **3**): Brown solid. M.p. 183–185° (MeOH/$CHCl_3$). $^1$H- and $^{13}$C-NMR: *Table 3*. EI-MS: 290 (5, $M^+$), 124 (100), 109 (85), 81 (47). HR-ESI-MS: 291.0875 ($[M+1]^+$, $C_{15}H_{15}O_6^+$; calc. 291.0869).

*Oxyresveratrol* (=*4-[(1*E*)-2-(3,5-Dihydroxyphenyl)ethenyl]benzene-1,3-diol*; **4**). Brown needles. M.p. 196–198° (MeOH/$CHCl_3$). $^1$H-NMR (400 MHz, $CD_3OD$): 6.98 (*d*, *J* = 1.8, H–C(3′)); 6.94 (*d*, *J* = 12.0, H–C(b)); 6.84 (*dd*, *J* = 8.1, 1.8, H–C(6′)); 6.77 (*d*, *J* = 12.0, H–C(a)); 6.73 (*d*, *J* = 8.1, H–C(5′)); 6.46 (*s*, H–C(2), H–C(6)); 6.18 (*s*, H–C(4)). $^{13}$C-NMR (100 MHz, $CD_3OD$): 159.4 (*s*, C(3), C(5)); 146.3 (*s*, C(2′)); 146.2 (*s*, C(4′)); 141.0 (*s*, C(1)); 130.9 (*s*, C(1′)); 129.6 (*d*, C(b)); 126.8 (*d*, C(a)); 120.2 (*d*, C(5′)); 116.4 (*d*, C(6′)); 113.7 (*d*, C(3′)); 105.7 (*d*, C(2), C(6)); 102.6 (*d*, C(4)). FAB-MS (pos.): 244 (100, $M^+$).

*Rhapontigenin* (=*5-[(1*Z*)-2-(3-Hydroxy-4-methoxyphenyl)ethenyl]benzene-1,3-diol*; **5**): Pale yellow needles. M.p. 186–187° (MeOH/$CHCl_3$). $^1$H-NMR (400 MHz, $C_5D_5N$): 7.39 (*s*, H–C(2′), H–C(6′)); 7.36 (*s*, H–C(2)); 7.22–7.19 (overlap, H–C(5), H–C(6), H–C(a), H–C(b)); 6.98 (*s*, H–C(4′)). $^{13}$C-NMR (100 MHz, $C_5D_5N$ ): 160.7 (*s*, C(3′), C(5′)); 149.0 (*s*, C(3)); 148.5 (*s*, C(4)); 140.9 (*s*, C(1′)); 130.6 (*s*, C(1)); 129.4 (*d*, C(b)); 127.1 (*d*, C(a)); 121.3 (*d*, C(6)); 116.8 (*d*, C(5)); 110.5 (*d*, C(2)); 105.9 (*d*, C(2′)); 103.6 (*d*, C(4′)). FAB-MS (pos.): 258 (100, $M^+$), 137 (11).

*Resveratrol* (=*5-[(1*E*)-2-(4-Hydroxyphenyl)ethenyl]benzene-1,3-diol*; **6**): Brown needles. M.p. 254–256° (MeOH/$CHCl_3$). $^1$H-NMR (400 MHz, $CD_3OD$): 7.34 (*d*, *J* = 8.1, H–C(2), H–C(6)); 6.95 (*d*, *J* = 16.1, H–C(b)); 6.79 (*d*, *J* = 16.1, H–C(a)); 6.75 (*d*, *J* = 8.1, H–C(3), H–C(5)); 6.43 (*s*, H–C(2′), H–C(6′)); 6.14 (*s*, H–C(4′)). $^{13}$C-NMR (100 MHz, $CD_3OD$): 159.6 (*s*, C(3′), C(5′)); 158.3 (*s*, C(4)); 141.3 (*s*, C(1′)); 130.4 (*s*, C(1)); 129.4 (*d*, C(2), C(6)); 128.8 (*d*, C(b)); 126.9 (*d*, C(a)); 116.5 (*d*, C(3), C(5)); 105.7 (*d*, C(2′), C(6′)); 102.6 (*d*, C(4′)). FAB-MS (pos.): 228 (100, $M^+$), 102 (62).

*Isorhapontigenin 3-(β-*D*-Glucopranoside)* (=*3-Hydroxy-5-[(1*E*)-2-(4-hydroxy-3-methoxyphenyl)-ethenyl]phenyl β-*D*-Glucopyranoside*; **7**): Brown solid. M.p. 144–146° (MeOH/$CHCl_3$). $^1$H-NMR (400 MHz, $CD_3OD$): 7.11 (br. *s*, H–C(2′)); 7.04 (*d*, *J* = 16.1, H–C(b)); 6.97 (*d*, *J* = 8.3, H–C(6′)); 6.89 (*d*, *J* = 16.1, H–C(a)); 6.79 (br. *s*, H–C(6)); 6.78 (*d*, *J* = 8.3, H–C(5′)); 6.63 (br. *s*, H–C(2)); 6.46 (br. *s*, H–C(4)); 3.89 (*s*, MeO); 4.91 (*d*, *J* = 7.6, H–C(1″)). $^{13}$C-NMR (100 MHz, $CD_3OD$): 160.4 (*d*, C(5)); 159.6 (*s*, C(3)); 149.2 (*s*, C(3′)); 147.7 (*s*, C(4′)); 141.4 (*s*, C(1)); 130.9 (*s*, C(1′)); 130.3 (*d*, C(b)); 126.9 (*d*, C(a)); 121.4 (*d*, C(2′)); 116.3 (*d*, C(5′)); 110.5 (*d*, C(6′)); 108.4 (*d*, C(2)); 107.0 (*d*, C(6)); 104.1 (*d*, C(4)); 102.3 (*d*, C(1″)); 78.0 (*d*, C(5″)); 77.8 (*d*, C(3″)); 74.9 (*d*, C(2″)); 71.4 (*d*, C(4″)); 62.6 (*t*, C(6″)); 56.4 (MeO). FAB-MS (pos.): 421 (10, $[M+H]^+$), 258 (9, $[M-Glc]^+$), 194 (8), 102 (100).

*Gnetifolin E* (=*4-[(1*E*)-2-(3,5-Dihydroxyphenyl)ethenyl]-2-methoxyphenyl β-*D*-Glucopyranoside*; **8**): Brown needles. M.p. 140–143° (MeOH/$CHCl_3$). $^1$H-NMR (500 MHz, $CD_3OD$): 7.11 (br. *s*, H–C(2′)); 7.11 (*d*, *J* = 8.2, H–C(5′)); 7.02 (*d*, *J* = 8.3, H–C(6′)); 6.97 (*d*, *J* = 16.1, H–C(b)); 6.88 (*d*, *J* = 16.1, H–C(a)); 6.51 (br. *s*, H–C(2), H–C(6)); 6.22 (br. *s*, H–C(4)); 4.92 (*d*, *J* = 7.1, H–C(1″)); 3.86 (*s*, MeO). $^{13}$C-NMR (125 MHz, $CD_3OD$): 159.4 (*s*, C(3), C(5)); 150.5 (*s*, C(3′)); 147.4 (*s*, C(4′)); 140.8 (*s*, C(1)); 133.8 (*s*, C(1′)); 129.1 (*d*, C(a)); 128.7 (*d*, C(b)); 120.9 (*d*, C(2′)); 117.5 (*d*, C(5′)); 111.1 (*d*, C(6′)); 106.1 (*d*, C(2), C(6)); 103.0 (*d*, C(4)); 102.4 (*d*, C(1″)); 77.9 (*d*, C(3″)); 77.6 (*d*, C(5″)); 74.7 (*d*, C(2″)); 71.1 (*d*, C(4″)); 62.3 (*t*, C(6″)); 56.7 (MeO). FAB-MS (pos.): 421 (15, $[M+H]^+$), 258 (44, $[M-Glc]^+$), 194 (10), 102 (100).

*Gnetifolin K* (=*4-[(1*E*)-2-[3-(β-*D*-Glucopyranosyloxyl)-5-hydroxyphenyl]ethenyl}-2-methoxyphenyl β-*D*-Glucopyranoside*; **9**): Brown solid. M.p. 178–180° (MeOH/$CHCl_3$). $^1$H-NMR (500 MHz,

$CD_3OD$): 7.16 (br. *s*, H–C(2′)); 7.13 (*d*, *J* = 8.8, H–C(5′)); 7.06 (*d*, *J* = 8.8, H–C(6′)); 7.05 (*d*, *J* = 16.1, H–C(b)); 6.95 (*d*, *J* = 16.1, H–C(a)); 6.82 (br. *s*, H–C(6)); 6.66 (br. *s*, H–C(2)); 6.49 (br. *s*, H–C(4)); 4.92 (*d*, *J* = 7.0, H–C(1″), H–C(1‴)); 3.92 (*s*, MeO). $^{13}$C-NMR (125 MHz, $CD_3OD$): 160.4 (*d*, C(5)); 159.9 (*s*, C(3)); 150.9 (*s*, C(3′)); 147.7 (*s*, C(1)); 147.7 (*s*, C(4′)); 133.9 (*s*, C(1′)); 129.6 (*d*, C(b)); 128.6 (*d*, C(a)); 121.1 (*d*, C(2′)); 117.9 (*d*, C(5′)); 111.4 (*d*, C(6′)); 108.7 (*d*, C(2)); 107.2 (*d*, C(6)); 104.6 (*d*, C(4)); 102.4 (*d*, C(1″)); 102.3 (*d*, C(1‴)); 78.1 (*d*, C(5‴)); 78.0 (*d*, C(5″));77.9 (*d*, C(3‴)); 77.8 (*d*, C(3″)); 74.9 (*d*, C(2″)); 74.8 (*d*, C(2‴)); 71.4 (*d*, C(4″)); 71.3 (*d*, C(4‴)); 62.6 (*t*, C(6″)); 62.5 (*t*, C(6‴)); 56.8 (MeO). FAB-MS (neg.): 582 (60, $M^-$), 419 (100, $[M - \text{Glc-H}]^-$), 339 (70), 265 (34), 212 (24).

*Pinosylvine* (*= 5-[(1Z)-2-Phenylethenyl]benzene-1,3-diol*; **10**): Brown solid. M.p. 153–155° (MeOH/$CHCl_3$). $^1$H-NMR (500 MHz, $CD_3OD$): 7.56 (*d*, *J* = 7.7, H–C(2), H–C(6)); 7.25 (*t*, *J* = 7.7, H–C(4)); 7.35 (*t*, *J* = 7.7, H–C(3), H–C(5)); 7.08 (*s*, H–C(a), H–C(b)); 6.59 (br. *s*, H–C(2′), H–C(6′)); 6.32 (*s*, H–C(4′)). $^{13}$C-NMR (125 MHz, $CD_3OD$): 159.6 (*s*, C(3′), C(5′)); 140.3 (*s*, C(1)); 138.3 (*s*, C(1′)); 129.7 (*d*, C(a)); 129.5 (*d*, C(2), C(6)); 129.1 (*d*, C(b)); 128.3 (*d*, C(4)); 127.3 (*d*, C(3), C(5)); 106.0 (*d*, C(2′), C(6′)); 103.2 (*d*, C(4′). FAB-MS (pos.): 212 (100, $M^+$).

*Gnetofuran B* (*= 2-(3-Hydroxy-5-methoxyphenyl)-4-methoxybenzofuran-5-ol*; **11**): Brown solid. M.p. 141–143° (MeOH/$CHCl_3$). $^1$H-NMR (500 MHz, $CD_3COCD_3$): 7.36 (*s*, H–C(3)); 7.11 (*d*, *J* = 8.8, H–C(6)); 7.01 (*t*, *J* = 2.2, H–C(2′)); 7.00 (*t*, *J* = 2.2, H–C(6′)); 6.88 (*d*, *J* = 8.8, H–C(7)); 6.45 (*t*, *J* = 2.2, H–C(4′)); 4.04 (*s*, MeO–C(5)); 3.82 (s, MeO–C(5′)). $^{13}$C-NMR (125 MHz, $CD_3COCD_3$): 162.3 (*s*, C(3′)); 159.8 (*s*, C(5′)); 156.3 (*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)); 114.6 (*d*, C(6)); 106.3 (*d*, C(7)); 105.3 (*d*, C(6′)); 102.8 (*d*, C(4′)); 102.5 (*d*, C(2′)); 100.4 (*d*, C(3)); 60.6 (*q*, *Me*O–C(4)); 56.6 (*q*, *Me*O–C(5′)). FAB-MS (pos.): 286 (72, $M^+$), 246 (39), 74 (100).

*Gnetifolin M* (*= 2-(3-Hydroxy-5-methoxyphenyl)benzofuran-4-ol*; **12**): Brown solid. M.p. 140–142° (MeOH/$CHCl_3$). $^1$H-NMR (500 MHz, $CD_3COCD_3$): 7.26 (*s*, H–C(3)); 7.12 (*dd*, *J* = 7.7, 8.3, H–C(6)); 7.05 (*d*, *J* = 8.3, H–C(7)); 6.99 (*s*, H–C(2′)); 6.96 (*s*, H–C(6′)); 6.68 (*d*, *J* = 7.7, H–C(5)); 6.43 (*s*, H–C(4′)); 3.83 (*s*, MeO). $^{13}$C-NMR (125 MHz, $CD_3COCD_3$): 162.4 (*s*, C(5′)); 159.8 (*s*, C(3′)); 157.3 (*s*, C(7a)); 155.0 (*s*, C(2)); 152.1 (*s*, C(4)); 133.2 (*s*, C(1′)); 126.3 (*d*, C(3)); 119.4 (*s*, C(3a)); 108.8 (*d*, C(5)); 105.1 (*d*, C(2′)); 103.6 (*d*, C(6)); 102.6 (*d*, C(4′)); 102.4 (*d*, C(6′)); 100.0 (*d*, C(7)); 55.6 (*q*, MeO). FAB-MS (pos.): 256 (100, $M^+$).

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