Five New Stilbene Dimers from the Lianas of *Gnetum hainanense*

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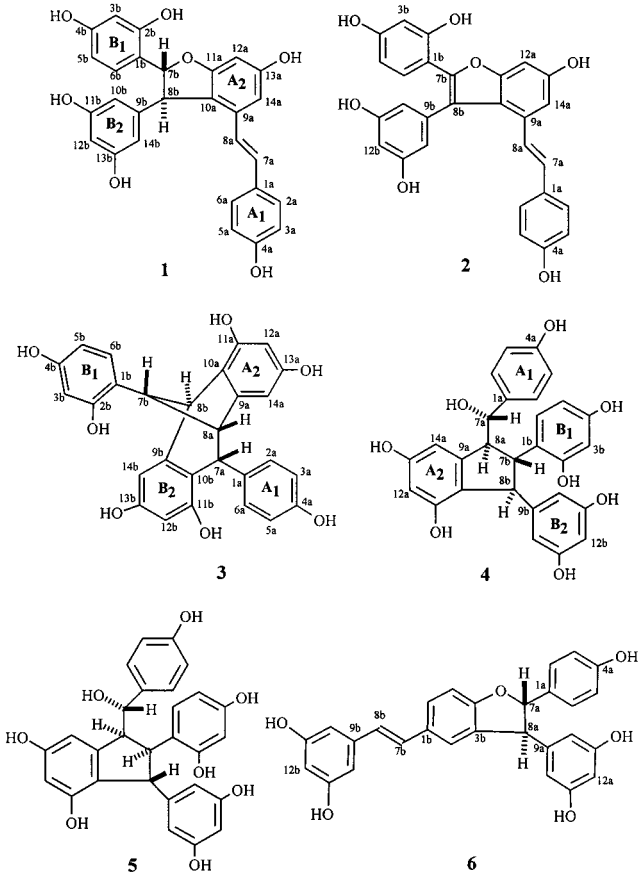
Five new stilbene dimers, gnetuhainins A−E (**1**−**5**), were isolated together with resveratrol *trans*-dehydrodimer (**6**), resveratrol, oxyresveratrol, and (−)-ϵ-viniferin from the lianas of *Gnetum hainanense*. Their structures and stereochemistry were determined on the basis of their chemical and spectral data. Compounds **1**−**5** are dimers formed by a resveratrol unit and an oxyresveratrol unit and belong to a new type of oligostilbenes polymerized from two different stilbene units.

Previous chemical studies on *Gnetum* species have revealed that they produce oligostilbenes.[1−12] Our research group has focused on the stilbenoids occurring in plants in recent years, and two *Gnetum* species, *G. parvifolium* and *G. montanum*, have been investigated.[7−13] As part of our research work, we investigated *G. hainanense*, which grows only in the southern part of the People's Republic of China, especially in Hainan Province. Besides resveratrol *trans*-dehydrodimer (**6**),[14] which was synthesized more than 20 years ago,[15] resveratrol,[7] oxyresveratrol,[16] and (−)-ϵ-viniferin,[17] five new compounds, named gnetuhainins A−E (**1**−**5**), were obtained from an EtOH extract of the lianas of *G. hainanense*. Because only gnetin D[1] was formed by a resveratrol unit and an oxyresveratrol unit among the known stilbene dimers, this report on **1**−**5** is of biosynthetic significance.

Results and Discussion

Gnetuhainin A (**1**) was obtained as pale white amorphous powder, $[\alpha]^{25}_D$ +13.2° (*c* 0.10, MeOH). Its molecular formula of $C_{28}H_{22}O_7$ was established by HREIMS, corresponding to a dimer of a resveratrol unit and an oxyresveratrol unit. The ^{1}H NMR spectrum showed two *ortho*-coupled doublets at δ 7.23 and 6.78 for ring A_1 (with each peak representing two protons); two *meta*-coupled doublets at δ 6.72 and 6.38 for ring A_2; a doublet at δ 7.02, a double doublet at δ 6.31, and a doublet at δ 6.47 of an ABX system for ring B_1; a triplet at δ 6.23 and a doublet at δ 6.32 (2H) of an AB_2 system for ring B_2; two coupled doublets at δ 6.94 and 6.76 for a *trans* double bond; and two coupled doublets for a dihydrobenzofuran moiety at δ 5.79 and 4.51. The ^{13}C NMR spectrum of **1** revealed the presence of two aliphatic carbons at δ 88.5 and 54.7, besides 26 aromatic and olefinic carbons between δ 96.0 and 161.7, and all protonated carbons were assigned from the HMQC spectrum. In the HMBC spectrum of **1** (Figure 1), the CH long-range correlations between H-7a/C-2(6)a, H-7b/C-2b,6b, and H-8b/C-10(14)b allowed the connection of **1** as indicated. The enhancements between H-7b/H-10(14)b and H-8b/H-6b observed in the NOESY spectrum (Figure 2) suggested a *trans* orientation between H-7b and H-8b. Thus, the relative configuration *rel*-(7b*S*,8b*S*) could be determined.

Gnetuhainin B (**2**) was obtained as a greenish amorphous powder, exhibiting white fluorescence under UV light at 254 nm. Its molecular formula of $C_{28}H_{20}O_7$, given by HREIMS, together with its ^{1}H and ^{13}C NMR data indicated



that **2** was also a dimer of a resveratrol unit and an oxyresveratrol unit. The ^{1}H NMR spectrum displayed similar patterns to those of **1** except that two aliphatic protons observed for **1** disappeared in **2**. Meanwhile, in the ^{13}C NMR spectrum of **2**, there were two quaternary carbons more than in that of **1** and no aliphatic carbon signals at all, which suggested that **2** was a dehydrogenated derivative of **1**. The key HMBC correlations (Figure 1) between H-2(6)a/C-7a, H-6b/C-7b, and H-10(14)b/C-8b confirmed the conclusion.

Gnetuhainin C (**3**) was obtained as a pale white amorphous powder, $[\alpha]^{25}_D$ +16.7° (*c* 0.027, MeOH). Its molecular formula of $C_{28}H_{22}O_7$ was established by HREIMS, which, along with its ^{1}H and ^{13}C NMR spectra, indicated that **3** was again a dimer of a resveratrol unit and an oxyresveratrol unit. The ^{1}H NMR spectrum of **3** presented four double doublets at δ 7.23, 6.73, 5.78, and 6.31 for ring A_1, which

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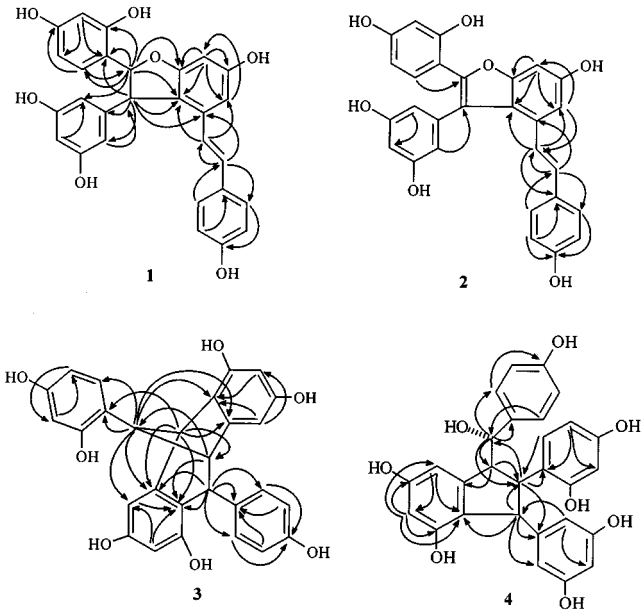

Figure 1. CH long-range correlations of **1**−**4** from their HMBC spectra.

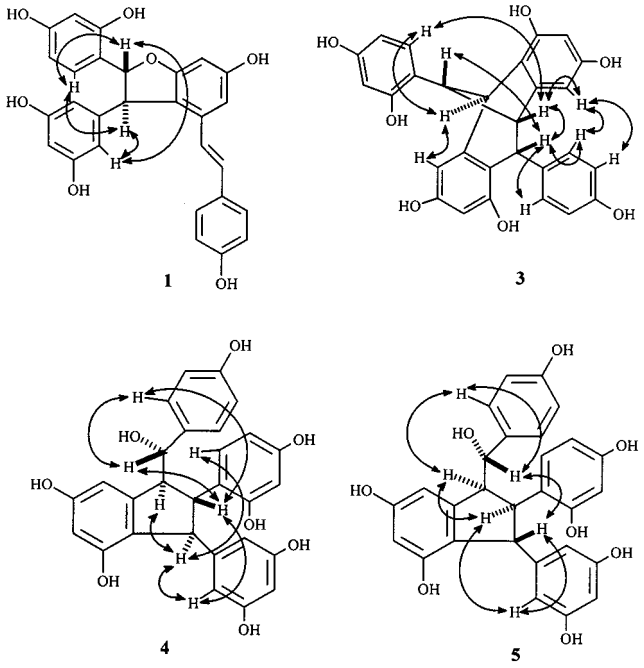

Figure 2. Significant NOE interactions of compounds **1**, **3**, **4**, and **5** from their NOESY spectra.

was fixed and could not rotate freely; two pairs of *meta*-coupled doublets at δ 5.96/5.13 and 6.37/6.06 for rings A_2 and B_2, respectively; a doublet at δ 6.50, a double doublet at δ 5.98, and a doublet at δ 6.30 of an ABX system for ring B_1; and four multicoupled signals at δ 4.44, 3.32, 3.76, and 3.98 for four aliphatic protons. The ^{13}C NMR spectrum of **3** showed the presence of four aliphatic carbons and 24 aromatic carbons. All of the ^{1}H and ^{13}C NMR signals mentioned above were similar to those of isoampelopsin F,[18] except that ring B_1 was a 2,4-dihydroxybenzene group in **3** instead of a 4-hydroxybenzene group. The HMBC spectrum (Figure 1) confirmed the bond connectivities proposed for **3**. The ^{1}H NMR spectrum of **3** was measured at room temperature and 90 °C, with no obvious differences observed, indicating that ring A_1 was fixed in an inflexible manner. On this basic skeleton, H-8a and H-8b gave *W*-type relationships, so a coupling between H-8a and H-8b was observed in the ^{1}H−^{1}H COSY spectrum. The NOE interactions (Figure 2) between H-7a/H-8a and H-7a/H-7b suggested that they were in a *cis* configuration, with H-8b located in a *trans* orientation because it showed no NOEs with other aliphatic protons. Other NOEs between H-8a/H-14a, H-8b/H-14b, H-14a/H-2a, and H-14a/H-3a supported the relative configuration of *rel*-(7a*R*,8a*S*,7b*S*,8b*R*) for **3**.

Gnetuhainins D (**4**) and E (**5**) were obtained as a mixture in the proportion of about 5:3 of **4** to **5**, but was not possible to separate them by HPLC. The HRFABMS gave a molecular formula of $C_{28}H_{24}O_8$ for **4** and **5**. The ^{1}H NMR spectrum of **4** exhibited two *ortho*-coupled doublets at δ 7.40 and 6.95 for ring A_1, with each peak integrating as two protons; two characteristic *meta*-coupled doublets at δ 6.07 and 5.47 for ring A_2; a doublet at δ 6.94, a double doublet at δ 6.29, and a doublet at δ 6.28 of an ABX system for ring B_1; a triplet at δ 6.29 and a doublet at δ 6.51 (2H) of an AB_2 system for ring B_2; and four multicoupled signals at δ 5.32, 3.30, 3.46, and 4.02 for four aliphatic protons. The ^{13}C NMR spectrum of **4** revealed the presence of four aliphatic carbons besides 24 aromatic carbons, of which one appeared at δ 83.4 and was assigned as an alcoholic carbon. To satisfy the 17 degrees of unsaturation, another ring must have been formed besides the four aromatic rings (A_1, A_2, B_1, B_2). In the HMBC spectrum of **4** (Figure 1), the cross-peak between H-2(6)a and C-7a, which was attached to a hydroxy group, indicated that C-7a was excluded from the additional ring. Therefore, considering that **4** is a dimer of a resveratrol unit and an oxyresveratrol unit, the other three aliphatic carbons probably formed a five-membered ring with two aromatic carbons as shown, which was confirmed by the cross-peaks in the HMBC spectrum. The stereochemistry of **4** was determined by analysis of its NOESY spectrum (Figure 2). The NOE interactions between H-7a/H-7b and H-8a/H-8b suggested a *cis* orientation for H-7a and H-7b as well as for H-8a and H-8b, and the NOE interactions between H-8b/H-2b revealed the *trans* relationship of H-7b and H-8b. Hence, the relative configuration of **4** was established as *rel*-(7a*S*,8a*R*,7b*S*,8b*S*). The ^{1}H and ^{13}C NMR spectra of **5** showed the same patterns as those of **4**, suggesting that **5** is a stereoisomer of **4**. The HMBC spectrum of **5** (Figure 1) confirmed the same connectivities as in **4**. In the NOESY spectrum of **5** (Figure 2), the NOE interactions between H-7a/H-8b and H-8a/H-7b indicated *cis* configurations between H-7a/H-8b and H-8a/H-7b, and a *trans* configuration between H-7b and H-8b was confirmed by the enhancement between H-7b and H-10(14)b. Accordingly, the relative configuration of **5** was *rel*-(7a*S*,8a*R*,7b*R*,8b*R*).

Experimental Section

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

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, identified by Prof. W.-Z. Song, Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College. A voucher specimen (no. 910920) has been deposited in the herbarium of this institute.

Table 1. ^{1}H and ^{13}C NMR Data for Compounds **1**−**3**[a]

	1		**2**		**3**	
position	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1a		128.9		129.2		134.4
2a	7.23 d (8.7)	127.8	7.02 d (8.7)	127.8	5.78 dd (8.7, 2.4)	129.1[b]
3a	6.78 d (8.7)	115.5	6.68 d (8.7)	115.4	6.31 dd (8.7, 2.4)	113.7
4a		158.1		157.0		155.3
5a	6.78 d (8.7)	115.5	6.68 d (8.7)	115.4	6.73 dd (8.7, 2.4)	114.3
6a	7.23 d (8.7)	127.8	7.02 d (8.7)	127.8	7.23 dd (8.7, 2.4)	129.2[b]
7a	6.94 d (16.5)	129.2	6.90 d (16.2)	132.0	4.44 d (5.4)	45.7
8a	6.76 d (16.5)	122.7	7.07 d (16.2)	122.1	3.32 d (5.4)	54.8
9a		135.4		131.8		147.0
10a		119.5		120.2		125.8
11a		161.7		155.4		155.9[c]
12a	6.38 d (2.1)	96.0	6.82 d (2.1)	96.6	5.96 d (2.4)	100.6
13a		158.6		157.2		156.4
14a	6.72 d (2.1)	103.1	7.07 d (2.1)	106.2	5.13 d (2.4)	105.6
1b		119.5		115.4		120.7
2b		155.5		155.4		151.9
3b	6.47 d (2.1)	102.6	6.37 d (2.1)	103.0	6.30 d (2.4)	102.1
4b		157.4		158.7		156.8
5b	6.31 dd (8.4,2.1)	106.2	6.20 dd (8.4,2.1)	106.8	5.98 dd (8.4,2.4)	105.7
6b	7.02 d (8.4)	127.0	6.97 d (8.4)	128.1	6.50 d (8.4)	127.9
7b	5.79 d (3.9)	88.5		149.5	3.76 s	52.7
8b	4.51 d (3.9)	54.7		118.6	3.98 s	47.9
9b		147.2		136.6		144.5
10b	6.32 d (2.1)	106.2	6.38 d (2.1)	109.3		113.5
11b		158.6		158.7		156.1[c]
12b	6.23 t (2.1)	100.9	6.39 t (2.1)	101.7	6.06 d (2.4)	100.8
13b		158.6		158.7		156.4
14b	6.32 d (2.1)	106.2	6.38 d (2.1)	109.3	6.37 d (2.4)	105.2

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

Table 2. ^{1}H and ^{13}C NMR Data for Compounds **4**−**6**[a]

	4		**5**		**6**	
position	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1a		131.2		130.8		131.6
2(6)a	7.40 d (8.4)	129.6	7.14 d (8.4)	129.2	7.15 d (8.4)	127.6
3(5)a	6.95 d (8.4)	115.4	6.81 d (8.4)	115.4	6.78 d (8.4)	115.3
4a		158.0		157.3		157.6
7a	5.32 d (10.5)	83.4	4.67 d (8.4)	78.2	5.42 d (7.8)	93.1
8a	3.30 t (10.5)	50.4	3.51 overlap	48.3	4.37 d (7.8)	57.0
9a		143.7		145.1		144.1
10a		123.4		121.8	6.14 d (2.1)	106.4
11a		154.5		154.3		158.9
12a	6.07 br s	102.8	6.19 d (1.9)	103.0	6.22 t (2.1)	106.4
13a		157.2		156.8		158.9
14a	5.47 br s	103.0	5.59 d (1.9)	104.4	6.14 d (2.1)	101.5
1b		117.7		115.8		130.9
2b		155.7		155.4	7.14 d (1.9)	122.9
3b	6.28 d (2.1)	101.8	6.29 d (2.1)	102.0		131.3
4b		157.6		157.5		159.5
5b	6.29 dd (8.4,2.1)	106.8	6.28 dd (8.4,2.1)	108.0	6.81 d (8.4)	109.3
6b	6.94 d (8.4)	125.7	6.64 d (8.4)	130.1	7.35 dd (8.4, 1.9)	127.8
7b	3.46 overlap	52.8	3.50 overlap	49.3	6.98 d (15.5)	128.0
8b	4.02 d (10.5)	51.3	4.10 d (7.2)	56.7	6.79 d (15.5)	126.4
9b		146.1		146.7		139.7
10(11)b	6.51 d (2.1)	106.8	6.28 d (2.1)	106.8	6.45 d (2.1)	104.6
11(13)b		159.0		158.6		158.7
14b	6.29 t (2.1)	101.3	6.28 t (2.1)	100.9	6.17 t (2.4)	101.9

[a] Measured in CD_3COCD_3 at 300 MHz for ^{1}H and 75 MHz for ^{13}C respectively, with all assignments confirmed by ^{1}H−^{1}H COSY, HMQC, HMBC, and NOESY spectra.

Extraction and Isolation. The dried and powdered lianas of *G. hainanense* (22 kg) were extracted with 95% EtOH by refluxing, and the crude extract (1.9 kg) obtained after removing solvent *in vacuo* was further extracted with EtOAc to provide 500 g of an EtOAc residue. The EtOAc portion (500 g) was subjected to a Si gel column (100−200 mesh, 10 × 150 cm) eluted with $CHCl_3$−MeOH, increasing the MeOH gradually to provide seven fractions (A−G). Resveratrol (2.4 g, 0.11%) and oxyresveratrol (200 mg, 0.0091%) were obtained from fraction C (41.3 g) by Si gel column chromatography (100−200 mesh, 5 × 100 cm) eluted with cyclohexane−acetone (1:1). Fraction E (81.7 g) was subjected to a Si gel column (100−200 mesh, 5 × 100 cm) eluted with cyclohexane−acetone (1:1) to afford fractions E_1−E_5. Fractions E_2 and E_4 were subjected to MDLC (Lobar column, RP_{18}, 43−63 μm, 2.5 × 31 cm) eluted with MeOH−H_2O (1:1) to afford **1** (38 mg, 0.0017%), **2** (14 mg, 0.00064%), **6** (3 mg, 0.00014%), and ϵ-viniferin (20 mg, 0.00091%) from fraction E_2, and **3** (5 mg, 0.00023%) and a mixture of **4** and **5** (50 mg, 0.0023%), which could not be separated by HPLC, from fraction E_4.

Gnetuhainin A (1): pale white amorphous powder; $[\alpha]^{25}_D$ +13.2° (*c* 0.10, MeOH); UV (MeOH) λ_{max} (log ϵ) 284 (4.2), 307

(4.3), 320 (4.3) nm; IR (KBr) ν_{max} 3342, 1693, 1604, 1514, 1454, 1265, 1157, 1122, 999, 835 cm^{-1}; ^1H (300 MHz) and ^{13}C (75 MHz) NMR data, see Table 1; EIMS *m/z* 470 $[M]^+$, 392, 365, 349, 259, 243, 124, 107, 95, 69; HREIMS *m/z* 470.1375 $[M]^+$ (calcd for $C_{28}H_{22}O_7$, 470.1366).

Gnetuhainin B (2): greenish amorphous powder, exhibiting white fluorescence under UV light (254 nm); UV (MeOH) λ_{max} (log ϵ) 284 (4.5), 320 (4.6), 356 (4.3) nm; IR (KBr) ν_{max} 3305, 1695, 1604, 1512, 1446, 1248, 1157, 999, 837 cm^{-1}; ^1H (300 MHz) and ^{13}C (75 MHz) NMR data, see Table 1; EIMS *m/z* 468 $[M]^+$, 361, 243, 229, 107, 95, 66; HREIMS *m/z* 468.1182 $[M]^+$ (calcd for $C_{28}H_{20}O_7$, 468.1209).

Gnetuhainin C (3): pale white amorphous powder; $[\alpha]^{25}_D$ +16.7° (*c* 0.028, MeOH); UV (MeOH) λ_{max} (log ϵ) 280 (4.3) nm; IR (KBr) ν_{max} 3330, 1612, 1512, 1460, 1329, 1236, 1171, 1016, 996, 839 cm^{-1}; ^1H (300 MHz) and ^{13}C (75 MHz) NMR data, see Table 1; EIMS *m/z* 470 $[M]^+$, 376, 360, 329, 266, 226, 197, 137, 123, 110; HREIMS *m/z* 470.1395 $[M]^+$ (calcd for $C_{28}H_{22}O_7$, 470.1366).

Gnetuhainin D (4) and gnetuhainin E (5): pale white amorphous powder; ^1H (300 MHz) and ^{13}C (75 MHz) NMR data, see Table 2; EIMS *m/z* 470 $[M - H_2O]^+$, 363, 347, 253, 215, 133, 123, 107, 77; HRFABMS *m/z* 471.1465 $[MH - H_2O]^+$ (calcd for $[C_{28}H_{25}O_8 - H_2O]$, 471.1444).

Resveratrol *trans*-dehydrodimer (6): pale white oil; ^1H (300 MHz) and ^{13}C (75 MHz) NMR data, see Table 2; EIMS *m/z* 454 $[M]^+$, 361, 347, 239, 227, 181, 107.

Resveratrol: colorless needles; mp 254−255 °C; ^1H NMR (300 MHz, in CD_3COCD_3) δ 7.38 (2H, d, J = 8.7 Hz, H-2, H-6), 6.82 (2H, d, J = 8.7 Hz, H-3, H-5), 7.00 (1H, d, J = 16.5 Hz, H-8), 6.83 (1H, d, J = 16.5 Hz, H-7), 6.52 (2H, d, J = 2.2 Hz, H-10, H-14), 6.27 (1H, t, J = 2.2 Hz, H-12); EIMS *m/z* 228 $[M]^+$, 211, 181, 157, 114.

Oxyresveratrol: pale yellow needles; mp 196−198 °C; ^1H NMR (300 MHz, in CD_3COCD_3) δ 6.45 (1H, d, J = 2.1 Hz, H-3), 6.37 (1H, dd, J = 8.4, 2.1 Hz, H-5), 7.37 (1H, d, J = 8.4 Hz, H-6), 7.30 (1H, d, J = 16.5 Hz, H-7), 6.85 (1H, d, J = 16.5 Hz, H-8), 6.50 (2H, d, J = 2.1 Hz, H-10, H-14), 6.20 (1H, t, J = 2.1 Hz, H-12); EIMS *m/z* 244 $[M]^+$, 226, 110.

(−)-ε-Viniferin: colorless amorphous powder; $[\alpha]^{20}_D$ −38.6° (*c* 0.12, MeOH); ^1H NMR (300 MHz, in CD_3COCD_3) δ 7.21 (2H, d, J = 8.7 Hz, H-2a, H-6a), 7.19 (2H, d, J = 8.4 Hz, H-2b, H-6b), 6.85 (2H, d, J = 8.7 Hz, H-3a, H-5a), 6.75 (2H, d, J = 8.4 Hz, H-3b, H-5b), 6.94 (1H, d, J = 16.2 Hz, H-8b), 6.73 (1H, d, J = 16.2 Hz, H-7b), 6.75 (2H, br s, H-12b, H-14b), 6.34 (1H, t, J = 2.2 Hz, H-12a), 6.26 (2H, d, J = 2.2 Hz, H-10a, H-14a), 5.44 (1H, d, J = 5.1 Hz, H-7a), 4.46 1H, d, J = 5.1 Hz, H-8a); EIMS *m/z* 454 $[M]^+$, 360, 347, 331, 267, 107.

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