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FOUR NEW GLUCOSIDES OF STILBENE OLIGOMERS FROM THE STEM OF *GNETUM GNEMONOIDES*

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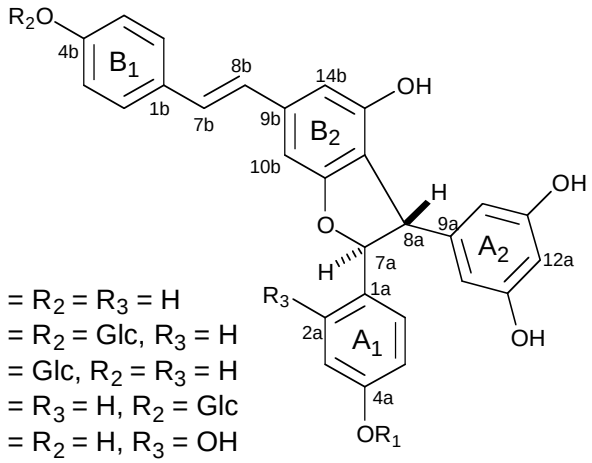
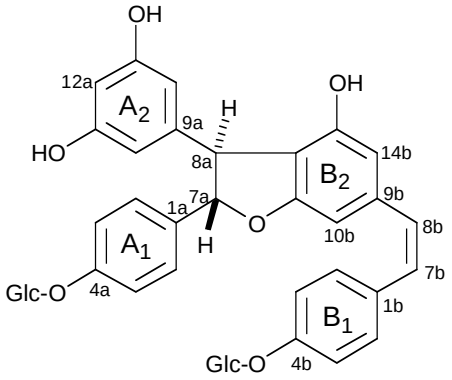
Abstract - Four new stilbene oligomeric glucosides, gnemonoside A, B, C and D, were isolated from the stem of *Gnetum gnemonoides* (BRONGN) along with four known stilbenoides, *trans*-resveratrol, gnetins C, D and E. The structures were elucidated on the basis of spectral evidence.

Gnetum gnemonoides (BRONGN) belongs to Gnetaceae, the leaves and fruits of the species are used as food and medicine in many parts of the tropical region.[1, 2] Various stilbene derivatives have been isolated from the Gnetaceaous plants,[3, 4] however, no literature has reported on the occurrence of oligomeric stilbene glycoside in the plant. This paper describes the isolation and structure elucidation of four new glucosides (gnemonoside A-D) of dimeric stilbenes in the stem of *G. gnemonoides*.

Gnetin C (**1**) was obtained as a brown amorphous powder and showed positive reaction to Gibbs reagent. The negative FAB-MS exhibited an $[M-H]^-$ ion peak at *m/z* 453, indicating the molecular weight to be 454. Its molecular formula $C_{28}H_{22}O_6$ was confirmed by negative HR-FAB-MS (453.1345). The ^1H NMR spectrum showed the presence of two sets of *ortho*-coupled protons assignable to two 4-hydroxyphenyl groups [δ 6.86 (2H, d, *J*= 8.8 Hz, H-3a, 5a), 7.23 (2H, d, *J*= 8.8 Hz, H-2a, 6a) and 6.86 (2H, d, *J*= 8.8 Hz, H-3b, 5b), 7.09 (2H, d, *J*= 8.8 Hz, H-2b, 6b)], a set of 3,5-dihydroxyphenyl group [δ 6.20 (2H, d, *J*= 2.0 Hz, H-10a, 14a), 6.26 (1H, t, *J*= 2.0 Hz, H-12a)] and a set of *meta*-coupled aromatic protons on a 1,3,4,5-tetrasubstituted benzene ring [δ 6.61 (1H, br s, H-14b), 6.73 (1H, br s, H-10b)]. A set of *trans*-coupled



1 $R_1 = R_2 = R_3 = H$
2 $R_1 = R_2 = Glc$, $R_3 = H$
4 $R_1 = Glc$, $R_2 = R_3 = H$
5 $R_1 = R_3 = H$, $R_2 = Glc$
6 $R_1 = R_2 = H$, $R_3 = OH$



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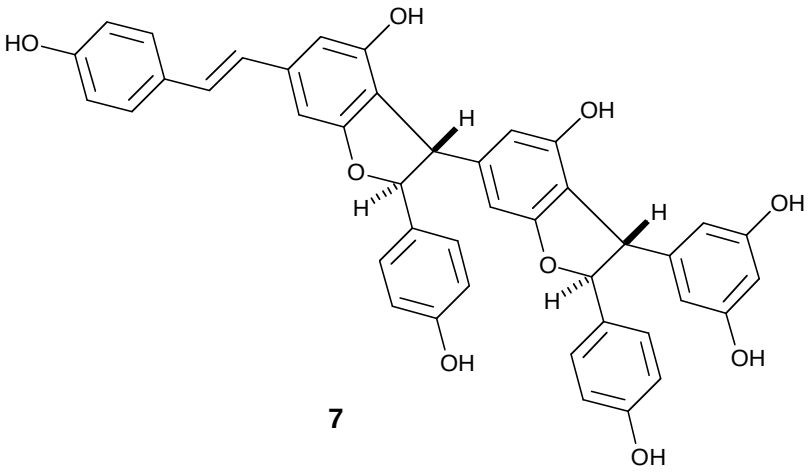

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Figure 1

olefinic protons [δ 6.99 (1H, d, *J*= 16.0 Hz, H-8b), 7.12 (1H, d, *J*= 16.0 Hz, H-7b)] and a set of mutually coupled aliphatic protons [δ 4.39 (1H, d, *J*= 4.5 Hz, H-8a), 5.39 (1H, d, *J*= 4.5 Hz, H-7a)] were also exhibited in the spectrum in addition to five phenolic hydroxyl groups [δ 8.18 (1H, br s, OH-13b), 8.20 (2H, br s, 2 x OH-11a, 13a), 8.48 (2H, br s, 2 x OH-4a, 4b)]. Analysis of the ^{1}H-^{1}H long range COSY spectrum revealed the following cross peak correlations: H-2a(6a)/H-7a, H-10a(14a)/H-8a, H-2b(6b)/H-7b and H-10b(14b)/H-8b. Similarly, correlations between C-7a/H-2a(6a), C-8a/H-10a(14a), C-7b/H-2b(6b) and C-8b/H-10b(14b) were observed in the COLOC spectrum, indicating that rings A_1, A_2, B_1 and B_2 were connected at C-7a, C-8a, C-7b, and C-8b, respectively. Significant correlations between C-11b/H-7a(8a) and C-12b/H-7a(8a) observed in the COLOC spectrum indicated that a resveratrol (ring A_1-C-7a-C-8a-ring A_2) formed a furan ring with ring B_2 of another resveratrol at C-11b and C-12b. The spectral data led to the revised assignment of some carbons earlier made in **1**[4] and allowed the confirmation of the planar structure of gnetin C (**1**).

Gnemonoside A (**2**) was obtained as a white amorphous powder and gave an $[M-H]^-$ ion peak at *m/z* 777 in the negative FAB-MS, suggesting the molecular formula to be $C_{40}H_{42}O_{16}$, which was supported by the negative ion HR-FAB-MS (*m/z* 777.2386). The ^{1}H and ^{13}C NMR spectral data (Table) showed the presence of two glucopyranosyl moieties at δ 4.84 [1H, d, *J*= 7.7 Hz, Glc(a)-H-1] and 4.88 [1H, d, *J*= 7.7 Hz, Glc(b)-H-1] accompanied with similar signals of **1**, suggesting that **2** is a diglucoside of **1**. Analysis of the HMQC and HMBC experiments enabled the assignment of all protonated and quaternary carbons

Table ^{13}C NMR spectral data of compounds (**1**-**5**)

	1[a]	**1**[b]	**2**[b]	**3**[b]	**4**[a]	**5**[a]
1a	134.2	132.1	135.2	135.2	136.9	134.0
2a(6a)	127.9	126.7	126.5	126.8	127.7	127.7
3a(5a)	116.5	115.5	116.4	116.5	117.7	116.2
4a	158.3	157.2	157.2	157.3	158.4	158.2
7a	93.8	92.0	91.6	91.8	93.4	93.4
8a	56.1	54.3	54.4	54.8	56.2	56.0
9a	146.9	145.0	144.8	145.0	146.3	146.1
10a(14a)	106.8	105.2	106.2	105.5	106.9	106.7
11a(13a)	159.7	158.4	158.4	158.6	159.8	159.6
12a	102.1	101.0	101.0	101.2	102.2	102.0
1b	130.1	128.1	130.8	130.4	130.1	131.8
2b(6b)	128.9	127.8	127.6	130.0	129.0	127.7
3b(5b)	116.3	115.2	116.4	116.0	116.6	117.5
4b	158.3	157.2	157.0	156.7	158.8	157.9
7b	129.3	128.1	127.7	129.4	128.0	128.4
8b	126.9	125.5	127.0	129.2	127.8	127.8
9b	141.3	139.6	139.4	139.1	141.5	140.5
10b	99.3	97.6	97.8	100.8	99.4	99.2
11b	163.3	161.4	161.4	161.2	163.3	163.1
12b	115.2	114.0	114.1	114.0	116.4	116.3
13b	155.6	154.5	154.6	154.6	155.7	155.4
14b	108.2	107.1	107.6	108.9	108.4	108.3
Glc-1a			100.4	100.5	102.1	101.7
1b			100.3	100.3		
2a(b)			73.2	73.4	74.9	74.7
			73.2	73.4		
3a(b)			76.6	76.6	78.2	77.9
			76.6	76.6		
4a(b)			69.7	69.8	71.5	71.2
			69.7	69.9		
5a(b)			77.0	77.1	78.0	77.8
			77.1	77.2		
6a(b)			60.7	60.0	62.8	62.6
			60.7	60.9		

a: $(CD_3)_2CO$, b: $(CD_3)_2SO$
All carbons were assigned by HMQC and HMBC (COLOC) spectrum.

as shown in Table. The positions of two glucose molecules were established with the aid of HMBC (Figure 3) and NOESY (Figure 2) experiments. The anomeric protons at δ 4.84 and 4.88 exhibited a cross peak correlation with the aromatic carbons at C-4a and C-4b respectively in the HMBC experiment. These positions were further confirmed by the results of NOESY experiment, in which the following correlations between Glc(a)-H-1 (δ 4.84) and H-3a(5a), and between Glc(b)-H-1 (δ 4.88) and H-3b(5b) were observed. Acid hydrolysis of **2** gave an aglycone, which was identified to gnetin C (**1**) by comparative TLC with an authentic sample. The structure of **2** was therefore characterized as gnetin C 4a, 4b-*O*-β-diglucopyranoside.

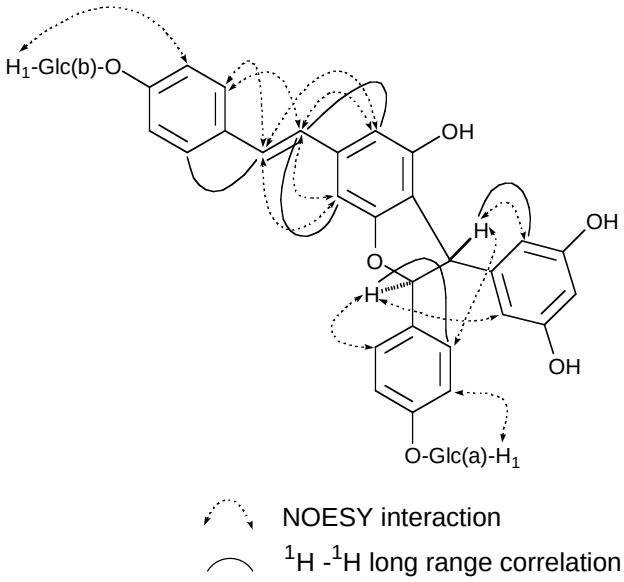


Figure 2

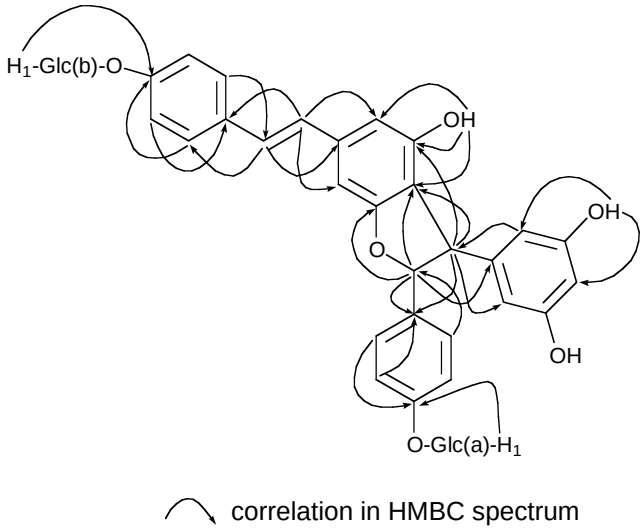
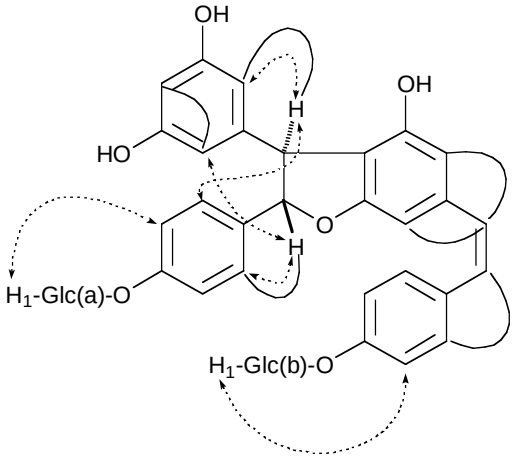


Figure 3

Gnemonoside B (**3**) was obtained as a white amorphous powder and showed a FAB-MS $[M-H]^-$ ion peak at *m/z* 777. The molecular formula of $C_{40}H_{42}O_{16}$ was supported by the HR-FAB-MS (*m/z* 777.2388). The ^1H and ^{13}C NMR spectral data of **3** were similar to those of **2** except for the appearance of signals due to *cis*-coupled olefinic protons at δ 6.45 (1H, d, *J*= 12.6 Hz, H-8b) and δ 6.50 (1H, d, *J*= 12.6 Hz, H-7b) for **3** in place of *trans*–coupled olefinic protons at δ 7.01 and 7.08 (each *J*= 16.0 Hz) for **2**. The ^1H NMR spectrum showed the presence of two sets of *ortho*-coupled protons assignable to two *para*-substituted phenyl groups [δ 7.03 (2H, d, *J*= 8.8 Hz, H-3a, 5a], 7.21 (2H, d, *J*= 8.8 Hz, H-2a, 6a) and 6.95 (2H, d, *J*= 8.8 Hz, H-3b, 5b), 7.24 (2H, d, *J*= 8.8 Hz, H-2b, 6b)], a set of 3,5-dihydroxyphenyl group in an A_2B spin system at δ 6.00 (2H, d, *J*= 2.2 Hz, H-10a, 14a), 6.06 (1H, t, *J*= 2.2 Hz, H-12a) and a set of *meta*-coupled protons on a 1,3,4,5-tetrasubstituted benzene ring [δ 6.29 (1H, d, *J*= 2.4 Hz, H-10b), 6.32 (1H, d, *J*= 2.4 Hz, H-14b)]. A set of methine protons at δ 4.21 (1H, d, *J*= 4.4 Hz, H-8a), 5.35 (1H, d, *J*= 4.4 Hz, H-7a) was also exhibited in the spectrum. Correlations between H-2a(6a)/H-7a, H-10a(14a)/H-8a, H-2b(6b)/H-7b and H-10b(14b)/H-8b observed in the ^1H-^1H long range COSY (Figure 4), and similar correlations also observed between H-2a(6a)/C-7a, H-10a(14a)/C-8a, H-2b(6b)/C-7b and H-10b(14b)/C-8b in the HMBC spectrum (Figure 5), indicated that rings A_1, A_2, B_1 and B_2 were attached at C-7a, C-8a, C-7b and C-8b, respectively. The HMQC and HMBC experiments enabled the assignment of all protonated and quaternary carbons in **3**. Analysis of the HMBC (Figure 5) and NOESY (Figure 4) experiments allowed the assignment of the two glucose molecules and their attaching positions. The relative configuration of **3** was established on the basis of NOESY correlation between H-7a/H-10a(14a) and H-8a/H-2a(6a), suggesting the relationship between H-7a and H-8a to be *trans*. Thus, the structure of gnemonoside B (**3**) was characterized as *cis*-gnetin C 4a, 4b-*O*-β-diglucopyranoside.

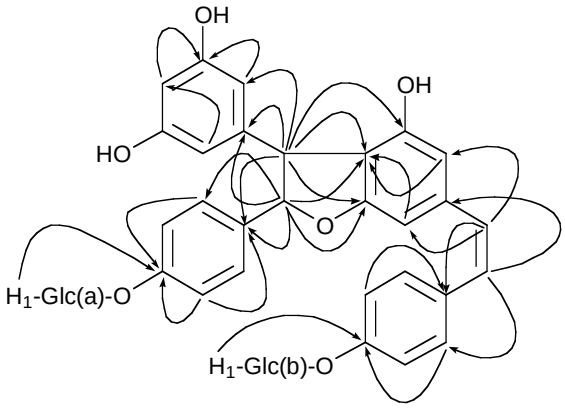
Gnemonoside C (**4**), a brown amorphous powder, showed strong fluorescence at 254 nm under UV radiation. It showed an $[M-H]^-$ ion peak at *m/z* 615 together with a fragment ion peak at *m/z* 453 $[M-Glc]^-$ in the negative FAB-MS. The molecular formula $C_{34}H_{32}O_{11}$ was established by the negative HR-FAB-MS (*m/z* 615.1872). The ^1H and ^{13}C NMR spectra exhibited similar patterns to those of **1** except the



NOESY interaction

^{1}H -^{1}H long range correlation

Figure 4



correlation in HMBC spectrum

Figure 5

appearance of one *O*-glucopyranosyl unit at δ 4.96 [1H, d, *J*= 7.3 Hz, Glc(a)-H-1, anomeric proton], which indicated that **4** is a monoglycoside of **1**. The position of glucose molecule was assigned with the aid of DIFNOE experiment. Irradiation of the anomeric proton at δ4.96 caused enhancement of the aromatic protons at δ 7.08, H-3a(5a), indicating that the glucose is attached at C-4a. The NOE also observed between H-7a/H-10a(14a) and H-8a/H-2a(6a) suggested a *trans* relationship between H-7a and H-8a and thus allowed the relative structure of **4** to be drawn as in Figure 1. All protonated carbons were assigned on the basis of ^{13}C-^{1}H COSY experiment, while the quaternary carbons were assigned by comparison with the chemical shifts of **1** and **2**. The structure of gnemonoside C (**4**) was characterized as gnetin C 4a-*O*-β-glucopyranoside.

Gnemonoside D (**5**) was isolated as a brown amorphous powder. Its molecular formula of $C_{34}H_{32}O_{11}$ was established by the results of the HR-FAB-MS (*m/z* 615.1869). An $[M-H]^-$ ion peak at *m/z* 615 was observed together with a fragment ion peak at *m/z* 453 $[M-H-Glc]^-$ in the negative FAB-MS. The ^{1}H and ^{13}C NMR spectral data resembled closely those of **4**, however, the position of *O*-glucosidic linkage is different from **4**. In the DIFNOE experiment the aromatic protons at δ 7.08, H-3b(5b) were enhanced when the anomeric proton at δ4.99 was irradiated, indicating that the glucose is linked to C-4b. The configuration of the furan ring was deduced to be *trans* from the result of NOE experiment as described in **4**. All protons and protonated carbons were assigned by the aid of ^{1}H-^{1}H COSY and HMQC experiments, while the quaternary carbons were assigned on the basis of comparison with **1** and **2**. Thereby the structure of gnemonoside D (**5**) was proposed to be gnetin C 4b-*O*-β-glucopyranoside.

Three known stilbenoids, gnetin D (**6**), gnetin E (**7**) and *trans*-resveratrol, 3,5,4'-trihydroxystilbene (**8**) were also isolated and identified by spectral analysis and comparison with authentic samples.

EXPERIMENTAL

General Method

^{1}H and $_{13}C$ NMR spectra were recorded on α-500 and EX 400 (JEOL) spectrophotometer. Chemical

shifts are shown as δ values with tetramethylsilane (TMS) as internal reference. Peak multiplicities are quoted in Hz. Negative ion FAB-MS and HR-FAB-MS were recorded on JMS-DA spectrometer equipped with a JMA 3500 data analysis system (JEOL). UV spectra was recorded on a UV2200 spectrometer (Shimadzu) and optical rotation was recorded on P-1020 (JASCO) polarimeter. Silica gel 60 (70-230 mesh, Merck), Sephadex LH-20 and ODS Sep-Pak C_{18} Cartridges Waters were used for column chromatography, while Kiesel-gel 60 F_{254} (Merck) was used for analytical and preparative TLC.

Plant Material

Stem of *Gnetum gnemonoides* (BRONGN) was collected in April 2000 at Bogor Botanical Garden, Indonesia.

Extraction and Isolation

The dried stem (1 kg) of *G. gnemonoides* was powdered and extracted successively with acetone (3 L for 7 days x 3) and methanol (3 L for 7 days x 3) at rt. The acetone extract (27 g) was chromatographed on silica gel with a mixture of $CHCl_3$-MeOH increasing polarity to give 33 fractions. Fractions 5, 6, 10 and 12 were further chromtographed several times in separate Sephadex LH 20 columns with acetone as eluting solvent to give **8** (21 mg), **1** (30 mg), **6** (11 mg) and **7** (35 mg), respectively. Fraction 14 ($CHCl_3$-MeOH, 8 : 2) was subjected to chromatography on Sephadex LH-20 with acetone as eluting solvent to give a mixture of **4** and **5** (25 mg), repeated chromatography of the mixture on reverse phase ODS eluted with H_2O-MeOH (7 : 3) achieved the separation of **4** (8 mg) and **5** (6 mg). Compounds (**2**) (60 mg) and (**3**) (30 mg) were obtained from the fraction 23 by repeated chromatography on ODS column using H_2O-MeOH (6 : 4) as eluting solvent.

Gnetin C (**1**) : A brown amorphous powder; negative HR-FAB-MS: $[M-H]^-$ *m/z* 453.1345 (Calcd 453.1338 for $C_{28}H_{21}O_6$); Negative FAB-MS: $[M-H]^-$ *m/z* 453; UV λmax (MeOH) nm: 224, 324; $[\alpha]_D$ 0° (*c*= 0.10, MeOH); ^{1}H NMR [400 MHz, $(CD_3)_2CO$]: δ 4.39 (1H, d, *J*= 4.5 Hz, H-8a), 5.39 (1H, d, *J*= 4.5 Hz, H-7a), 6.20 (2H, d, *J*= 2.0 Hz, H-10a,14a), 6.26 (1H, t, *J*= 2.0 Hz, H-12a), 6.61 (1H, br s, H-14b), 6.73 (1H, br s, H-10b), 6.86 (4H, d, *J*= 8.8 Hz, H-3a,5a and H-3b,5b), 6.99 (1H, d, *J*=16.0 Hz, H-8b), 7.09 (2H, d, *J*= 8.8 Hz, H-2b,6b), 7.12 (1H, d, *J*= 16.0 Hz, H-7b), 7.23 (2H, d, *J*= 8.8 Hz, H-2a,6a), 8.18 (1H, br s, OH-13b), 8.20 (2H, br s, 2xOH-11a,13a), 8.48 (2H, br s, 2xOH-4a,4b); The ^{13}C NMR spectral data are listed in Table.

Gnemonoside A (**2**) : A white amorphous powder; negative HR-FAB-MS: $[M-H]^-$ *m/z* 777.2386 (Calcd 777.2395 for $C_{40}H_{41}O_{16}$); negative ion FAB-MS: $[M-H]^-$ *m/z* 777; UV λmax (MeOH) nm: 222, 323; $[\alpha]_D$ – 8° (*c*= 0.10, pyridine); ^{1}H NMR [500 MHz, $(CD_3)_2SO$]: δ 4.32 (1H, d, *J*= 4.2 Hz, H-8a), 5.40 (1H, d, *J*= 4.2 Hz, H-7a), 6.00 (2H, d, *J*= 2.1 Hz, H-10a,14a), 6.05 (1H, t, *J*= 2.1 Hz, H-12a), 6.51 (1H, d, *J*=1.8 Hz, H-14b), 6.70 (1H, d, *J*= 1.8 Hz, H-10b), 7.01 (1H, d, *J*= 16.0 Hz, H-8b), 7.03 (4H, d, *J*= 8.8 Hz, H-3a,5a and H-3b,5b), 7.08 (1H, d, *J*= 16.0 Hz, H-7b), 7.22 (2H, d, *J*= 8.8 Hz, H-2a,6a), 7.52 (2H, d, *J*= 8.8 Hz, H-2b,6b), 9.10 (2H, br s, 2xOH-11a,13a), 9.37 (1H, br s, OH-13b), 3.16 [2H, m, Glc(a,b)-H-4], 3.25 [2H,

m, Glc(a,b)-H-2], 3.29 [2H, m, Glc(a,b)-H-3], 3.33 [2H, m, Glc(a,b)-H-5], 3.45, 3.68 [2H each, m, Glc(a,b)-H-6], 4.84 [1H, d, *J*= 7.7 Hz, Glc(a)-H-1], 4.88 [1H, d, *J*= 7.7 Hz, Glc(b)-H-1]; The ^{13}C NMR spectral data are shown in Table.

Gnemonoside B (**3**) : A white amorphous powder; negative ion HR-FAB-MS: $[M-H]^-$ *m/z* 777.2388 (Calcd 777.2395 for $C_{40}H_{41}O_{16}$); negative ion FAB-MS: $[M-H]^-$ *m/z* 777; UV λmax (MeOH) nm: 212, 284; $[\alpha]_D$ - 46° (*c*= 0.10, MeOH); ^{1}H NMR [500 MHz, $(CD_3)_2SO$]: δ 4.21 (1H, d, *J*= 4.4 Hz, H-8a), 5.35 (1H, d, *J*= 4.4 Hz, H-7a), 6.00 (2H, d, *J*= 2.2 Hz, H-10a,14a), 6.06 (1H, t, *J*= 2.2 Hz, H-12a), 6.29 (1H, d, *J*= 2.4 Hz, H-10b), 6.32 (1H, d, *J*= 2.4 Hz, H-14b), 6.45 (1H, d, *J*= 12.6 Hz, H-8b), 6.50 (1H, d, *J*= 12.6 Hz, H-7b), 6.95 (2H, d, *J*= 8.8 Hz, H-3b,5b), 7.03 (2H, d, *J*= 8.8 Hz, H-3a,5a), 7.21 (2H, d, *J*= 8.8 Hz, H-2a,6a), 7.24 (2H, d, *J*= 8.8 Hz, H-2b,6b), 9.14 (2H, br s 2xOH-11a,13a), 9.29 (1H, br s, OH-13b), 3.17 [2H, m, Glc(a,b)-H-4], 3.26 [2H, m, Glc(a,b)-H-2], 3.35-3.46 [4H, m, Glc(a,b)-H-3,5], 3.51, 3.75 [2H each, m, Glc(a,b)-H-6], 4.995 [1H, d, *J*= 7.2 Hz, Glc(a)-H-1], 4.997 [1H, d, *J*= 7.2 Hz, Glc(b)-H-1]; The ^{13}C NMR spectral data are listed in Table.

Gnemonoside C (**4**): A brown amorphous powder; negative ion HR-FAB-MS: $[M-H]^-$ *m/z* 615.1872 (Calcd 615.1866 for $C_{34}H_{31}O_{11}$); negative ion FABMS: $[M-H]^-$ *m/z* 615; UV λmax (MeOH) nm: 221, 324; $[\alpha]_D$ – 39° (*c*= 0.10, MeOH); ^{1}H NMR [400 MHz,$(CD_3)_2CO$]: δ 4.40 (1H, d, *J*= 4.8 Hz, H-8a), 5.44 (1H, d, *J*= 4.8 Hz, H-7a), 6.18 (2H, d, *J*= 1.8 Hz, H-10a,14a), 6.22 (1H, t, *J*= 1.8 Hz, H-12a), 6.60 (1H, br s, H-14b), 6.72 (1H, br s, H-10b), 6.85 (2H, d, *J*= 8.8 Hz, H-3b,5b), 6.98 (1H, d, *J*= 16.0 Hz, H-8b), 7.08 (2H, d, *J*= 8.8 Hz, H-3a,5a), 7.11 (1H, d, *J*= 16.0 Hz, H-7b), 7.30 (2H, d, *J*= 8.8 Hz, H-2a,6a), 7.45 (2H, d, *J*= 8.8 Hz, H-2b,6b), 8.16 (1H, br s, OH-13b), 8.17 (2H, br s, 2xOH-11a,13a), 8.51 (1H, br s, OH-4b); 3.40-3.82 [4H, m, Glc(a)-H-2,3,4,5], 3.88 [2H, m, Glc(a)-H-6], 4.96 [1H, d, *J*= 7.3 Hz, Glc(a)-H-1]; The ^{13}C NMR spectral data are shown in Table.

Gnemonoside D (**5**) : A brown amorphous powder; negative ion HR-FAB-MS: $[M-H]^-$ *m/z* 615.1869 (Calcd 615.1866 for $C_{34}H_{31}O_{11}$); negative ion FAB-MS: $[M-H]^-$ *m/z* 615; UV λmax (MeOH) nm: 224; $[\alpha]_D$ – 57° (*c*= 0.08, MeOH); ^{1}H NMR [500 MHz, $(CD_3)_2CO$]: δ 4.32 (1H, d, *J*= 4.9 Hz, H-8a), 5.38 (1H, d, *J*= 4.9 Hz, H-7a), 6.17 (2H, d, *J*= 2.0 Hz, H-10a,14a), 6.25 (1H, t, *J*= 2.0 Hz, H-12a), 6.61 (1H, br s, H-14b), 6.72 (1H, br s, H-10b), 6.85 (2H, d, *J*= 8.8 Hz, H-3a,5a), 6.99 (1H, d, *J*= 16.0 Hz, H-8b), 7.08 (2H, d, *J*= 8.8 Hz, H-3b,5b), 7.12 (1H, d, *J*= 16.0 Hz, H-7b), 7.20 (2H, d, *J*= 8.8 Hz, H-2a,6a), 7.51 (2H, d, *J*= 8.8 Hz, H-2b,6b), 8.19 (2H, br s, 2xOH-11a,13a), 8.55 (1H, br s, OH-4a), 8.20 (1H, br s, OH-13b), 3.48-3.51 [4H, m, Glc(b)-H-2,3,4,5], 3.86 [2H, m, Glc(b)-H-6], 4.99 [1H, d, *J*= 7.6 Hz, Glc(b)-H-1]; The ^{13}C NMR spectral data are listed in Table.

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