Three New Trimeric Stilbenes from *Gnetum gnemon*

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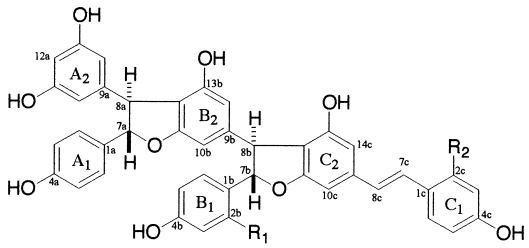
Three stilbene trimers (gnemonols D, E, F) were isolated from the root of *Gnetum gnemon.* The structures were determined by spectroscopic analysis. In addition, the antioxidant activity of the compounds on lipid peroxide inhibition and super oxide scavenging activity were also investigated.

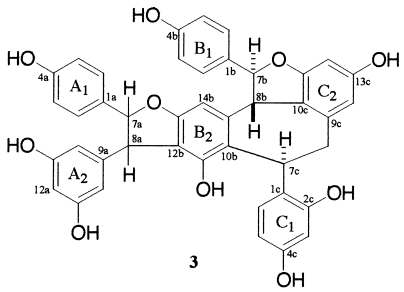
Key words *Gnetum gnemon*; Gnetaceae; stilbene trimer; antioxidant activity

With the recent isolation of many stilbene oligomers,[1—3] their various biological activities such as blood sugar reduction,[4] induction of apoptosis in colon cancer,[5] *etc*. have been revealed. Our phytochemical attention is therefore drawn to the plants of Gnetaceae which are known to contain stilbenoids[6] and have been ethnobotanically used as folk medicine as well as food.[7,8] In our previous investigation of the Gnetaceaous plants, the occurrence of stilbenoid constituents in some *Gnetum* species was reported.[9—13] This paper deals with the isolation and structure determination of three new stilbene trimers, gnemonols D (**1**), E (**2**), and F (**3**) from the root of *Gnetum gnemon.* The structures of the compounds were determined by spectroscopic methods. The effects of the compounds on lipid peroxide inhibition and scavenging ability for super oxide in a xanthine–xanthine oxidase system were also conducted. All the compounds exhibited considerable antioxidant activity.

Gnemonol D (**1**), $[\alpha]_D = -22°$, showed a positive reaction to Gibbs reagent. The negative FAB-MS exhibited an $[M-H]^-$ ion peak at *m/z* 695, indicating the molecular weight to be 696. The molecular formula of $C_{42}H_{32}O_{10}$ was deduced by the high-resolution (HR) negative FAB-MS (*m/z* 695.1920). The ^{1}H-NMR spectrum (Table 1) exhibited the signals of two sets of *ortho*-coupled aromatic protons on *p*-substituted phenyl moieties [δ 6.78 (2H, d, J=8.8 Hz, H-3a, 5a), 7.14 (2H, d, J=8.8 Hz, H-2a, 6a); 6.80 (2H, d, J=8.8 Hz, H-3b, 5b), 7.19 (2H, d, J=8.8 Hz, H-2b, 6b)], two sets of *meta*-coupled protons on 1,3,4,5-tetrasubstituted benzene rings [δ 6.18 (1H, br s, H-14b), 6.28 (1H, br s, H-10b); 6.57 (1H, br s, H-14c), 6.63 (1H, br s, H-10c)], and a set on 3,5-dihydroxyphenyl group [δ 6.13 (2H, d, J=2.0 Hz, H-10a, 14a), 6.19 (1H, t, J=2.0 Hz, H-12a)]. The spectrum also showed the presence of a set of protons on a 1,2,4-trisubtituted benzene ring in an ABX system [δ 6.42 (1H, d, J=2.4 Hz, H-3c), 6.34 (1H, dd, J=2.4, 8.3 Hz, H-5c), 7.37 (1H, d, J=8.3 Hz, H-6c)], and a set of *trans*-coupled olefinic protons [δ 6.92 (1H, d, J=16.1 Hz, H-8c), 7.33 (1H, d, J=16.1 Hz, H-7c)]. Two sets of mutually coupled methines [δ 4.33 (1H, d, J=5.4 Hz, H-8a), 5.32 (1H, d, J=5.4 Hz, H-7a); 4.42 (1H, d, J=4.4 Hz, H-8b), 5.42 (1H, d, J=4.4 Hz, H-7b)] and eight phenolic hydroxyl protons [δ 8.40 (2H, br s, OH-4a, 4b), 8.11 (2H, br s, OH-11a, 13a), 8.01 (1H, br s, OH-13b), 8.55 (1H, br s, OH-2c), 8.36 (1H, br s, OH-4c), 8.17 (1H, br s, OH-13c)] were further observed in the spectrum. The molecular formula ($C_{42}H_{32}O_{10}$), ^{1}H- and ^{13}C-NMR spectral data (Table 1) revealed that **1** is a trimeric stilbene. All protonated and quaternary carbons were assigned with the aid of ^{13}C–^{1}H shift correlation spectroscopy (^{13}C–^{1}H COSY) and correlation spectroscopy involving long-range coupling (COLOC). The following correlations C-2a(6a)/H-7a, C-10a(14a)/H-8a, C-2b(6b)/H-7b, C-10b(14b)/H-8b, C-2c(6c)/H-7c, and C-10c(14c)/H-8c observed in the COLOC spectrum (Fig. 2) and H-2a(6a)/H-7a, H-10a(14a)/H-8a, H-2b(6b)/H-7b, H-10b(14b)/H-8b, H-6c/H-7c, and H-10c(14c)/H-8c in the long-range ^{1}H–^{1}H COSY spectrum (Fig. 3) revealed the linkages of C-1a/C-7a, C-9a/C-8a, C-1b/C-7b, C-9b/C-8b, C-1c/C-7c, and C-9c/C-8c, respectively. The correlations be-



1: R_1 = H, R_2 = OH
2: R_1 = OH, R_2 = H



3

H-7a/8a = *trans*

Fig. 1

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Table 1. NMR Spectral Data of **1**—**3**

Position	**1**[a]		**2**[a]		**3**[a]	
	δ_C[b]	δ_H[d]	δ_C[b]	δ_H[d]	δ_C[c]	δ_H[e]
1a	133.7		133.7		133.9	
2a/6a	128.0	7.14 (d, 8.8)	128.0	7.20 (d, 8.8)	127.9	7.11 (d, 8.4)
3a/5a	116.0	6.78 (d, 8.8)	116.0	6.84 (d, 8.8)	116.2	6.79 (d, 8.4)
4a	159.4		158.0		158.3	
7a	93.8	5.32 (d, 5.4)	93.7	5.37 (d, 6.0)	93.8	5.30 (d, 5.1)
8a	56.0	4.33 (d, 5.4)	55.9	4.40 (d, 6.0)	56.2	4.47 (d, 5.1)
9a	146.0		145.9		145.9	
10a/14a	106.8	6.13 (d, 2.0)	106.8	6.19 (d, 2.0)	106.8	6.22 (d, 2.0)
11a/13a	159.4		159.3		159.7	
12a	101.9	6.19 (t, 2.0)	101.9	6.24 (t, 2.0)	102.1	6.22 (t, 2.0)
1b	134.0		120.6		131.8	
2b	127.6	7.19 (d, 8.8)	155.8		130.1	7.24 (d, 8.8)
3b	116.1	6.80 (d, 8.8)	103.4	6.50 (d, 2.0)	116.1	6.76 (d, 8.8)
4b	159.1		158.70		158.6	
5b	116.1	6.80 (d, 8.8)	107.2	6.31 (dd, 2.0, 8.4)	116.1	6.76 (d, 8.8)
6b	127.6	7.19 (d, 8.8)	127.5	7.05 (d, 8.4)	130.1	7.24 (d, 8.8)
7b	93.5	5.42 (d, 4.4)	89.1	5.84 (d, 2.9)	88.4	5.94 (d, 10.8)
8b	55.9	4.42 (d, 4.4)	54.2	4.52 (d, 2.9)	49.9	4.71 (d, 10.8)
9b	146.6		147.0		143.1	
10b	101.0	6.28 (br s)	101.3	6.50 (br s)	123.5	
11b	162.8		162.5		152.1	
12b	114.1		113.8		114.5	
13b	155.38		155.0		160.5	
14b	108.2	6.18 (br s)	108.3	6.28 (br s)	99.2	6.45 (br s)
1c	117.2		129.9		120.7	
2c	156.9		128.6	7.44 (d, 8.8)	156.5	
3c	103.6	6.42 (d, 2.4)	116.3	6.85 (d, 8.8)	106.7	6.12 (d, 2.4)
4c	158.1		158.0		157.9	
5c	108.4	6.34 (dd, 2.4, 8.3)	116.3	6.85 (d, 8.8)	103.8	6.22 (dd, 2.4, 8.8)
6c	128.3	7.37 (d, 8.3)	128.6	7.44 (d, 8.8)	128.5	7.04 (d, 8.8)
7c	124.5	7.33 (d, 16.1)	129.0	7.11 (d, 16.4)	32.7	5.07 (t, 3.9)
8c	126.2	6.92 (d, 16.1)	126.7	6.97 (d, 16.4)	34.9	3.41 (dd, 3.9, 17.7) 3.21 (dd, 3.9, 17.7)
9c	142.1		141.0		138.6	
10c	99.2	6.63 (br s)	99.2	6.79 (br s)	119.0	
11c	163.0		163.3		160.6	
12c	114.6		115.4		95.6	6.14 (br s)
13c	155.4		155.5		159.1	
14c	107.6	6.57 (br s)	108.0	6.62 (br s)	108.5	6.31 (br s)
OH-4a		8.40 (br s)		8.46 (br s)		8.47 (br s)
OH-11a/13a		8.11 (br s)		8.18 (br s)		8.20 (br s)
OH-2b				8.73 (br s)		
OH-4b		8.40 (br s)		8.29 (br s)		8.50 (br s)
OH-11b						7.77 (br s)
OH-13b		8.01 (br s)		8.00 (br s)		
OH-2c		8.55 (br s)				7.65 (br s)
OH-4c		8.36 (br s)		8.52 (br s)		8.11 (br s)
OH-13c		8.17 (br s)		8.24 (br s)		8.27 (br s)

a) acetone-d_6. *b*) 100 MHz. *c*) 75 MHz. *d*) 400 MHz. *e*) 300 MHz.

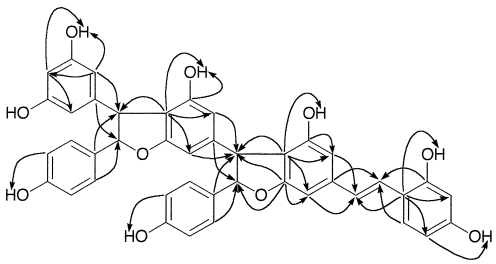

Fig. 2. Correlations in the COLOC Spectrum of **1**

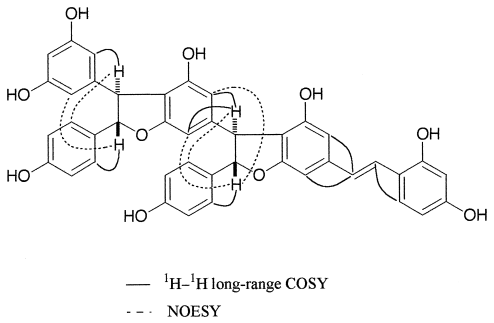

Fig. 3. Correlations in the ^{1}H–^{1}H Long-Range COSY and NOESY Spectra of **1**

tween C-12b/H-8a and C-11c(12c)/H-8b in the COLOC spectrum showed that a resveratrol unit A is connected to a second resveratrol unit B which in turn is connected to a third resveratrol unit C through C-8a/C-12b and C-8b/C-12c, respectively. The correlation of a quaternary carbon at δ 156.9 (C-2c) with an olefinic proton at δ 7.33 (H-7c) in the COLOC spectrum showed that a hydroxyl group is substituted at C-2c on ring C_1, which is also supported by the upper field chemical shift of C-1c (δ 117.2) and the appearance of a set of protons in an ABX system. The presence of the dihydrofuran ring (7b-8b-12c-11c-O) was deduced by the correlation of C-11c/H-7b in the COLOC spectrum. The existence of a second dihydrofuran ring (7a-8a-12b-11b-O) was revealed from the molecular formula and degrees of unsaturation. The compound showed a close resemblance to gnetin E,[14] except for the presence of an additional hydroxyl group attached to ring C_1. The correlations between H-2a(6a)/H-8a, H-10a(14a)/H-7a, H-2b(6b)/H-8b, and H-10b(14b)/H-7b in the nuclear Overhauser and exchange spectroscopy (NOESY) spectrum showed a *trans* orientation of the two dihydrofuran rings. The relative structure of **1** was drawn in relation to gnetin E.

Gnemonol E (**2**), $[\alpha]_D = -14°$, reacted positively with Gibbs reagent. The molecular formula of $C_{42}H_{32}O_{10}$ was deduced by high-resolution negative FAB-MS (*m/z* 695.1921). All protonated and quaternary carbons in **2** were assigned with the help of ^{13}C–^1H COSY, COLOC (Fig. 4), and long-range ^1H–^1H COSY (Fig. 5) experiments. The ^1H-NMR spectra of **2** showed a similar set of protons as that of **1**, but in the case of **2**, C-2b on ring B_1 is substituted with a hydroxyl group instead of C-2c on ring C_1 as in **1**. The correlations between C-2c(6c)/H-7c, C-1c/H-8c, and C-2b/H-7b, and a relatively upper field (δ 120.6) C-1b/H-8b,OH-2b in the COLOC spectrum (Fig. 4) and the correlations in the long-range ^1H–^1H COSY spectrum (Fig. 5) between H-2c(6c)/H-7c and H-6b/H-7b revealed that the ABX-coupled proton system was related to ring B_1 instead of ring C_1 as in compound **1**. The relative stereochemistry of chiral centers at two dihydofurans was determined in a NOESY experiment (Fig. 5) in a similar way as in **1**.

Gnemonol F (**3**), $[\alpha]_D = -18°$, showed a positive reaction to Gibbs reagent. Its molecular formula of $C_{42}H_{32}O_{10}$ was deduced by high-resolution negative FAB-MS (*m/z* 695.1920). The ^1H- and ^{13}C-NMR spectra (Table 1) indicated that **3** is a stilbene trimer. The ^1H-NMR spectrum revealed the presence of two 4-hydroxyphenyl groups (rings A_1, B_1), a 1,2,3,5-tetrasubstituted benzene ring (ring C_2), a 1,2,3,4,5-pentasubstituted benzene ring (ring B_2), a 1,2,4-trisubstituted benzene ring (ring C_1), and a 3,5-dihydroxyphenyl group (ring A_2). A pair of mutually coupled methine protons (H-7a/8a), and a set of mutually coupled methine and methylene (H-7c/H-8c) along with signals of eight phenolic hydroxyl groups were also seen in the spectrum. The correlations observed in the heteronuclear multiple-bond connectivity (HMBC) spectrum (Fig. 6) between H-7a/C-2a(6a), H-8a/C-10a(14a), H-7b/C-2b(6b), H-14b/C-8b, H-7c/C-2c(6c), and H-7c/C-9c and the correlations in the long-range ^1H–^1H COSY spectrum (Fig. 7) between H-2a(6a)/H-7a, H-10a(14a)/H-8a, H-2b(6b)/H-7b, H-14b/H-8b, H-6c/H-7c, and H-14c/H-8c revealed the following linkages C-1a/C-7a, C-8a/C-9a, C-1b/C-7b, C-8b/C-9b, C-1c/C-7c, and C-8c/C-9c, respectively. The correlations also observed in the HMBC spectrum between H-8a/C-12b(11b), H-8b/C-10c, and H-7c/C-9b(11b) revealed the respective connections of C-8a/C-12b, C-8b/C-10c, and C-7c/C-10. The correlations of H-3c, H-5c, H-7c, and OH-3c with a quaternary carbon at δ 120.7 (C-1c) in the HMBC spectrum confirmed the position of the hydroxyl group to be at C-2 on ring C_1, which is supported by the appearance of a set of protons in an ABX system on a 1,2,4-trisubstituted benzene ring (ring C_1) and the upper field shift of C-1c. In the NOESY experiment (Fig. 7), the correlations [H-7a/H-

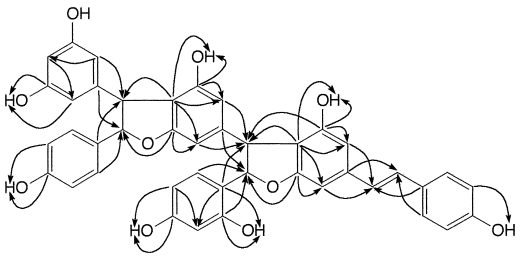

Fig. 4. Correlations in the COLOC Spectrum of **2**

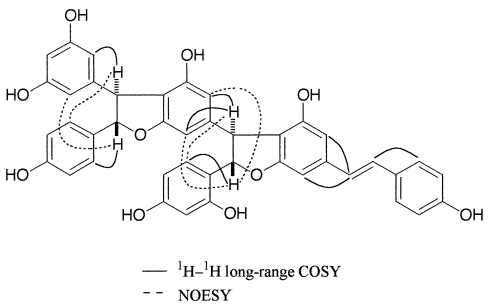

Fig. 5. Correlations in the ^1H–^1H Long-Range COSY and NOESY Spectra of **2**

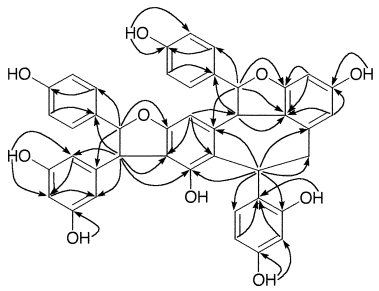

Fig. 6. Correlations in the HMBC Spectrum of **3**

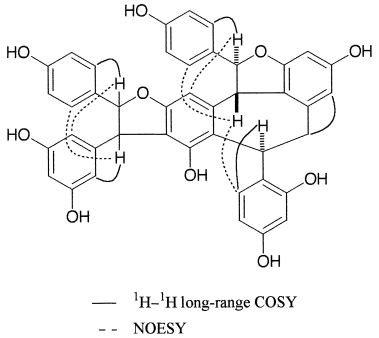

Fig. 7. Correlations in the ^1H–^1H Long-Range COSY and NOESY Spectra of **3**

Table 2. Super Oxide Scavenging Activity and Lipid Peroxide Inhibition

	IC_{50} (μM)	
	Super oxide scavenging activity	Lipid peroxide inhibition
Gnemonol D (**1**)	60	*a)*
Gnemonol E (**2**)	72	47
Gnemonol F (**3**)	13	*a)*
Gnemonol A	65	22
Gnetol	66	61
ε-Viniferin	20	33

a) >100 mM.

10a(14a), H-8a/H-2a(6a), and H-7b/H-14b, H-8b/H-2b(6b)] revealed the orientation of the two dihydrofuran rings to be *trans*. The protons (H-7a/8a and H-7b/8b) in the dihydrofuran rings in **3** showed different coupling constant values (5.1 and 10.8), sometimes the *J* values of the methine protons in the dihydrofuran rings appeared to be different. Similar phenomena were also observed in miyabenol C (1.5, 5.5 Hz),[15] α-viniferin (3.0, 6.0, 10.0),[16] and ampelopsin A (11.7).[17] The H-8b (β) and H-7c (α) configurations were deduced by the correlation between H-8b/H-6c observed in the NOESY experiment and subsequently allowed the relative structure of **3** to be drawn as in Fig. 1. However, no NOE was observed between H-7a(8a) and H-7b(8b) nor H-7c(8c) to allow the complete relative structure of **3** to be determined.

Compounds **1**, **2**, and **3** showed super oxide scavenging activity[18] at 60, 72, and 13 μM (IC_{50}) respectively, and in lipid peroxide inhibitory activity,[19,20] **2** exhibited inhibitory activity at 47 μM (IC_{50}). The results of some other stilbenoids isolated in *Gnetum* species are listed in Table 2. The super oxide scavenging activity and lipid peroxide inhibition showed by the compounds, in addition to other activities such as blood sugar reduction and antiinflammatory activities exhibited by other stilbenoids also found in abundance in *Gnetum* species, revealed that the Gnetaceous plants are an important functional food.

Experimental

General Methods ^{1}H- and ^{13}C-NMR spectra were recorded on EX-400 (JEOL) and AL-300 spectrometers. Chemical shift values are shown as δ values with tetramethylsilane (TMS) as an internal reference. Peak multiplicities are quoted in Hertz. Negative-ion FAB-MS were measured on a JMS-DX 300 spectrometer equipped with a JMA 3500 data analysis system (JEOL), and optical rotations were recorded on a P-1020 (JASCO) polarimeter. UV spectra were recorded on a UV 2200 spectrometer (Shimadzu). Silica gel 60 (70—230 mesh, Merk), Sephadex L-H 20 (Pharmacia), and ODS (100—200 mesh, Fuji Silysia Chemical) were used for column chromatography. Kiesel-gel 60_{254} (Merck) was used for analytical and preparative TLC.

Extraction and Isolation The dried root of *G. gnemon* (2.0 kg), collected in April 2001 in the Bogor Botanical Garden, Indonesia, was powdered and extracted successively with acetone and methanol. The acetone extract of *G. gnemon* (60 g) was chromatographed on silica gel eluted with a mixture of $CHCl_3/CH_3OH$ with increasing polarity to give 11 fractions (fr. A—K). Fr. D was subjected to VLC on ODS eluted with CH_3OH/H_2O 1 : 1 to give 10 subfractions (fr. D_1—D_{10}). Further purification of fr. D_7 by preparative TLC developed with benzene/AcOEt/acetone/H_2O (40 : 30 : 30 : 1) gave **3** (10 mg). Fr. E was chromatographed on Sephadex LH-20 eluted with CH_3OH to give 20 subfractions (fr. E_1—E_{20}). Fr. E_8—E_{13} were combined and subjected to chromatography on Sephadex LH-20 eluted with CH_3OH to give **2** in the initial fractions and **1** (45 mg) in the final fractions. Compound **2** (80 mg) was further purified by preparative TLC developed with $CHCl_3/CH_3OH/H_2O$ (30 : 10 : 1) and $CHCl_3$/AcOEt/acetone/EtOH/H_2O (32 : 8 : 8 : 8 : 1), respectively.

Gnemonol D (**1**): A white amorhous powder; negative-ion HR-FAB-MS $[M-H]^-$ *m/z*: 695.1920 (Calcd for $C_{42}H_{31}O_{10}$: 695.1917); negative-ion FAB-MS $[M-H]^-$ *m/z*: 695; UV λ_{max} (MeOH) nm: 224, 286, 332; $[\alpha]_D$ −22° (*c*=0.2, MeOH). The ^{1}H- and ^{13}C-NMR spectral data are listed in Table 1.

Gnemonol E (**2**): A white amorphous powder; negative-ion HR-FAB-MS $[M-H]^-$ *m/z*: 695.1921 (Calcd for $C_{42}H_{31}O_{10}$: 695.1917); negative-ion FAB-MS $[M-H]^-$ *m/z*: 695; UV λ_{max} (MeOH) nm: 222, 286, 327; $[\alpha]_D$ −14° (*c*=0.4, MeOH). The ^{1}H- and ^{13}C-NMR spectral data are listed in Table 1.

Gnemonol F (**3**): A white amorphous powder; negative-ion HR-FAB-MS $[M-H]^-$ *m/z*: 695.1920 (Calcd for $C_{42}H_{31}O_{10}$: 695.1917); negative-ion FAB-MS $[M-H]^-$ *m/z*: 695; UV λ_{max} (MeOH) nm: 208, 283; $[\alpha]_D$ −18° (*c*=0.1, MeOH). The ^{1}H- and ^{13}C-NMR spectral data are listed in Table 1.

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