Five Stilbene Glucosides from *Gnetum gnemonoides* and *Gnetum africanum*

by **Ibrahim Iliya**[a]), **Toshiyuki Tanaka***[b]), **Munekazu Iinuma**[a]), **Miyuki Furusawa**[b]), **Zulfiqar Ali**[b]), **Ken-ichi Nakaya**[b]), **Jin Murata**[c]), and **Dedy Darnaedi**[d])

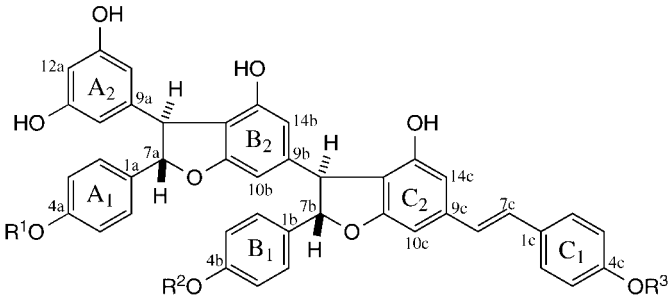
[a]) Gifu Pharmaceutical University, 5-6-1, Mitahora-higashi, Gifu 502-8585, Japan
[b]) Gifu Prefectural Institute of Health and Environmental Sciences, 1-1 Naka-fudogaoka, Kakamigahara 504-0838, Japan (Tel: 0583-80-2120, fax: 0583-71-5016, e-mail: yhy06063@nifty.ne.jp)
[c]) Botanical Gardens, Koishikawa, Graduate School of Science, University of Tokyo, 3-7-1, Hakusan, Bunkyo-Ku, Tokyo, 112-0001, Japan
[d]) Indonesian Institute of Sciences, Jalan Ir. H. Juanda 13, Bogor 16122, Indonesia

Five new stilbene glucosides, gnemonosides F, G, H, I, and J were isolated from the stem lianas of *Gnetum gnemonoides* BRONGN and *Gnetum africanum* WELW along with nine known stilbenoids. The structures of the new compounds were elucidated as gnetin E 4a,4b,4c-*O*-*β*-triglucopyranoside (**2**), gnetin E 4a,4c-*O*-*β*-diglucopyranoside (**3**), gnetin C 4a,4b,11a-*O*-*β*-triglucopyranoside (**4**), gnetin D 4a,4b-*O*-*β*-diglucopyranoside (**5**), and gnetuhainin A 4a,4b-*O*-*β*-diglucopyranoside (**6**) on the basis of spectroscopic evidence.

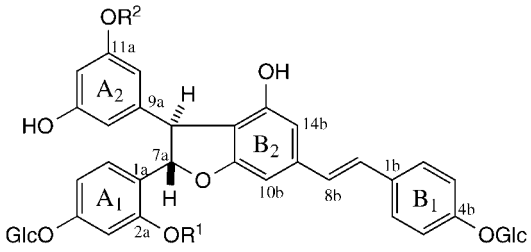
Introduction. – The family of Gnetaceae comprises of *ca*. 40 species, distributed in the tropical rain forest. Many species in the family of Gnetaceae are used as food [1][2], as well as medicines and are known to contain stilbenoids [3]. In our previous report on the chemical constituents of *G. gnemoniodes* [4], the structures of dimeric stilbene glucosides were discussed. Further investigation of the polar fractions of *G. gnemonoides* and *G. africanum* resulted in the isolation of five new stilbenoids; gnemonosides F (**2**), G (**3**), H (**4**), I (**5**), and J (**6**). In addition, gnetin E and eight known stilbene glucosides; gnemonoside A (**7**), gnemonoside B, resveratroloside, resveratrol 3,4′-*O*-*β*-diglucopyranoside, piceatanol 4′-*O*-*β*-glucopyranoside, piceatanol 3,4′-*O*-*β*-diglucopyranoside, gnetofolin E, and gnetofolin K were also isolated. The structures of the compounds were determined by spectroscopic analysis.

Results and Discussion. – The polar fractions of acetone extracts of the stem lianas of *G. gnemonoides* and *G. africanum* were subjected to column chromatographic techniques (silica gel, *Sephadex LH-20* and *Sek-Pak* C_{18} cartridges (reverse-phase (RP) chromotography) to lead to the isolation of gnemonosides F (**2**) and G (**3**) from *G. gnemonoides*, gnemonoside I (**5**) and J (**6**) from *G. africanum*, and gnemonoside H (**4**) from both species.

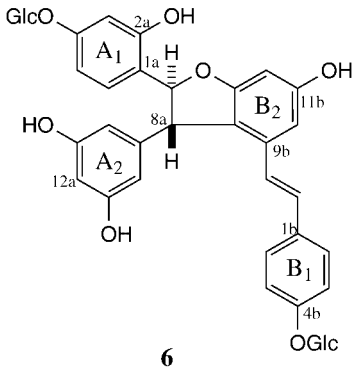
Gnemonoside F (**2**), a white amorphous powder, showed a strong reaction to *Gibbs* reagent. The $[M-H]^-$ ion peak at *m*/*z* 1165 in the negative FAB-MS corresponded to the molecular formula $C_{60}H_{62}O_{24}$. The ^{1}H-NMR spectrum showed the presence of three 4-hydroxyphenyl groups at 7.03 (*d*, *J* = 8.3, H−C(3a), H−C(5a)) and 7.23 (*d*, *J* = 8.3, H−C(2a), H−C(6a)), 7.03 (*d*, *J* = 8.8, H−C(3b), H−C(5b)) and 7.28 (*d*, *J* = 8.8, H−C(2b), H−C(6b)), and 7.03 (*d*, *J* = 8.3, H−C(3c), H−C(5c)) and 7.54 (*d*, *J* = 8.3,



1 $R^1 = R^2 = R^3 = H$ (Gnetin E)
2 $R^1 = R^2 = R^3 = Glc$
3 $R^1 = R^3 = Glc$, $R^2 = H$



4 $R^1 = H$, $R^2 = Glc$
5 $R^1 = OH$, $R^2 = H$
7 $R^1 = H$, $R^2 = H$ (Gnemonoside A)



6

H–C(2c), H–C(6c)), two sets of *meta*-coupled aromatic H-atoms on a 1,3,4,5-tetrasubstituted benzene ring at 6.16 (br. *s*, H–C(14b)) and 6.23 (br. *s*, H–C(10b)), and 6.55 (br. *s*, H–C(14c)) and 6.75 (br. *s*, H–C(10c)), and a set of 3,5-dihydroxyphenyl groups at 6.00 (*d*, $J = 2.2$, H–C(10a), H–C(14a)) and 6.05 (*t*, $J = 2.2$, H–C(12a)). The presence of two pairs of CH H-atoms at 4.24 (*d*, $J = 5.4$, H–C(8a)) and 5.36 (*d*, $J = 5.4$, H–C(7a)), and 4.36 (*d*, $J = 4.2$, H–C(8b)) and 5.50 (*d*, $J = 4.2$, H–C(7b)), a pair of olefinic H-atoms at 7.04 (*d*, $J = 16.6$, H–C(8a) and 7.11 (*d*, $J = 16.6$, H–C(7c)), and signals due to three anomeric H-atoms at 4.87 (*d*, $J = 7.5$, Glc–H–C(1a), H–C(1b)) and 4.89 (*d*, $J = 7.5$, Glc–H–C(1c)) were also observed in the spectrum in addition to four phenolic OH groups at 9.13 (br. *s*, OH–C(11a), OH–C(13a)), 9.27 (OH–C(13b)), and 9.45 (br. *s*, OH–C(13c)). The ^{1}H- and ^{13}C-NMR spectral data (*Tables 1* and *2*) showed a closed resemblance to those of gnetin E (**1**) [5]. The presence of three anomeric H-atoms and the molecular weight indicated that **2** is a triglucoside of gnetin E. The correlations in COLOC spectrum (*Fig. 1*) observed between C(11b)/H–C(7a,8a), C(12b)/H–C(7a,8a), C-(11c)/H–C(7b,8b), and C(12c)/H–C(7b,8b) revealed the respective linkages between C(7a)/C(11b), C(8a)/C(12b), C(7b)/C(11c), and C(8b)/C(12c). The C–H COSY and COLOC spectra allowed the assignment of all protonated and quaternary C-atoms in **2**. Although no correlation was observed between the anomeric H-atoms and corresponding aglycone C-atoms in the COLOC spectrum, the chemical shifts of *ca.* 0.29 ppm downfield observed at H–C(3a,5a), H–C(3b,5b), and H–C(3c,5c) as compared to those of **1**, indicated that the three glucose molecules must be attached to

Table 1. *^{1}H-NMR Data* (*J* [Hz]) *of Compounds* **1**–**6**

H-Atom	**1**[a])	**2**[a])	**3**[b])	**4**[a])	**5**[a])	**6**[a])
H–C(2a)	7.16 (*d*, 8.8)	7.23 (*d*, 8.3)	7.28 (*d*, 8.8)	7.27 (*d*, 8.8)		
H–C(3a)	6.74 (*d*, 8.8)	7.03 (*d*, 8.3)	7.07 (*d*, 8.8)	7.09 (*d*, 8.8)	6.22 (*d*, 2.0)	6.63 (*d*, 2.0)
H–C(5a)	6.74 (*d*, 8.8)	7.03 (*d*, 8.3)	7.07 (*d*, 8.8)	7.09 (*d*, 8.8)	6.51 (*dd*, 2.0, 8.8)	6.40 (*dd*, 2.0, 8.4)
H–C(6a)	7.16 (*d*, 8.8)	7.23 (*d*, 8.3)	7.28 (*d*, 8.8)	7.27 (*d*, 8.8)	7.08 (*d*, 8.8)	6.95 (*d*, 8.4)
H–C(7a)	5.27 (*d*, 6.0)	5.36 (*d*, 5.4)	5.43 (*d*, 5.6)	5.37 (*d*, 4.8)	5.67 (*d*, 5.0)	5.60 (*d*, 3.6)
H–C(8a)	4.22 (*d*, 6.0)	4.24 (*d*, 5.4)	4.38 (*d*, 5.6)	4.38 (*d*, 4.8)	4.35 (*d*, 5.0)	4.38 (*d*, 3.6)
H–C(10a)	5.97 (*d*, 2.0)	6.00 (*d*, 2.2)	6.19 (*d*, 2.0)	6.44 (*t*, 2.0)	6.21 (*d*, 2.0)	6.10 (*d*, 2.0)
H–C(12a)	6.03 (*t*, 2.0)	6.05 (*t*, 2.2)	6.24 (*t*, 2.0)	6.37 (*t*, 2.0)	6.12 (*t*, 2.0)	6.03 (*t*, 2.0)
H–C(14a)	5.97 (*d*, 2.0)	6.00 (*d*, 2.2)	6.19 (*d*, 2.0)	6.23 (*t*, 2.0)	6.21 (*d*, 2.0)	6.10 (*d*, 2.0)
H–C(2b/6b)	7.10 (*d*, 8.4)	7.28 (*d*, 8.8)	7.25 (*d*, 8.8)	7.40 (*d*, 8.8)	7.47 (*d*, 8.8)	7.28 (*d*, 8.4)
H–C(3b/5b)	6.74 (*d*, 8.4)	7.03 (*d*, 8.8)	6.85 (*d*, 8.8)	7.11 (*d*, 8.8)	7.06 (*d*, 8.8)	6.95 (*d*, 8.4)
H–C(7b)	5.40 (*d*, 4.0)	5.50 (*d*, 4.2)	5.48 (*d*, 4.4)	7.07 (*d*, 16.0)	7.05 (*d*, 16.0)	6.87 (*d*, 16.0)
H–C(8b)	430 (*d*, 4.0)	4.36 (*d*, 4.2)	4.49 (*d*, 4.4)	6.97 (*d*, 16.0)	6.95 (*d*, 16.0)	6.67 (*d*, 16.0)
H–C(10b)	6.16 (br. *s*)	6.23 (br. *s*)	6.33 (br. *s*)	6.67 (br. *s*)	6.69 (br. *s*)	6.31 (br. *s*)
H–C(14b)	6.13 (br. *s*)	6.16 (br. *s*)	6.25 (br. *s*)	6.54 (br. *s*)	6.50 (br. *s*)	6.60 (br. *s*)
H–C(2c/6c)	7.40 (*d*, 8.4)	7.54 (*d*, 8.3)	7.52 (*d*, 8.8)			
H–C(3c/5c)	6.76 (*d*, 8.4)	7.03 (*d*, 8.3)	7.07 (*d*, 8.8)			
H–C(7c)	7.03 (*d*, 16.0)	7.11 (*d*, 16.6)	7.15 (*d*, 16.0)			
H–C(8c)	6.91 (*d*, 16.0)	7.04 (*d*, 16.6)	7.05 (*d*, 16.0)			
H–C(10c)	6.67 (br. *s*)	6.75 (br. *s*)	6.74 (br. *s*)			
H–C(14c)	6.50 (br. *s*)	6.55 (br. *s*)	6.64 (br. *s*)			

[a]) $(CD_3)_2SO$. [b]) $(CD_3)_2SO$.

Table 2. *^{13}C-NMR Data of Compounds* **1**–**6**

C-Atom	**1**[a])	**2**[a])	**3**[b])	**4**[a])	**5**[a])	**6**[a])
C(1a)	131.7	135.4	132.6	130.8	122.3	121.5
C(2a)	127.2	127.1	127.6	126.5	156.4	155.8
C(3a)	115.3	116.5	117.6	116.3	102.0	103.4
C(4a)	157.3	157.24	157.3	157.04	157.7	157.0
C(5a)	115.3	116.5	117.6	116.3	107.1	106.0
C(6a)	127.2	127.1	127.6	126.5	128.2	127.3
C(7a)	91.9	92.1	93.4	91.5	89.7	89.2
C(8a)	54.1	54.6	56.1	60.4	54.5	55.1
C(9a)	145.7	144.7	146.7	144.6	146.0	146.8
C(10a)	105.5	105.6	106.8	107.7	106.5	105.5
C(11a)	158.4	158.4	159.6	157.01	159.3	158.4
C(12a)	100.8	101.2	101.9	103.5	101.4	100.9
C(13a)	158.4	158.4	159.6	158.7	159.3	158.4
C(14a)	105.5	105.6	106.8	107.2	106.5	105.5
C(1b)	128.1	134.95	134.2	130.8	131.5	130.9
C(2b/6b)	126.8	126.7	127.7	127.6	128.6	127.5
C(3b/5b)	115.3	116.5	116.1	116.4	117.1	117.0
C(4b)	157.3	157.35	158.3	157.16	158.1	157.5
C(7b)	92.4	91.6	93.7	128.4	128.3	128.5
C(8b)	54.4	54.4	56.0	127.7	126.9	123.7
C(9b)	144.7	145.2	146.2	140.1	140.0	140.9
C(10b)	99.4	99.8	101.0	96.8	99.8	117.0
C(11b)	161.5	161.2	162.4	161.4	163.2	161.0
C(12b)	115.5	114.2	115.4	114.5	115.9	98.9
C(13b)	154.6	154.74	155.5	155.1	155.6	158.1
C(14b)	107.3	107.5	108.5	107.8	108.2	103.4
C(1c)	132.2	131.0	131.4			
C(2c/6c)	127.9	127.8	128.4			
C(3c/5c)	115.3	116.6	117.4			
C(4c)	157.3	157.41	157.0			
C(7c)	128.2	131.0	129.3			
C(8c)	125.5	127.2	128.4			
C(9c)	139.5	139.7	140.2			
C(10c)	97.8	98.9	98.6			
C(11c)	161.0	161.7	161.8			
C(12c)	115.5	115.5	115.9			
C(13c)	154.6	154.85	155.5			
C(14c)	106.9	107.8	108.3			

[a]) $(CD_3)_2SO$. [b])$(CD_3)_2CO$.

C(4a), C(4b), and C(4c), respectively, and thus planar structure **2** was assigned to gnetin E 4a,4b,4c-*O*-*β*-triglucopyranoside. The relative configurations of the stereogenic centers were assigned by comparison with the chemical-shift values of the corresponding dihydrofuran rings of **1** in the ^{1}H- and ^{13}C-NMR spectra.

Gnemonoside G (**3**), a white amorphous powder, gave positive reaction to *Gibbs* reagent. The UV absorption bands at λ [nm] 207, 285, 315 showed the presence of aromatic rings and a strong conjugation in the molecule. The molecular formula of $C_{54}H_{52}O_{19}$ was deduced from the negative FAB-MS $[M-H]^-$ ion peak at *m*/*z* 1003. The

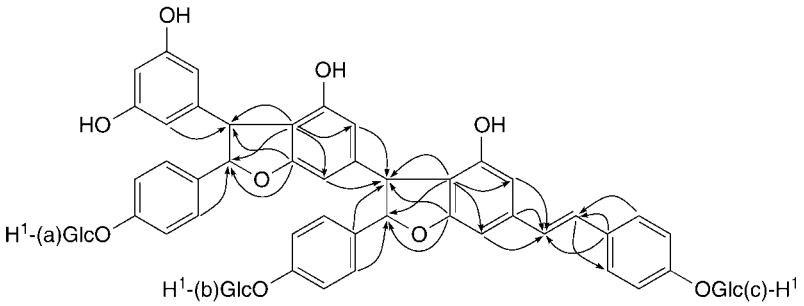


Fig. 1. *Correlations in the COLOC spectrum of* **2**

^{1}H-NMR spectrum exhibited the presence of three 4-hydroxyphenyl groups (rings A_1, B_1, and C_1), two sets of a *meta*-coupled aromatic H-atom on a 1,3,4,5-tetrasubstituted benzene ring (rings B_2 and C_2), and a set on a 3,5-dihydroxyphenyl group (ring A_2). Signals of a pair of olefinic H-atoms (H−C(7c/8c)), of two pairs of methine protons (H−C(7a/8a), H−C(7b/8b)) and of two anomeric H-atoms at 4.98 ($d, J = 8.4$, Glc−H−C(1a)) and 5.00 ($d, J = 7.8$, Glc−H−C(1b)) were also observed in the spectrum in addition to five phenolic OH signals. The ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*) of **3** showed a closed similarity to those of **2**, except that **3** exhibited the presence of two anomeric H-atom signals. The chemical-shift values (*ca.* 0.32 ppm) towards downfield observed for H−C(3a/5a) and H−C(3c/5c) as compared to those of H−C(3b/5b) suggested that the two sugar moieties were attached to C(4a) and C(4c). The results of the differential NOE experiments (*Fig. 2*) confirmed the positions of the glucose moieties, and irradiation of the anomeric protons at 4.98 and 5.00 resulted in significant NOEs at 7.07 H−C(3a/5a) and H−C(3c/5c), revealing the positions of the glucose moieties to be at C(4a) and C(4c), respectively. The *trans*-orientation of dihydrofuran rings was also determined by the differential NOE (*Figs. 2* and *3*). Thereby, confirming the structure **3** as gnetin E 4a,4c-*O*-β-diglucopyranoside.

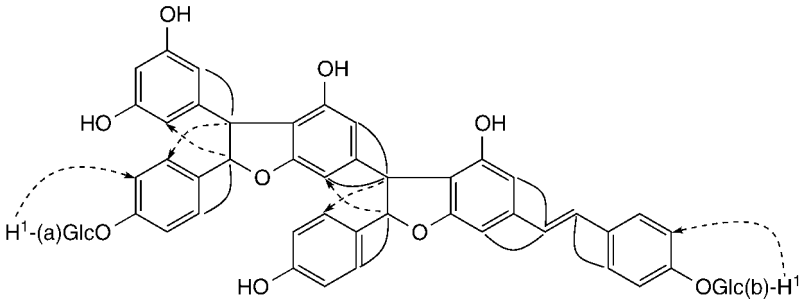


Fig. 2. *Correlations in the* ^{1}*H,*^{1}*H-long-range COSY* (⌒) *and differential NOE spectra* (↷) *of* **3**

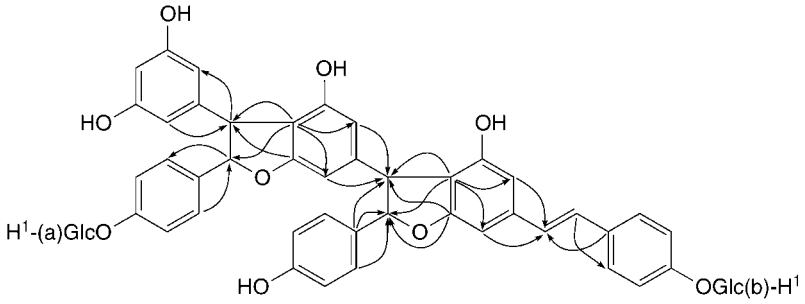


Fig. 3. *Correlations in the COLOC spectrum of* **3**

Gnemonoside H (**4**) was obtained as a brown amorphous powder. The UV spectrum showed absorption bands at λ [nm] 206, 282, 307. The molecular formula of $C_{46}H_{52}O_{21}$ was supported by the negative FAB-MS $[M-H]^-$ ion peak at *m/z* 939. Analysis of the ^{1}H-NMR spectrum revealed the presence of two 4-hydroxyphenyl groups (ring A_1, B_1), a set of *meta*-coupled aromatic H-atoms on a 1,3,4,5-tetrasubstituted benzene ring (ring B_2), and a set on a 1,3,5-trisubstituted benzene ring (ring A_2). The presence of a pair of olefinic H-atoms at 6.97 ($d, J=16.0$, H–C(8b)) and 7.07 ($d, J=16.0$, H–C(7b)]; a pair of CH-coupled H-atoms 4.38 ($d, J=4.8$, H–C(8a)) and 5.37 ($d, J=4.8$, H–C(7a)) and signals of three anomeric H-atom signals at 4.70, 4.83, 4.86 ($d, J=7.5$, H–C(1) of Glc(1), Glc(2), Glc(3)) were also observed in the spectrum. These results showed that **4** is a dimeric stilbene glucoside. The ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*) showed a closed resemblance to those of **7** [4], except that **4** showed the appearance a 1,3,5-trisubstituted benzene ring (ring A_2) in place of 3,5-dihydroxyphenyl group. All quaternary C-atoms in **4** were assigned by comparison with **7** and piceid. In the ^{1}H,^{1}H long-range COSY (*Fig. 4*), the correlations observed between H–C(7a)/H–C(2a/6a), H–C(8a)/H–C(10a/14a), H–C(7b)/H–C(2b/6b), and H–C(8b)/H–C(10b/14b) revealed the linkages of C(7a)/C(1a), C(8a)/C(9a), C(7b)/C(1b), and C(8b)/C(9b), respectively. The chemical shift of *ca.* 2.0 ppm toward upfield observed for C(11a) and the appearance of a 1,3,5-trisubstituted benzene ring (ring A_2) in **4**, as compared to 3,5-dihydroxyphenyl group

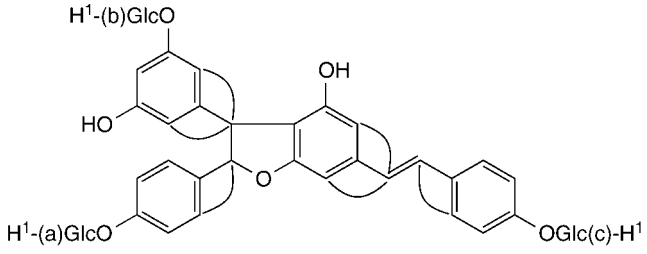


Fig. 4. *Correlations in the ^{1}H,^{1}H-long-range COSY spectrum of* **4**

(ring A_2) in **7**, revealed that an additional glucose molecule is attached at C(11a), and, thus, the structure of **4** is gnetin C 4a,4b,11a-*O*-*β*-triglucopyranoside.

Gnemonoside I (**5**), a white amorphous powder, showed a positive reaction to *Gibbs* reagent. The molecular formula of $C_{40}H_{42}O_{17}$ was deduced by negative FAB-MS $[M-H]^-$ at *m*/*z* 793. The ^{1}H-NMR spectrum showed the presence of aromatic H-atoms on a 4-hydroxyphenyl group (ring B_1), a set on a 1,2,4-trisubstituted benzene ring in an *ABX* spin system (ring A_1), and a set on a 3,5-dihydroxyphenyl group (ring A_2). The spectrum also exhibited a set of *meta*-coupled aromatic H-atoms on a 1,3,4,5-tetrasubstituted benzene ring (ring B_2), a pair of olefinic H-atoms at 6.95 (*d*, $J = 16.0$, H–C(8b)) and 7.05 (*d*, $J = 16.0$, H–C(7b)), and two anomeric H-atoms at 4.69 (*d*, $J = 7.6$, H–C(1) of Glc(a)) and 4.87 (*d*, $J = 7.6$, H–C(1) of Glc(b)). These results suggested that **5** is a dimeric stilbene composed of an oxyresveratrol unit (ring A_1-7a-8a-ring A_2) and a resveratrol unit (ring B_1-7a-8a-ring B_2). The ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*) of **5** showed the presence of two glucose moieties accompanied by similar signals of gnetin D [5], which indicated that **5** is a diglucoside of gnetin D. All quaternary C-atoms and the relative configuration of **5** were assigned by comparison with those of gnetin D and **7**. Subsequently the structure of **5** was characterized as gnetin D 4a, 4b-di-*O*-*β*-diglucopyranoside.

Gnemonoside J (**6**), a white amorphous powder, gave an $[M-H]^-$ ion peak at *m*/*z* 793 in the negative FAB-MS suggesting the molecular formula $C_{40}H_{42}O_{17}$. The ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*) of **6** showed the closed resemblance to gnetuhainin A [6], in addition to two glucose moieties. These results suggested **6** to be a diglucoside of gnetuhainin A. Analysis of the ^{1}H,^{1}H long-range COSY of **6** allowed the respective linkages of the CH and olefinic H-atoms to their aromatic rings. The assignment of quaternary C-atoms and the relative configuration was accomplished by comparison with **7**. Resveratrol 3,4′-*O*-*β*-diglucopyranoside [7], piceatanol 4′-*O*-*β*-glucopyranoside [8], piceatanol 3,4′-*O*-*β*-diglucopyranoside, and gnetofolin K [9] were also isolated from the stem of *G. africanum*. Gnemonosides A (**7**), and B, resveratroloside [10], gnetofolin E [11], and gnetin E were obtained from both *G. africanum* and *G. gnemonoides*. The structures of the compounds were determined by spectroscopic analysis and comparison with authentic samples.

Experimental Part

General. Anal. TLC: *Merck* Kieselgel F_{254} (0.25 mm), Prep. TLC: *Merck* Kieselgel gel F_{254} (0.5 mm). The following adsorbents were used for column chromatography (CC): Merck Kieselgel *60*, *Sephadex LH 20*, and *Sek-Pak* C_{18} cartridges (*Waters*). Optical Rotations: *JASCO P-1020* polarimeter. UV Spectra: *Shimadzu UV-2200* spectrophotometer. ^{1}H- and ^{13}C-NMR spectra: *JEOL EX-400* with TMS as an internal standard. FAB-MS Spectra: *JOEL JMX-DX-300*.

Plant Materials. The stems of *G. gnemonoides* were collected at Bogor, Indonesia, in April 2000, and the stems of *G. africanum* were obtained at Nsukka, Nigeria, in March 2001.

Extraction and Isolation. The dried stems of *G. gnemonoides* (1.0 kg) were powdered and extracted with acetone and MeOH (3 × weekly each), successively. The acetone extract (27.0 g) was chromatographed on silica gel eluted with a mixture of $CHCl_3$/MeOH of increasing polarity to give 33 fractions. *Fractions 24–33* were combined and subjected to reserved-phase (RP) CC on *Sek-Pak* C_{18} cartridges to give 12 fractions. Further purification of *Fr. 2* by prep. TLC with AcOEt/$CHCl_3$/MeOH/H_2O 20 : 10 : 12 : 5 gave **4** (9.0 mg). *Fr. 8–12* were combined and subjected to further RP chromatography to give **2** (47.0 mg) and **3** (15.0 mg).

The dried stems (1.3 kg) of *G. africanum* were treated as the same way as those of *G. gneomoides* to give acetone extract (35.0 g). The acetone extract was also subjected to similar chromatography procedure as described above resulted into 26 fractions. *Fr. 23–26* were combined and subjected to RP-CC (*Sek-Pak C_{18}*; H_2O/MeOH 1:9) to give 10 fractions. Compound **4** (5.0 mg) was obtained from *Fr. 3* in a pure form. Compound **5** (7.5 mg) and **6** (9.0 mg) were obtained from *Fr. 8* by repeated RP-CC (H_2O/MeOH 3:7).

Gnemonoside F (= *Gnetin* E *4a,4b,4c*-O-*β-Triglucopyranoside*; **2**). A white amorphous powder. $[\alpha]_D = -23$ ($c = 0.11$, MeOH). UV: 206, 220, 320. ^{1}H-NMR (400 MHz, $(CD_3)_2SO$): glucose moieties: 3.25 (*m*, H–C(4) of Glc(a,b,c)); 3.33 (*m*, H–C(2) of Glc(a,b,c)); 3.34 (*m*, H–C(3) of Glc(a,b,c)); 3.40 (*m*, H–C(5) of Glc(a,b,c)); 3.47, 3.70 (*m*, H–C(6) of Glc(a,b,c)); 4.87 (*d*, $J = 7.5$, H–C(1) of Glc(a,b)); 4.89 (*d*, $J = 7.5$, H–C(1) of Glc(c)); 9.13 (br. *s*, OH–C(11a), OH–C(13a)); 9.27 (br. *s*, OH–C(13b)); 9.47 (br. *s*, OH–C(13c)). ^{13}C-NMR (100 MHz,$(CD_3)_2SO$): glucose moieties: 60.9 (C(6) of Glc(a,b,c)); 68.9 (C(4) of Glc(a,b,c)); 73.4 (C(2) of Glc(a,b,c)); 76.8 (C(3) of Glc(a,b,c)); 77.2 (C(5) of Glc(a,b,c)); 100.5 (C(1) of Glc(a,b,c)). The ^{1}H- and ^{13}C-NMR aglycone unit: *Tables 1* and *2*. FAB-MS (neg.): 1165 ($[M-H]^-$).

Gnemonoside G (= *Gnetin* E *4a,4c*-O-*β-Diglucopyranoside*; **3**). A white amorphous powder. $[\alpha]_D = -27$ ($c = 0.114$, MeOH). UV: 207, 285, 315. ^{1}H-NMR (400 MHz, $(CD_3)_2CO$): glucose moieties: 3.45 (*m*, H–C(4) of Glc(a,b)); 3.53 (*m*, H–C(2) of Glc(a,b)); 3.57 (*m*, H–C(3), H–C(5) of Glc(a,b)); 3.74, 3.88 (*m*, 2 H–C(6) of Glc(a,b)); 4.98 (*d*, $J = 8.4$, H–C(1) of Glc(a)); 5.00 (*d*, $J = 7.8$, Glc(b)). ^{13}C-NMR (100 MHz, $(CD_3)_2CO$): glucose moieties: 62.7 (C(6) of Glc(a,b)); 71.4 (C(4) of Glc(a,b)); 74.4 (C(2) of Glc(a,b)); 77.7 (C(3) of Glc(a,b)); 77.9 (C(5) of Glc(a,b)); 101.89 (C(1) of Glc(a)); 101.84 (C(1) of Glc(b)). ^{1}H- and ^{13}C-NMR of aglycone moiety: *Tables 1* and *2*. FAB-MS (neg.): 1003 ($[M-H]^-$).

Gnemonoside H (= *Gnetin C 4a,4b,11a*-O-*β-Triglucopyranoside*; **4**). A brown amorphous powder. $[\alpha]_D = -43$ ($c = 0.05$, MeOH). UV: 206, 282, 308. ^{1}H-NMR (400 MHz, $(CD_3)_2SO$): glucose moieties: 2.98–3.48 (*m*, H–C(2), H–C(3), H–C(4), H–C(5) of Glc(a,b,c)); 3.70, 3.83 (*m*, H–C(6) of Glc(a,b,c)); 4.70*, 4.83*, 4.86 (*d*, $J = 7.5$, H–C(1) of Glc(a,b,c)). ^{13}C-NMR (100 MHz, $(CD_3)_2SO$): glucose moieties: 60.37, 60.69, 60.73 (C(6) of Glc(a,b,c)); 69.48, 69.64, 69.71 (C(4) of Glc(a,b,c)); 73.20, 73.22, 73.27 (C(2) of Glc(a,b,c)); 76.22, 76.58, 76.61 (C(3) of Glc(a,b,c)); 77.11, 77.14, 77.17 (C(5) of Glc(a,b,c)); 100.4 (C(1) of Glc(a,b,c)). ^{1}H- and ^{13}C-NMR of aglycone unit: *Tables 1* and *2* (*: interchangeable). FAB-MS (neg.): 939 ($[M-H]^-$). HR-FAB-MS (neg.): 939.2929 ($[M-H]^-$, $C_{54}H_{51}O_{19}$; calc. 939.2923).

Gnemonoside I (= *Gnetin D 4a,4b*-O-*β-Diglucopyranoside*; **5**). A white amorphous powder. $[\alpha]_D = -30$ ($c = 0.10$, MeOH). UV: 206, 285, 320. ^{1}H-NMR (400 MHz, $(CD_3)_2SO$): glucose moieties: 3.15–3.45 (*m*, H–C(2), H–C(3), H–C(4), H–C(5) of Glc(a,b)); 3.47, 3.68 (*m*, 2 H–C(6) of Glc(a,b)); 4.69, 4.87 (*d*, $J = 7.6$, H–C(1) of Glc(a,b)). ^{13}C-NMR (100 MHz, $(CD_3)_2SO$): glucose moieties: 62.5 (C(6) of Glc(a,b)); 71.4 (C(4) of Glc(a,b)); 74.85, 74.91 (C(2) of Glc(a,b)); 77.6 (C(3) of Glc(a,b)); 78.05, 78.16 (C(5) of Glc(a,b)); 101.4 (C(1) of Glc(a,b)). ^{1}H- and ^{13}C-NMR of aglycone units: *Tables 1* and *2*. FAB-MS (neg.): 793 ($[M-H]^-$). HR-FAB-MS (neg.): 739.2352 ($[M-H]^-$, $C_{40}H_{41}O_{17}$; calc. 793.2343).

Gnemonoside J (= *Gnetihainin A 4a,4b*-O-*β-Diglucopyranoside*; **6**). A white amorphous powder. $[\alpha]_D = -19$ ($c = 0.12$, MeOH). UV: 206, 285, 317. ^{1}H-NMR (400 MHz, $(CD_3)_2SO$): glucose moieties: 3.15–3.32 (*m*, H–C(2), H–C(3), H–C(4), H–C(5) of Glc(a,b)); 3.64, 3.82 (*m*, H–C(6) of Glc(a,b)); 4.72 (*d*, $J = 7.2$, H–C(1) of Glc(a)); 4.84 (*d*, $J = 7.6$, H–C(1) of Glc(a)). ^{13}C-NMR (100 MHz, $(CD_3)_2SO$): glucose moieties: 60.6 (C(6) of Glc(a,b)); 69.6 (C(4) of Glc(a,b)); 73.2 (C(2) of Glc(a,b)); 76.55, 76.63 (C(3) of Glc(a,b)); 77.1 (C(5) of Glc(a,b)); 100.3, 100.4 (C(1) of Glc(a,b)). ^{1}H- and ^{13}C-NMR of aglycone units: *Tables 1* and *2*. FAB-MS (neg.): 793 ($[M-H]^-$). HR-FAB-MS (neg.): 793.2350 ($[M-H]^-$, $C_{40}H_{41}O_{17}$; calc. 793.2343).

REFERENCES

[1] H. M. Burkill, 'The Useful Plants of West Africa', Royal Botanical Garden Kew, 1994, *2*, 168.
[2] K. S. Huang, R. L. Li, Y. H. Wang, M. Lin, *Planta Med*. **2001**, *67*, 61.
[3] S. Sotheeswaran, V. Pasupathy, *Phytochemistry* **1993**, *31*, 1083.
[4] I. Iliya, T. Tanaka, M. Furasawa, Z. Ali, K. Nakaya, M. Iinuma, Y. Shirataki, J. Murata, D. Darnaedi, *Heterocyles* **2001**, *55*, 2123.
[5] A. P. Lins, M. N. de S. Ribeiro, O. R. Gottlieb, H. E. Gottlieb, *J. Nat. Prod*. **1982**, *45*, 754.
[6] K.-S. Huang, Y.-H. Wang, R.-L. Li, M. Lin, *J. Nat. Prod*. **2000**, *63*, 86.
[7] K. S. Ko, *Arch. Pharmacol. Res.* **2000**, *32*, 159.
[8] Y. Kashida, G. Nonaka, I. Nishioka, M. Nishizawa, T. Yamagishi, *Chem. Pharm. Bull*. **1988**, *36*, 1545.

[9] Q. Xu, M. Lin, *Chinese Chemical Lett*. **1997**, *8*, 509.
[10] John Gorham 'The Biochemistry of the Stilbenoids', Chapman & Hall, London, 1995, 222.
[11] M. Lin, J. B. Li, S. Z. Li, D. Q. Yu, X. T. Liang, *Phytochemistry* **1992**, *31*, 633.

Received April 26, 2002