Four New Stilbene Oligomers in the Root of *Gnetum gnemon*

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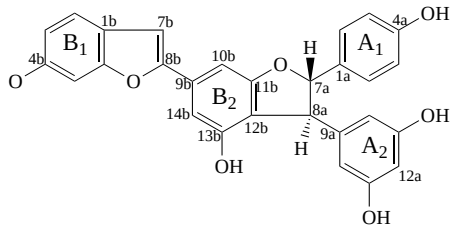
Four new stilbene oligomers, gnemonols G, H, I, and J (**1**–**4**), were isolated from acetone extract of the root of *Gnetum gnemon* along with five known stilbenoids, ampelopsin E, *cis*-ampelopsin E, gnetins C, D, and E. The structures were elucidated on the basis of spectroscopic evidence.

Introduction. – The genus *Gnetum* (Gnetaceae) comprises *ca.* 40 species and is known to contain stilbenoids [1–4]. Various species in the family have been used as folk medicines for the treatment of arthritis, bronchitis, and asthma [2]. In continuation of our studies of *Gnetum* plants [5–8], we report in this paper the isolation and structure elucidation of two novel (gnemonols G (**1**) and H (**2**)) and two new (gnemonols I (**3**) and J (**4**)) stilbene oligomers together with five known stilbenoides, ampelopsin E, *cis*-ampelopsin E [9], and gnetin C, D, and E [10] from acetone-soluble part of the root of *Gnetum gnemon*. The compounds were purified by column chromatography over silica gel, *Sephadex LH-20*, ODS, and PTLC. The structures were characterized on the basis of their spectral data.

Results and Discussion. – Gnemonol G (**1**), a brown amorphous powder, showed a positive reaction to *Gibbs* reagent. The characteristic UV absorption bands at 283, 321, 335 nm showed the presence of a furan ring in the molecule. The negative FAB-MS exhibited an $[M-H]^-$ ion peak at *m*/*z* 467, indicating a molecular weight of 468. The molecular formula $C_{28}H_{20}O_7$ was deduced from HR-FAB-MS *m*/*z* 467.4545 $[M-H]^-$. The ^{1}H-NMR spectrum showed the signals of a set of *ortho*-coupled H-atoms on a *p*-substituted phenyl moiety (7.23 (*d*, *J* = 8.5, H–C(2a), H–C(6a)); 6.85 (*d*, *J* = 8.5, H–C(3a), H–C(5a)), a set of protons in A_2B system on 1,3,5-trisubstituted benzene ring (6.19 (*d*, *J* = 2.2, H–C(10a), H–C(14a)); 6.25 (*t*, *J* = 2.2, H–C(12a))) and a set of *meta*-coupled H-atoms on a 1,2,3,5-tetrasubstituted benzene ring at 6.97 (br. *s*, H–C(10b), H–C(14b)). A set of H-atoms in an *ABX* system on a 1,2,4-trisubstituted benzene ring (7.42 (*d*, *J* = 8.3, H–C(6b)); 7.01 (*d*, *J* = 2.2, H–C(3b)); 6.82 (*dd*, *J* = 8.3, 2.2, H–C(5b))) and a H-atom on 2,3,5-trisubstituted furan ring at 7.12 (br. *s*, H–C(7b)) were also observed in the spectrum. Furthermore, a set of mutually coupled methines (5.43 (*d*, *J* = 4.9, H–C(7a)); 4.43 (*d*, *J* = 4.9, H–C(8a))) and five phenolic OH H-atoms were shown in the spectrum. The ^{1}H- and ^{13}C-NMR spectral data (*Tables 1* and *2*)



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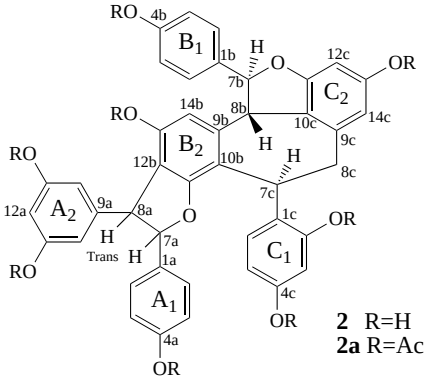
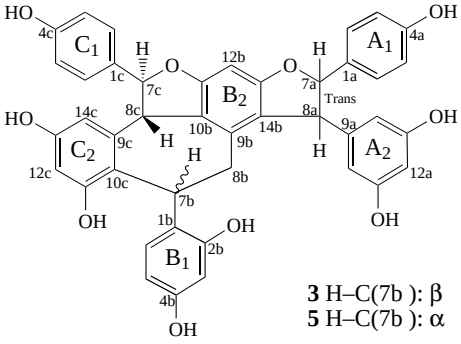
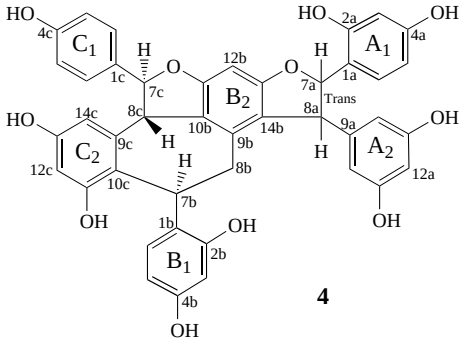


2 R=H
2a R=Ac



3 H–C(7b): β
5 H–C(7b): α



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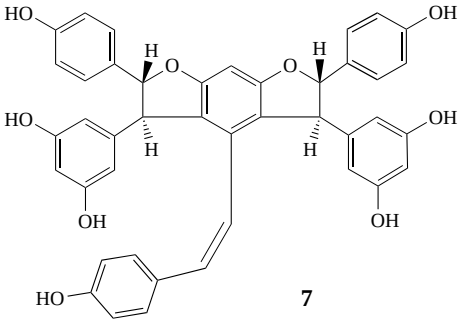

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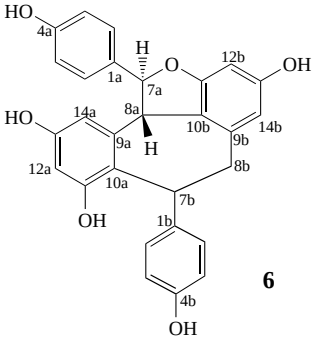

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suggested **1** to be a dimer of resveratrol units. In the HMBC spectrum, the long-range connectivities (*Fig. 1*) between H–C(7a)/C(2a,6a), H–C(8a)/C(10a,14a), H–C(7b)/C(1b,2b), H–C(10b,14b)/C(8b) showed the respective connections between C(1a)/C(7a), C(9a)/C(8a), C(1b)/C(7b), and C(9b)/C(8b). The correlations in the long range ^{1}H,^{1}H-COSY spectrum (*Fig. 1*) between H–C(2a,6a)/H–C(7a), H–C(10a,14a)/H–C(8a) further confirmed the linkages between C(1a)/C(7a) and C(9a)/C(8a). The HMBC correlation between H–C(8a)/C(12b) showed that a

Table 1. *^{1}H-NMR Data of* **1**–**4**

H-Atom	**1**[a]) (*J* [Hz])	**2**[a]) (*J* [Hz])	**3**[b]) (*J* [Hz])	**4**[b]) (*J* [Hz])
H–C(2a)	7.23 (*d*, 8.5)	7.22 (*d*, 8.4)	6.79 (*d*, 8.8)	–
H–C(3a)	6.85 (*d*, 8.5)	6.83 (*d*, 8.4)	6.83 (*d*, 8.8)	6.42 (*d*, 2.4)
H–C(5a)	6.85 (*d*, 8.5)	6.83 (*d*, 8.4)	6.83 (*d*, 8.8)	6.22 (*dd*, 8.4, 2.4)
H–C(6a)	7.23 (*d*, 8.5)	7.22 (*d*, 8.4)	6.79 (*d*, 8.8)	6.96 (*d*, 8.4)
H–C(7a)	5.43 (*d*, 4.9)	5.37 (*d*, 5.6)	5.07 (*d*, 6.8)	5.76 (*d*, 3.0)
H–C(8a)	4.43 (*d*, 4.9)	4.37 (*d*, 5.6)	3.91 (*d*, 6.8)	4.26 (*d*, 3.0)
H–C(10a)	6.19 (*d*, 2.2)	6.11 (*d*, 2.0)	6.11 (br. *s*)	6.34 (*d*, 2.1)
H–C(12a)	6.25 (*t*, 2.2)	6.16 (*t*, 2.0)	6.21 (br. *s*)	6.20 (*t*, 2.1)
H–C(14a)	6.19 (*d*, 2.2)	6.11 (*d*, 2.0)	6.11 (br. *s*)	6.34 (*d*, 2.1)
H–C(2b)	–	7.20 (*d*, 8.4)	–	–
H–C(3b)	7.01 (*d*, 2.2)	6.76 (*d*, 8.4)	6.35 (*d*, 2.4)	6.12 (*d*, 2.4)
H–C(5b)	6.82 (*dd*, 8.3, 2.2)	6.76 (*d*, 8.4)	5.98 (*dd*, 8.3, 2.4)	6.17 (*dd*, 8.4, 2.4)
H–C(6b)	7.42 (*d*, 8.3)	7.20 (*d*, 8.4)	6.16 (*d*, 8.3)	6.47 (*d*, 8.4)
H–C(7b)	7.12 (br. *s*)	5.76 (*d*, 11.2)	5.15 (br. *s*)	4.91 (*t*, 3.9)
H–C(8b)	–	4.57 (*d*, 11.2)	3.17 (*dd*, 13.8, 5.9), 2.85 (br. *d*, 13.8)	3.30 (br. *d*, 17.4), 2.90 (br. *d*, 17.4)
H–C(10b)	6.97 (br. *s*)[c])	–	–	–
H–C(12b)	–	–	5.92 (br. *s*)	6.28 (br. *s*)
H–C(14b)	6.97 (br. *s*)[c])	6.33 (br. *s*)	–	–
H–C(2c)	–	–	7.51 (*d*, 8.8)	7.16 (*d*, 8.7)
H–C(3c)	–	6.29 (*d*, 2.4)	6.95 (*d*, 8.8)	6.75 (*d*, 8.7)
H–C(5c)	–	6.18 (*dd*, 8.4, 2.4)	6.95 (*d*, 8.8)	6.75 (*d*, 8.7)
H–C(6c)	–	7.00 (*d*, 8.4)	7.51 (*d*, 8.8)	7.16 (*d*, 8.7)
H–C(7c)	–	4.95 (br. *s*)	5.80 (*d*, 9.3)	5.87 (*d*, 10.8)
H–C(8c)	–	3.45 (*dd*, 17.5, 2.5), 3.35 (*dd*, 17.5, 3.2)	5.19 (*d*, 9.3)	4.58 (*d*, 10.8)
H–C((12c)	–	6.10 (br. *s*)	6.24 (br. *s*)[c])	6.36 (br. *s*)
H–C(14c)	–	6.31 (br. *s*)	6.24 (br. *s*)[c])	6.35 (br. *s*)
HO–C(2a)	–	–	–	8.50 (br. *s*)
HO–C(4a)	8.54 (br. *s*)	8.37 (br. *s*)	8.41 (br. *s*)	8.17 (br. *s*)
HO–C(11a/13a)	8.16 (br. *s*)	8.04 (br. *s*)	8.14 (br. *s*)	8.13 (br. *s*)
HO–C(2b)	–	–	8.23 (br. *s*)	8.13 (br. *s*)
HO–C(4b)	8.43 (br. *s*)[d])	8.42 (br. *s*)	7.97 (br. *s*)	7.94 (br. *s*)
HO–C(13b)	8.33 (br. *s*)[d])	7.85 (br. *s*)	–	–
HO–C(2c)	–	7.54 (br. *s*)	–	–
HO–C(4c)	–	7.98 (br. *s*)	8.62 (br. *s*)	8.42 (br. *s*)
HO–C(11c)	–	-	7.70 (br. *s*)	8.76 (br. *s*)
HO–C(13c)	–	8.15 (br. *s*)	8.05 (br. *s*)	8.14 (br. *s*)

[a]) 300 MHz, (D_6)Acetone. [b]) 400 MHz, (D_6)Acetone. [c]) Overlapped. [d]) Interchangeable.

resveratrol unit A is connected to another resveratrol-like unit B through a bond at C(8a) and C(12b). The correlation in the HMBC spectrum between a quaternary C-atom C(2b) (δ 156.8) with an aromatic methine H–C(7b) (δ 7.12) suggested that C(2) on the ring B_1 was occupied with an oxygenated function, which was supported by the upfield shift (δ 122.6) of the signal of C(1b) and the appearance of the signals of the aromatic protons (H–C(3b, 5b, and 6b)) as an *ABX* system. The correlation in the HMBC spectrum (*Fig. 1*) between H–C(10b)/C(8b) and H–C(7b)/C(8b,1b,2b) revealed the presence of a trisubstituted furan ring (C(8b)–C(7b)–C(1b)–C(2b)–O). The presence of a dihydrofuran ring

Table 2. *^{13}C-NMR Data of* **1**–**4**

C-Atom	**1**[a])	**2**[a])	**3**[b])	**4**[b])
C(1a)	133.5	134.2	133.5	121.0
C(2a)	127.9	127.6	129.4	156.0
C(3a)	116.2	116.0	116.1	103.5
C(4a)	158.3	158.0	158.2	158.9
C(5a)	116.2	116.0	116.1	107.4
C(6a)	127.9	127.6	129.4	127.6
C(7a)	93.8	93.3	95.0	89.2
C(8a)	55.9	56.6	55.8	55.7
C(9a)	146.0	146.1	148.3	147.4
C(10a)	106.7	106.6	107.1	107.2[c])
C(11a)	159.7	159.2	159.4	159.7
C(12a)	102.1	101.7	101.7	102.0
C(13a)	159.7	159.2	159.4	159.7
C(14a)	106.7	106.6	107.1	107.2[c])
C(1b)	122.6	131.6	123.2	120.2
C(2b)	156.8[c])	130.0	155.7	156.4
C(3b)	98.4	115.9	102.8	103.7
C(4b)	156.8[c])	158.4	156.9	157.8
C(5b)	113.3	115.9	106.2	107.2[c])
C(6b)	122.1	130.0	131.7	128.6
C(7b)	102.4	88.4	35.4	32.0
C(8b)	155.6	50.1	32.8	31.6
C(9b)	133.9	141.9	136.8	135.0
C(10b)	98.0	117.0	119.6	120.0
C(11b)	163.2	160.8	159.8	160.3
C(12b)	116.1	112.6	89.1	90.4
C(13b)	155.8	152.9	161.3	161.5
C(14b)	105.7	96.6	121.4	121.3
C(1c)		120.3	133.9	131.5
C(2c)		156.9	130.2	129.9
C(3a)		103.6	116.4	116.1
C(4c)		157.6	158.4	158.5
C(5c)		106.4	116.4	116.1
C(6c)		128.3	130.2	129.9
C(7a)		34.2	93.6	88.4
C(8a)		34.9	52.3	49.3
C(9c)		138.6	141.9	143.0
C(10c)		119.0	121.9	120.5
C(11c)		160.5	157.3	155.6
C(12c)		95.6	101.9	101.7
C(13c)		158.7	156.6	157.4
C(14c)		108.2	106.8	105.3

[a]) 75 MHz, (D_6)Acetone. [b]) 100 MHz, (D_6)Acetone. [c]) Overlapped.

(C(7a)–C(8a)–C(12b)–C(11b)–O) was also shown by the correlation between H–C(7a)/C(11b). The *trans*-orientation of the dihydrofuran ring was deduced from the NOEs (*Fig. 1*) observed between H–C(7a)/H–C(10a,14a) and H–C(8a)/H–C(2a,6a) in the NOESY spectrum. These results allowed the relative structure of **1** to be drawn as given above.

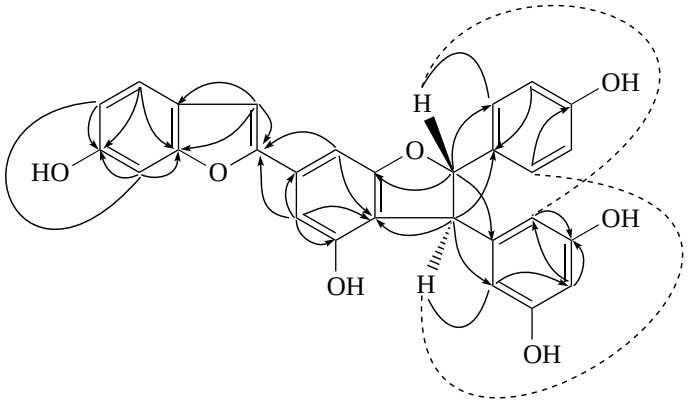

Fig. 1. *Correlations in the HMBC spectrum* (↷), *in the* $^1H,^1H$ *long-range COSY spectrum* (⌒), *and in NOESY spectrum* (⌒) *of* **1**

Gnemonol H (**2**), a brown amorphous powder, showed positive reaction to the *Gibbs* reagent. The negative FAB-MS exhibited an $[M-H]^-$ ion peak at *m*/*z* 695. The molecular formula $C_{42}H_{32}O_{10}$ was deduced from HRFAB-MS *m*/*z* 695.1920 $[M-H]^-$. The ^{1}H-NMR spectrum exhibited signals of two sets of A_2B_2 H-atoms on two 4-hydroxybenzene rings (7.22 (*d*, *J* = 8.4, H−C(2a), H−C(6a)); 6.83 (*d*, *J* = 8.4, H−C(3a), H−C(5a)); 7.20 (*d*, *J* = 8.4, H−C(2b), H−C(6b)); 6.76 (*d*, *J* = 8.4, H−C(3b), H−C(5b)), a set of *AB* H-atoms on 1,2,3,5-tetrasubstituted benzene ring (6.31 (br. *s*, H−C(14c)); 6.10 (br. *s*, H−C(12c))) and a set of A_2B H-atoms on a 1,3,5-trisubstituted benzene ring (6.16 (*t*, *J* = 2.0, H−C(12a)); 6.11 (*d*, *J* = 2.0, H−C(10a), H−C(14a))). The spectrum also showed a set of protons in *ABX* system on the 1,2,4-trisubstituted benzene ring (7.00 (*d*, *J* = 8.4, H−C(6c)); 6.29 (*d*, *J* = 2.4, H−C(3c)); 6.18 (*dd*, *J* = 8.4, 2.4, H−C(5c))) and an aromatic H-atom on 1,2,3,4,5-pentasubstituted benzene ring (6.33 (br. *s*, , H−C(14b))). Furthermore, two sets of mutually coupled methines (5.37 (*d*, *J* = 5.6, H−C(7a)); 4.37 (*d*, *J* = 5.6, H−C(8a)); 5.76 (*d*, *J* = 11.2, H−C(7b)); 4.57 (*d*, *J* = 11.2, H−C(8b))), a set of mutually coupled CH and CH_2 H-atoms (4.95 (br. *s*, H−C(7c)); 3.45 (*dd*, *J* = 17.5, 2.5, H−C($8c_a$)), 3.35 (*dd*, *J* = 17.5, 3.2, H−C($8c_b$))), and eight phenolic OH H-atoms were observed in the spectrum. Considering the molecular formula and the ^{1}H- and ^{13}C-NMR spectral data (*Tables 1* and *2*), **2** is a trimer of resveratrol units. The correlations in the HMBC spectrum (*Fig. 2*) H−C(7a)/C(2a,6a), H−C(8a)/C(10a,14a), H−C(7b)/C(2b,6b), H−C(8b)/C(14b), and H−C(6c)/C(7c), and long-range ^{1}H,^{1}H-COSY correlations (*Fig. 3*) between H−C(2a,6a)/H−C(7a), H−C(10a,14a)/H−C(8a), H−C(2b,6b)/H−C(7b), H−C(14b)/H−C(8b), and H−C(6c)/H−C(7c), revealed the respective linkages between C(1a)/C(7a), C(8a)/C(9a), C(1b)/C(7b), C(8b)/C(9b), and C(1c)/C(7c). The HMBC correlation between H−C(7c)/C(10b,11b) showed the connectivity of C(7c) and C(10b). In the HMBC spectrum, the correlations of H−C(3c, 5c, and 7c) with a relatively upfield-shifted quaternary C-atom C(1c) (δ 120.3) revealed an OH group at C(2) of the ring C_1, which is also supported by the appearance of aromatic protons (H−C(3c,5c,6c)) in an *ABX* system. The presence of a dihydrofuran ring (C(7a)−C(8a)−C(12b)−C(11b)−O) was supported by the HMBC correlation

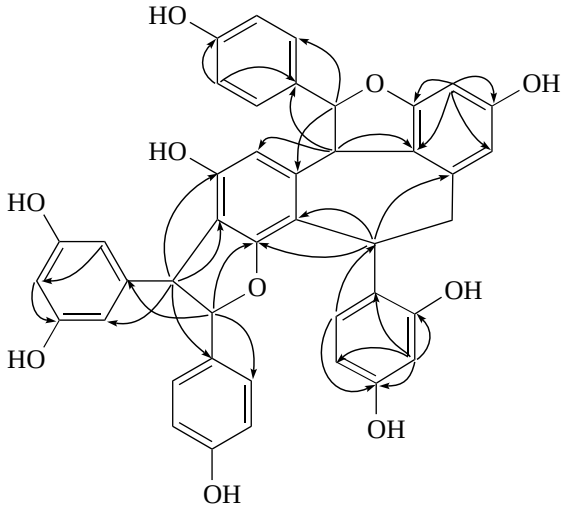

Fig. 2. *Correlations in the HMBC spectrum of* **2**

between H–C(7a)/C(11b). The presence of a second dihydrofuran ring (C(7b)–C(8b)–C(10c)–C(11c)–O) and a seven-membered ring (C(8b)–C(9b)–C(10b)–C(7c)–(8c)–C(9c)–(10c)) fused with this dihydrofuran ring was deduced from the molecular formula and the degrees of unsaturation. The condensation of ampelopsin B (**6**) [11] with a resveratrol at C(11a) and C(12a) might constitute the formation of the planar skeleton of **2**. The NOEs between H–C(7a)/H–C(10a,14a), H–C(8a)/H–C(2a,6a), and H–C(7b)/H–C(14b), H–C(8b)/H–C(2b,6b) in the NOESY spectrum (*Fig. 3*) revealed a *trans*-orientation of the two dihydrofuran rings. Similarly, the NOEs between H–C(8b)/H–C(6c)

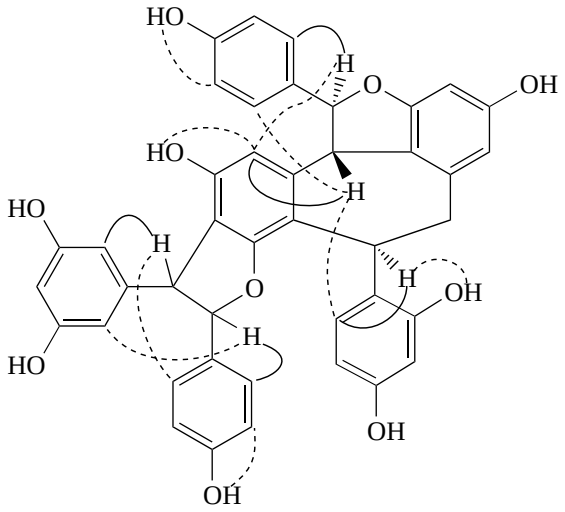

Fig. 3. *Correlations in the* $^1H,^1H$ *long-range COSY spectrum* (⌒) *and in NOESY spectrum* (⋰) *of* **2**

revealed the relative configurations at C(8b) and C(7c) to be β and α, respectively. Thus, the relative structure of **2** corresponds to that shown above.

Gnemonol I (**3**) is a stereoisomer of gnemonol A (**5**) [7]. The NMR chemical shifts (^{1}H and ^{13}C) were assigned with the aid of HMBC spectrum (*Fig. 4*). The relative configurations at C(8c) and C(7b), β and β were confirmed by NOEs observed

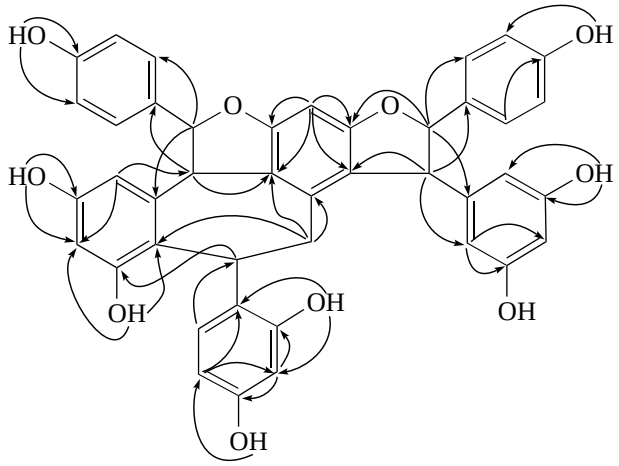

Fig. 4. *Correlations in the HMBC spectrum of* **3**

between H–C(8c)/H–C(7b) in the NOESY spectrum. Then, the relative structure of **3** is as given above. Condensation of ampelopsin B (**6**) [11] with a resveratrol at C(13b) and C(14b) led to **3**. Enzymatically, **3** will also be formed through *cis*-ampelopsin E (**7**), which has been isolated from the same species.

Gnemonol J (**4**) is also a trimer of resveratrol units. The ^{1}H- and ^{13}C-NMR spectral data assigned on the basis of correlations in the HMBC spectrum (*Fig. 5*) showed

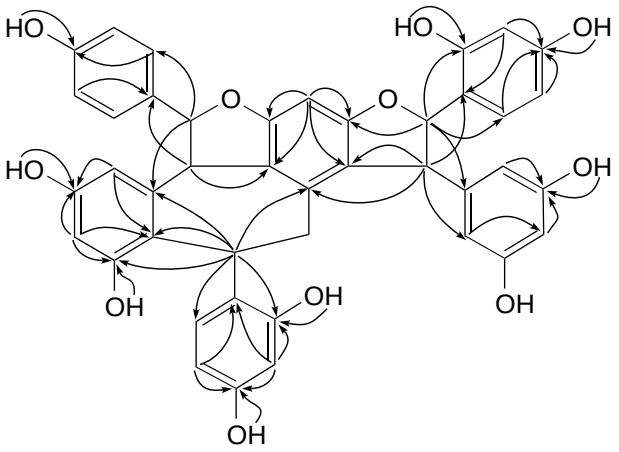

Fig. 5. *Correlations in the HMBC spectrum of* **4**

similarity to **3**. The differences were that **4** had another OH group at C(2a) compared with **3**, and the relative configurations at C(8c) (β) and C(7b) (α) were supported by the NOEs observed between H–C(8c)/H–C(6c) in the NOESY spectrum. The relative structure of **4** was as shown above, and, accordingly, **4** is a hydroxy derivative of gnemonol A (**5**) [7].

cis-Ampelopsin E (**7**) is the first enantiomer isolated ($[\alpha]_D = +118$). Previously, it has been reported by *Oshima* and *Ueno* [9] as a racemate.

Experimental Part

General. Anal. TLC: *Merck* Kieselgel F_{254} (0.25 mm). Prep. TLC: *Merck* Kieselgel F_{254} (0.5 mm). Column Chromatography (CC): *Merck* Kieselgel *60* (70–230 mesh), *Sephadex LH-20*, and *Merck Sep-Pak* C_{18} and tC_{18} cartridges. Optical Rotation: *JASCO P-1020* polarimeter. UV Spectra: *Shimadzu UV-2200* spectrophotometer. NMR Spectra: *EX-400* and *AL 300* spectrometers (*JEOL*) with TMS as an internal standard. FAB-MS: *JOEL JMX-DX-300*.

Plant Material. Root of *Gnetum gnemon* was collected in April 2001 at Bogor Botanical Garden, Indonesia.

Extraction and Isolation. The dried root of *G. gnemon* (2.0 kg) was powdered and extracted successively with acetone, MeOH, and 70% MeOH. The acetone extract (60 g) was chromatographed on silica gel eluted with a mixture of $CHCl_3$/MeOH by increasing polarity to give 11 fractions ($A-K$). *Fr. B* was chromatographed over an *ODS Sep-Pak* C_{18} cartridge eluted with MeOH/H_2O 1:1 to give 20 subfractions (20 ml each, B_1-B_{20}). Compound **1** (8 mg) was obtained from subfractions $B_{17}-B_{20}$ after purification by CC with *Sephadex LH-20* (MeOH), and gnetin C (30 mg) was also obtained from subfractions B_9-B_{16}. *Fr. D* was subjected to VLC on *ODS* eluted with MeOH/H_2O 1:1 to give 10 subfractions (D_1-D_{10}). Further purification of subfraction D_8 by prep. TLC with benzene/AcOEt/acetone/H_2O 40:30:30:1 gave **2** (12 mg). Ampelopsin E (70 mg) and *cis*-ampelopsin E (**5**, 67 mg) were obtained from subfraction D_2 by CC over *ODS* eluted with MeOH/H_2O 1:1. *Fr. E* was chromatographed over *Sephadex LH-20* (MeOH) to give 40 subfractions (30 ml each, E_1-E_{40}). Compound **3** (20 mg) was purified from subfractions E_5-E_9 by prep. TLC with benzene/AcOEt/acetone/H_2O 40:30:30:1 and $CHCl_3$/AcOEt/acetone/EtOH/H_2O 32:8:8:8:1. Compound **4** (13 mg) was obtained from *Fr. G* after purification by CC with *Sephadex LH-20* (MeOH) and C_{18} *SepPak* cartridge eluted with MeOH/H_2O 25:75. Gnetin E (1.5 g) and D (29 mg) were obtained from *Fr. C* by VLC on *ODS* eluted with MeOH/H_2O 1:1.

Acetylation of **2**. Gnemonol H (5 mg) was dissolved in a mixture of pyridine (0.5 ml) and Ac_2O (0.5 ml). The mixture was treated in a usual manner after stirring at r.t. for 20 h. The crude product (7.3 mg) was purified by prep. TLC with hexane/acetone 3:2 to afford an octa-acetate **2a** as an amorpous white solid (5 mg).

Gnemonol G (**1**). A brown amorphous powder. $[\alpha]_D = -33$ ($c = 0.16$, MeOH). UV: 224, 256, 283, 321, 335. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*, resp. FAB-MS (neg.): 467 ($[M-H]^-$). HR-FAB-MS (neg.): 467.4545 ($[M-H]^-$, $C_{28}H_{19}O_7$; calc. 467.4542).

Gnemonol H (**2**). A brown amorphous powder. $[\alpha]_D = +36$ ($c = 0.12$, MeOH). UV: 208, 283. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*, resp. FAB-MS (neg.): 695 ($[M-H]^-$). HR-FAB-MS (neg.): 695.120 ($[M-H]^-$, $C_{42}H_{31}O_{10}$; calc. 695.1917).

Gnemonol H Octaacetate (**2a**). ^{1}H-NMR ((D$_6$)acetone, 400 MHz): 7.49 (d, $J = 8.8$, H–C(2a), H–C(6a)); 7.40 (d, $J = 8.8$, H–C(2b), H–C(6b)); 7.35 (d, $J = 8.8$, H–C(6c)); 7.18 (d, $J = 8.8$, H–C(3a), H–C(5a)); 7.11 (d, $J = 8.8$, H–C(3b), H–C(5b)); 6.92 (dd, $J = 8.8, 2.4$, H–C(5c)); 6.90 (t, $J = 2.0$, H–C(12a)); 6.83 (d, $J = 2.0$, H–C(10a), H–C(14a)); 6.82 (d, $J = 2.4$, H–C(3c)); 6.68 (s, H–C(14b)); 6.65 (d, $J = 2.0$, H–C(14c)); 6.45 (d, $J = 2.0$, H–C(12c)); 6.07 (d, $J = 10.8$, H–C(7b)); 5.69 (d, $J = 8.8$, H–C(7a)); 5.02 (br. s, H–C(7c)); 4.62 (d, $J = 8.8$, H–C(8a)); 4.49 (d, $J = 10.8$, H–C(8b)); 3.67, 3.46 (br. d, $J = 15.2$, 2 H–C(8c)); 2.10, 2.23, 2.24, 2.25, 2.27 (8 AcO).

Gnemonol I (**3**). A brown amorphous powder. $[\alpha]_D = -70$ ($c = 0.37$, MeOH). UV: 209, 285. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*, resp. FAB-MS (neg.): 695 ($[M-H]^-$). HR-FAB-MS (neg.): 695.1914 ($[M-H]^-$, $C_{42}H_{31}O_{10}$; calc. 695.1917).

Gnemonol J (**4**). A brown amorphous powder. $[\alpha]_D = -168$ ($c = 0.12$, MeOH). UV: 212, 284. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*, resp. FAB-MS (neg.): 711 ($[M-H]^-$). HR-FAB-MS (neg.): 711.1940 ($[M-H]^-$, $C_{42}H_{31}O_{11}$; calc. 711.1945).

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