Preparation on Oligostilbenes of Isorhapontigenin by Oxidative Coupling Reaction

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Four new compounds 1—4 were obtained from an oxidative coupling reaction of (*E*)-isorhapontigenin using $FeCl_3$ as oxidant. Their structures and stereochemistry were determined on the basis of spectroscopic evidence [UV, IR, MS, ^{1}H-, ^{13}C-NMR, NOE and 2D NMR], and their possible formation mechanisms were also discussed, respectively.

Key words oxidative coupling reaction; isorhapontigenin; oligostilbene; ferric chloride

An oxidative coupling reaction of (*E*)-isorhapontigenin (**8**) using $FeCl_3$ as an oxidant afforded ten oligostilbenes. In previous paper, we determined the structures of three major products, shegansu B, bisisorhapontigenin A and B.[1] Further investigation resulted in the structural identification of four minor products: bisisorhapontigenin C (**1**), bisisorhapontigenin D (**3**), triisorhapontigenin A (**2**) and tetraisorhapontigenin A (**4**) (Fig. 1). They are all new oligostilbenes of isorhapontigenin. The structures of the remaining three compounds have not been identified due to scarcity. This paper describes the structure and stereochemistry identification of the four new minor products on the basis of spectra analysis, and discussed their possible formation mechanisms.

Results and Discussion

The natural stilbene (*E*)-isorhapontigenin (**8**) from *Gnetum montanum* was treated with $FeCl_3$ in acetone at room temperature for 36 h to afford ten products. The structures of four minor products: **1**—**4** were established as follows:

Compound **1** was obtained as light yellowish amorphous powder. The molecular ion peak at *m/z* 514 in EI-MS, combined with its elementary analysis, ^{1}H- and ^{13}C-NMR spectra indicated that the molecular formula of $C_{30}H_{26}O_8$, suggesting that **1** was an isorhapontigenin dimer. The UV spectrum of **1** displayed absorption bands at λ_{max} 284, 334 nm, suggesting the presence of strong conjugated system in the molecule. The IR spectrum of **1** exhibited the existence of hydroxyl, aromatic groups and *trans* olefinic carbons. The ^{1}H-NMR spectrum of **1** showed the presence of two methoxyls, two aliphatic protons due to a dihydrobenzofuran moiety, two olefinic protons, and eleven aromatic protons, including two *meta*-coupled protons for ring B_2, two ABX systems for ring A_1 and ring B_1, and an AB_2 system for ring A_2. Its ^{13}C-NMR spectrum exhibited 24 signals representing 30 carbons, including 13 quaternary carbons, 15 tertiary carbons and two methoxyl carbons. Comparing the ^{1}H- and ^{13}C-NMR spectra of **1** with those of bisisorhapontigenin A (**5**) showed that the chemical shifts of 7a, 8a protons (δ *ca.* 4.5 ppm and *ca.* 5.5 ppm) in ^{1}H-NMR and 10b, 11b quaternary carbons (δ *ca.* 110 ppm and *ca.* 162 ppm) in ^{13}C-NMR were similar,[1] suggesting that the structure of **1** was similar to that of **5**, except for the relative positions of ring A_1 and A_2 which were interchanged. Thus, **1** was determined as an isorhapontigenin dimer polymerized by head to head (Fig. 1).

In order to clarify the stereochemistry of H-7a and H-8a, NOE experiment (Fig. 2) was carried out. The NOEs between H-7a and H-2a, H-6a, H-10a, H-14a; H-8a and H-10a, H-14a indicated *trans* orientation for H-7a and H-8a. Therefore, the stereochemistry of **1** was shown in structure **1**.

Compound **2** is a light yellowish amorphous powder. The HR EI-MS *m/z* 771.2445 $[M+H]^+$, in combination with its ^{1}H- and ^{13}C-NMR spectra revealed the molecular formula of $C_{45}H_{38}O_{12}$ (771.2442 calcd for $C_{45}H_{38}O_{12}$), which indicated that **2** could be an isorhapontigenin trimer. Its UV spectrum was similar to that of **1**, suggesting the presence of strong conjugated system. The IR spectrum of **2** indicated the presence of hydroxyl, aromatic group and *trans* olefinic bond. The ^{1}H-NMR spectrum of **2** indicated the presence of three methoxyls, four aliphatic methines due to two dihydrobenzofuran moiety and two *trans* olefinic protons, as well as 16 aromatic protons, which were attributed to three sets of ABX system for ring A_1, ring B_1 and ring C_1, one set of AB_2 system for ring A_2, and two sets of *meta*-coupled protons for ring B_2 and ring C_2. The ^{13}C-NMR spectrum of **2** showed 35 signals representing 45 carbons (including 20 quaternary carbons, 22 tertiary carbons and 3 methoxyl carbons). The chemical shifts (95—162 ppm) of C-9b, C-9c, C-10b, C-10c, C-11b, C-11c in **2** were similar to those of C-9b, C-10b, C-11b in compound **5**, indicating that the coupling route of **2** was similar to that of **5**. Therefore, The skeleton of **2** was similar to that of miyabenol C (**6**),[2] a resveratrol trimer. The connectivities for each isorhapontigenin were futher confirmed by HMBC cross-peaks between H-8a and C-9b; H-7a and C-11b; H-7b and C-10c, C-11c; H-8b and C-9b, C-10b, C-10c, C-11c (Fig. 3).

The stereochemistry of **2** was determined on the basis of NOESY experiment (Fig. 3). The interactions between H-7a and H-2a, H-6a, H-10(14)a; H-8a and H-2a, H-6a, H-10(14)a demonstrated *trans* orientation of H-7a and H-8a. The NOEs between H-7b and H-2b, H-14b indicated *cis* orientation of H-7b and ring B_2. The cross-peaks between H-8b and H-2b, H-6b, H-14b revealed *cis* orientation of H-8b and ring B_1. These evidences supported a *trans* orientation of H-7b and H-8b. Accordingly, the stereochemistry of **2** was clarified as shown in structure **2** (Fig.1).

Compound **3** was obtained as light yellowish crystals. The molecular ion peak at *m/z* 514 (M^+) in EI-MS, combined with the elementary analysis gave the molecular formula of $C_{30}H_{26}O_8$, which suggested that compound **3** was an isorhapontigenin dimer. The UV spectrum of **3** revealed the

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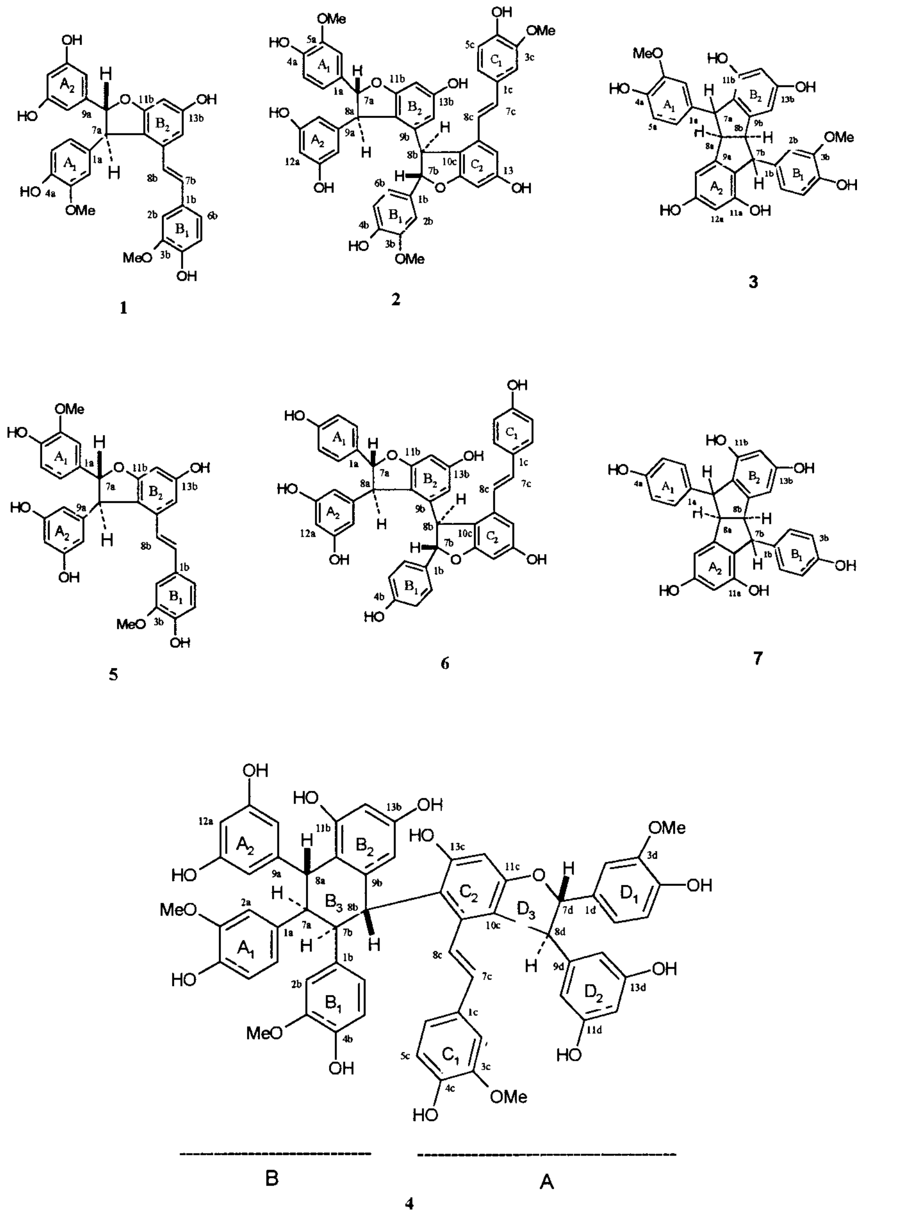

Fig. 1. Structures of Compounds **1**—**7**

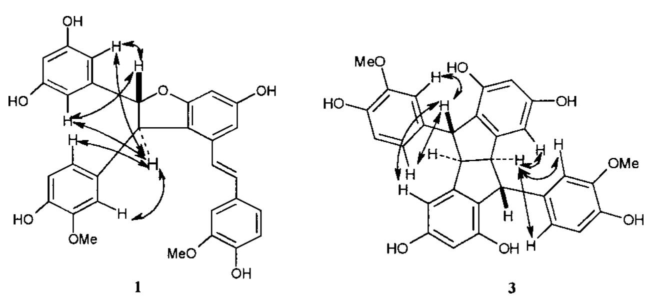

Fig. 2. Significant NOE Interactions of **1** and **3**

absence of *trans* olefinic protons in the molecule. Its IR spectrum exhibited the existence of hydroxyl and aromatic groups. The ^{1}H-NMR spectrum of **3** showed signals for two methoxyls, two aliphatic methines due to two fused five-membered ring, two sets of symmetric ABX system due to ring A_1 and B_1, and two sets of symmetrical *meta*-coupled protons due to ring A_2 and B_2. The ^{13}C-NMR spectrum displayed 15 signals representing 30 carbons (14 quaternary carbons, 14 tertiary carbons and two methoxyl carbons). Analysis of ^{1}H-, ^{13}C-NMR spectra and molecular formula indicated that **3** has a symmetric skeleton similar to that of pallidol (**7**) as shown in Fig. 1.[3)]

The stereochemistry of **3** was further established on the basis of the NOE experiment (Fig. 2). The NOE enhancements between H-7a with H-2a, H-6a, H-14a, and H-8a with H-2a, H-6a, H-14a suggested *trans* relationship between H-7a and H-8a as well as H-7b and H-8b. Therefore, **3** was determined as shown in structure **3** (Fig. 1).

Compound **4** was obtained as brown amorphous powder. The UV spectrum of **4** indicated characteristic absorptions of stilbene skeleton with hydroxyl group. The FTMS 1068 (M^{+}+H+K) was in agreement with a molecular fomula of $C_{60}H_{52}O_{16}$, which in combination with its ^{1}H- and ^{13}C-NMR spectra indicated that **4** could be a tetramer of isorhaponti-

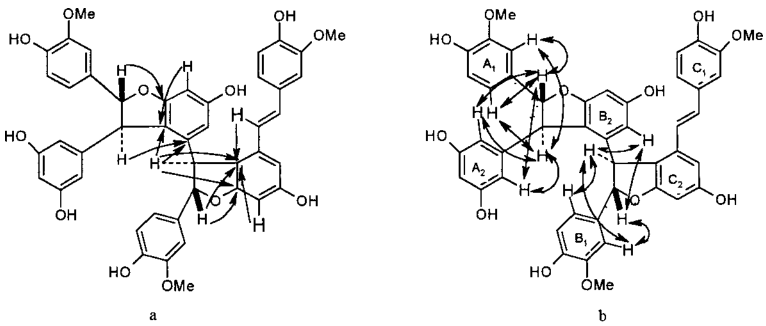

Fig. 3. Selected HMBC (a) and NOESY (b) Correlations of **2**

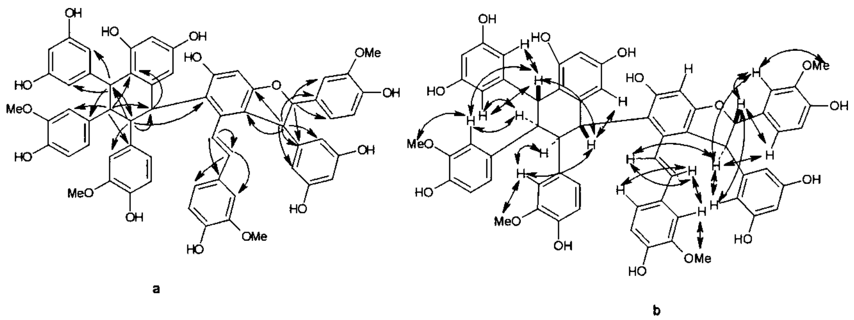

Fig. 4. Significant HMBC (a) and NOESY (b) Correlations of **4**

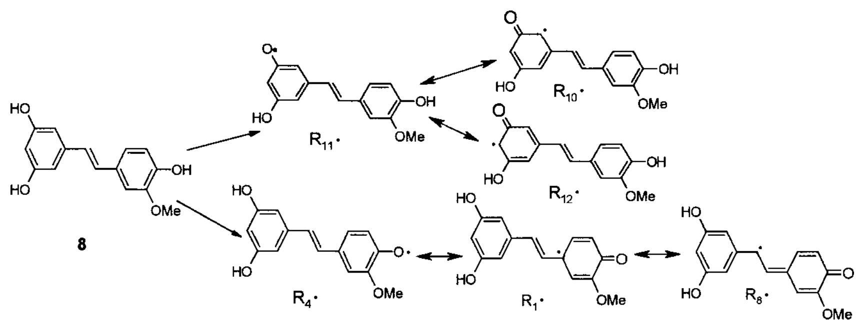

Fig. 5. Possible Free Radicals in the Oxidative Coupling of Isorhapontigenin.

genin.

The [1]H-NMR spectrum of **4** showed signals for four isorhapontigenin units (Table 3). Two of them formed a bis-isorhapontigenin A unit in which C-14c was substituted (part A of **4**), showing the following signals: two sets of ABX system for ring D_1 and C_1, one set of AB_2 system for ring D_2, two coupled aliphatic protons for dihydrobenzofuran moiety, two *trans* olefinic protons, an isolated aromatic proton and two singlets for two methoxyl groups. The other two isorhapontigenin units formed another dimer (part B of **4**) having a six-membered ring skeleton , which was deduced from the following signals: two sets of ABX system for ring A_1 and B_1, one set of AB_2 system for ring A_2, two *meta*-coupled doublet for ring B_2, four aliphatic protons for ring B_3, which formed a six-membered ring with two aromatic carbons, and two singlets for two aromatic methoxyl groups. The connectivities between parts A and B were confirmed by CH long-range correlations in the HMBC spectrum (Fig. 4). The key correlations between H-7b/C-8a, C-14c, C-8b supported that part A and part B were connected through a linkage between C-8b and C-14c as depicted in structure **4**. The relationships between H-8a/C-1a, C-7a, C-10(14)a C-7b; H-7a/C-1a, C-2a, C-6a, C-1b, C-8b, C-10b and H-8b/C-7b, C-10b confirmed the type of connection for two isorhapontigenins. Therefore, **4** was determined as shown in structure **4** (Fig. 1), which is a novel isorhapontigenin tetramer.

The stereochemistry of **4** was determined on the basis of NOESY experiment (Fig. 4). The NOEs between H-7a and H-2a, H-10(14)a; H-8a and H-2a, H-10(14)a suggested a *trans* orientation of H-7a and H-8a. Interactions between H-8a and H-8b, H-2a; H-7b and H-2b; H-8b and H-8a, H-2b, H-14b indicated a *cis* orientation of ring A_1, ring B_1 and H-8a, H-8b. The cross-peaks between H-7d and H-2d, H-6d, H-10(14)d; H-8d and H-2d, H-6d, H-10(14)d, H-8c indicated a *trans* orientation of H-7d and H-8d. Therefore, the stereochemistry of **4** was elucidated as shown in structure **4**.

In the course of oxidative coupling reaction, (*E*)-isorhapontigenin was presumably converted into phenoxyl radical intermediates by $FeCl_3$ to afford $R_1\cdot$, $R_4\cdot$, $R_8\cdot$, $R_{10}\cdot$ and $R_{11}\cdot$ radicals (Fig. 5). On the basis of this assumption, the possible mechanisms for the formation of compounds **1**—**4** were presumed as follows:

The coupling of $R_{11}\cdot$ and $R_8\cdot$ radicals yield an unstable quinone intermediate **9**, which generated **1** *via* spontaneous cyclization as shown in Fig. 6. The formation of product **2** would be possibly rationalized by coupling reaction of three molecules of **8** as shown in Fig. 7. The first procedure, combination of R_8· and R_{10}· radicals produced the intermediate **10**, which generated compound **5** through cyclization. The second step, **5** was converted into radical **11** by $FeCl_3$, which coupled with radical R_{10}· to afford quinone intermediate **12**. At last, spontaneous cyclization of **12** yield compound **2**. The $C\beta$–$C\beta$ coupling of two R_8· radicals gave a mixture of *erythro*- and *threo*-bisquinone methides as the intermediate. Addition of the aromatic ring to two bisquinone methides groups in *threo*-bisquinone (**13**) yield the corresponding compound **3** as shown in Fig. 8. The formation of product **4** would be possibly explained by Diels-Alder cycloaddition and oxidative coupling reaction of four molecules of **8** as shown in Fig. 9. Dimerization between two (*E*)-isorhapontigenin *via* the *exo* complex produced a head to head connected dimer (**14**), which was a trisubstituted aryltetralin. Simultaneously, compound **5** was converted into radical **15** by ferric chloride. Then, coupling of intermediate **14** and radical **15** generated compound **4**. Compound **5** obtained as a major product in this reaction further confirmed the mechanism.

Experimental

General Experimental Procedures IR spectra were run on a Perkin Elmer 683 infrared spectrometer in KBr pellets. UV spectrum were taken on a Shimadzu UV-300 spectrophotometer. NMR spectra were carried out on AM 500 using TMS as internal standard. FTMS spectra were taken on an ZAB-2F and 711 mass spectrometer and HPLC on waters 411.

Extraction and Isolation of Isorhapontigenin Acetone extract of *Gnetum montanum* (15 g) was subjected to ODS column chromatography (RP-18, 35—75 μm) with $CHCl_3$–MeOH–H_2O (8 : 1.5 : 1, lower layer) as eluent to afford crude isorhapontigenin, which was crystallized in MeOH/H_2O to give light yellow nubby crystal of (*E*)-isorhapontigenin (10.7 g), mp 172—175 °C.

Oxidative Coupling Reaction of Isorhapontigenin A solution of (*E*)-isorhapontigenin (5 g, 0.019 mol) in acetone (20 ml) was cooled to 0 °C in ice bath, to which a solution of $FeCl_3 \cdot 6H_2O$ (4 g, 0.015 mol) in water (30 ml)

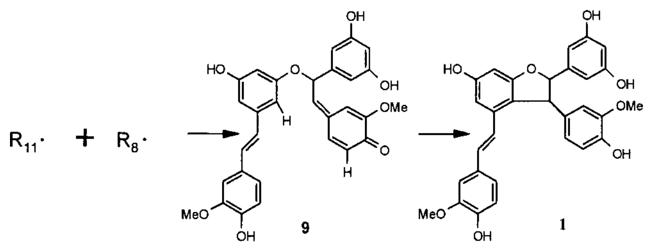

Fig. 6. Postulated Intermediates for the Formation of Compound **1**

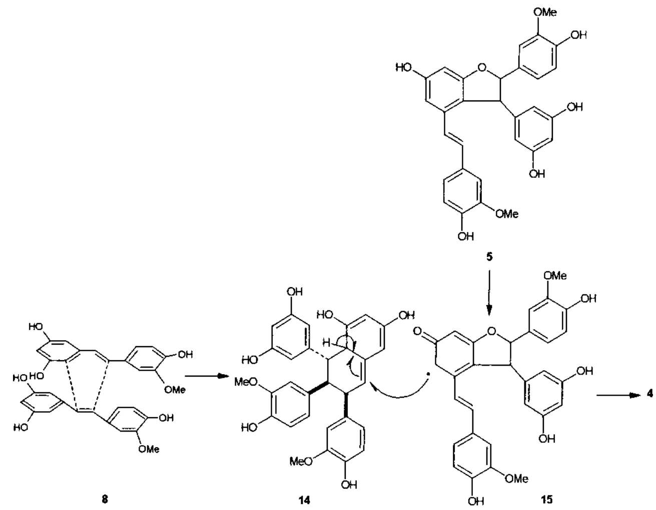

Fig. 9. Postulated Intermediates for the Formation of Compound **4**

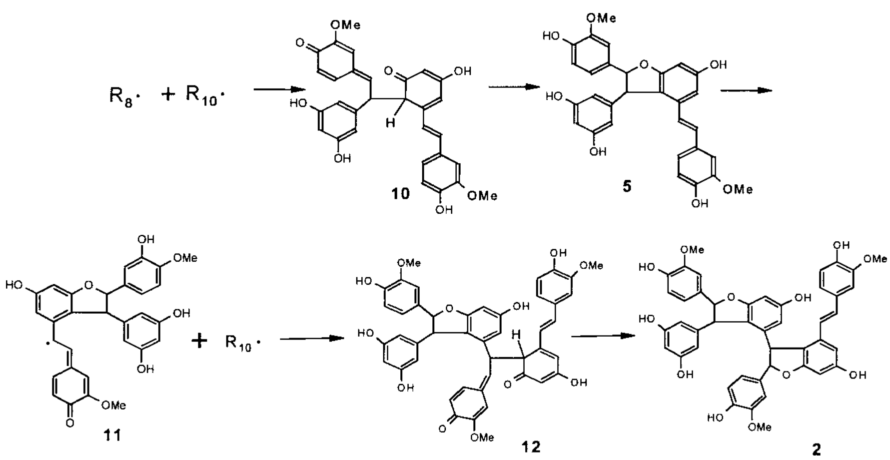

Fig. 7. Postulated Intermediates for the Formation of Compound **2**

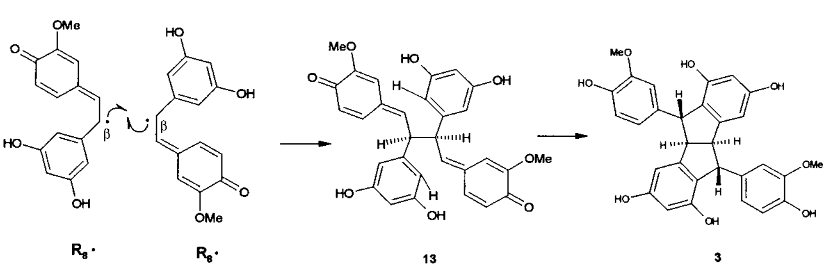

Fig. 8. Postulated Intermediates for the Formation of Compound **3**

was added. The reactant was stirred under N_2 and kept for 36 h at room temperature. After removal of the acetone in low temperature, the solution was extracted with EtOAc, and the combined EtOAc extract was dried over anhydrous Na_2SO_4 for 24 h. Then it was concentrated *in vacuo* to yield a residue of about 5 g.

Isolation of the Reaction Products The residue was dissolved in EtOH and mixed with silica gel (60—100 mesh, 25 g). After dryness, the mixture was subjected to a silica gel column eluting with $CHCl_3$–MeOH–*n*-hexane–EtOAc–H_2O (7.5 : 1.1 : 1.0 : 0.5 : 0.08) to give fractions I—IX: Fraction I: crystallization in MeOH/H_2O gave isorhapontigenin (1.026 g). Fraction III: concentration *in vacuo* afforded compound **5** (988 mg). Fraction IV: evaporation *in vacuo* afforded shegansu B (200 mg), light brown amorphous powder. Fraction V: removal of the solvent *in vacuo* afforded bisisorhapontigenin B (200 mg). Fraction VI: purification by semipreparative HPLC eluted with MeOH–H_2O (155 : 145) gave compound **2** (17 mg, 0.34%). Fraction VII: separation by ODS column chromatography (RP-18, 35—75 μm) with MeOH–H_2O (6 : 4) as eluent provided Fractions 1—12. Fraction 6 afforded compound **3** (30 mg, 0.60%) crystallized from MeOH–H_2O (2 : 3). Fraction VIII: ODS column chromatography (RP-18, 35—75 μm) using MeOH–H_2O (65 : 35) as fluid phase afforded Fraction 1—16. Fraction 13 and 14 were combined and evaporated to yield compound **1** (27 mg, 0.54%). Fraction IX: separation through ODS column chromatography (RP-18, 35—75 μm)

Table 1. ^{1}H- and ^{13}C-NMR Data for Compounds **1** and **3** (δ in ppm and J in Hz)[a]

Position	**1**		**3**	
	δ_H	δ_C	δ_H	δ_C
1a		134.1		138.5 s
2a	6.55 d, 1.6	108.6	6.79 d, 2.0	112.2 d
3a		147.5		145.6 s
4a		148.4		150.2 s
5a	6.56 d, 8.2	115.5	6.66 d, 8.1	115.5 d
6a	6.49 dd, 1.6, 8.2	121.5	6.52 dd, 8.1, 2.0	120.3 d
7a	4.55 d, 5.6	58.0	4.52 s	54.3 d
8a	5.40 d, 5.6	94.2	3.80 s	60.4 d
9a		146.9		148.1 s
10a	6.17 d, 2.1	106.8		122.9 s
11a		159.7		159.2 s
12a	6.04 t, 2.1	101.7	6.46 d, 2.0	102.3 d
13a		159.7		155.5 s
14a	6.17 d, 2.1	106.8	6.16 d, 2.0	103.4 d
1b		130.3		138.5 s
2b	6.79—6.81 m	115.8	6.79 d, 2.0	112.2 d
3b		147.4		145.6 s
4b		148.5		150.2 s
5b	6.79—6.81 m	115.8	6.66 d, 8.1	115.5 d
6b	6.79—6.81 m	119.2	6.52 dd, 8.1, 2.0	120.3 d
7b	6.57 d, 16.6	134.0	4.52 s	54.3 d
8b	5.54 d, 16.6	122.0	3.80 s	60.4 d
9b		133.1		148.1 s
10b		119.8		122.9 s
11b		162.5		159.2 s
12b	6.54 br s	91.2	6.46 d, 2.0	102.3 d
13b		159.7		155.5 s
14b	6.97 br s	110.3	6.16 d, 2.0	103.4 d
OCH_3	3.80 s	56.0	3.74 s	56.2 q
OCH_3	3.69 s	56.2	3.74 s	56.2 q

a) Measured in CD_3COCD_3 at 500 MHz for ^{1}H-NMR, and 125 MHz for ^{13}C-NMR, respectively.

Table 3. ^{1}H- and ^{13}C-NMR Data for Compound **4** (δ in ppm and J in Hz)[a]

Position	δ_H	δ_C	Position	δ_H	δ_C
1a		137.9	1c		130.7
2a	6.57 d, 2.0	111.9	2c	6.45 d, 2.0	109.7
3a		145.4	3c		146.8
4a		147.8	4c		145.2
5a	5.70 d, 8.0	115.0	5c	6.70 d, 8.0	115.5
6a	6.34 dd, 8.0, 2.0	119.8	6c	6.49 dd, 8.0, 2.0	120.0
7a	4.22 m	56.7	7c	6.08 d, 16.5	133.7
8a	3.02 m	59.9	8c	6.04 d, 16.5	126.6
9a		146.2	9c		133.7
10a	6.03 m	105.4	10c		119.6
11a		159.2	11c		160.2
12a	6.16 t, 2.0	100.9	12c	6.37 s	97.5
13a		159.2	13c		159.3
14a	6.03 m	105.4	14c		122.9
1b		135.8	1d		133.7
2b	6.68 br s	114.7	2d	6.94 d, 2.0	110.3
3b		145.1	3d		144.6
4b		144.5	4d		147.7
5b	6.52 d, 8.0	114.5	5d	6.80 d, 8.0	115.5
6b	6.73 d, 8.0	123.2	6d	6.75 dd, 8.0, 2.0	119.7
7b	4.18 d, 12.5	53.6	7d	5.22 d, 8.0	94.2
8b	4.63 d 12.5	54.8	8d	4.40 d, 8.0	58.4
9b		146.4	9d		146.4
10b		123.6	10d	6.03 m	106.9
11b		155.2	11d		159.2
12b	6.39 br s	102.6	12d	6.09 t, 2.0	101.3
13b		157.1	13d		159.2
14b	5.89 br s	106.0	14d	6.03 m	106.9
3aCH_3	3.56 s	55.8	3cCH_3	3.73 s	55.9
3bCH_3	3.48 s	55.5	3dCH_3	3.77 s	56.2

a) Measured in CD_3COCD_3 at 500 MHz for ^{1}H-NMR, and 125 MHz for ^{13}C-NMR, respectively.

Table 2. ^{1}H- and ^{13}C-NMR Data for Compound **2** (δ in ppm and J in Hz)[a]

Position	δ_H	δ_C	Position	δ_H	δ_C	Position	δ_H	δ_C
1a		131.5	1b		141.9	1c		127.9
2a	6.71 d, 1.5	110.1	2b	6.43 d, 1.8	110.1	2c	6.92 d, 1.8	110.4
3a		147.6	3b		147.6	3c		147.6
4a		147.4	4b		146.7	4c		146.7
5a	6.45 d, 8.3	115.2	5b	6.59 d, 8.3	115.4	5c	6.59 d, 8.3	115.7
6a	6.55—6.58 m	117.8	6b	6.64 dd, 1.8, 8.3	117.8	6c	6.55—6.58 m	119.3
7a	5.24 d, 6.0	93.3	7b	5.13 br s	90.8	7c	6.83 d, 16.3	130.4
8a	4.52 d, 6.0	55.0	8b	4.24 br s	55.2	8c	5.56 d, 16.3	121.1
9a		145.6	9b		131.7	9c		134.2
10a	6.00 br s	105.3	10b		117.1	10c		120.2
11a		158.9	11b		160.3	11c		160.5
12a	5.91 t, 2.1	101.2	12b	6.15 d, 2.1	95.3	12c	6.53 br s	96.5
13a		158.9	13b		159.0	13c		147.4
14a	6.00 br s	105.3	14b	5.93 d, 2.1	106.5	14c	6.27 br s	103.5
OCH_3	3.56 s	55.5	OCH_3	3.59 s	55.5	OCH_3	3.54 s	55.3

a) Measured in CD_3COCD_3 at 500 MHz for ^{1}H-NMR, and 125 MHz for ^{13}C-NMR, respectively.

eluted with $CHCl_3$–cyclohexane–MeOH–EtOAc–Me_2CO–HOAc (600 : 150 : 150 : 300 : 75 : 2.5) afforded Fraction 1—22, among them, Fraction 4 was concentrated to dryness to afforded compound **4** (18 mg, 0.36%).

6-Hydroxy-2-(3,5-dihydroxyphenyl)-3-(3-methoxy-4-hydroxyphenyl)-4-(*E*)-(3-methoxy-4-hydroxystyryl)-2,3-dihydrobenzofuran (**1**): Yellowish amorphous powder. UV λ_{max} (EtOH) nm (log ε): 285 (4.10), 335 (sh) (4.14). IR (KBr) cm^{-1}: 3418, 1604, 1515, 1451, 1273, 1158, 960, 870. EI-MS *m*/*z*: 514 (M^+). *Anal.* Calcd for $C_{30}H_{26}O_8$: C, 60.67; H, 5.26. Found: C, 67.28; H, 4.62. ^{1}H- and ^{13}C-NMR (acetone-d_6) see Table 1.

6-Hydroxy-2-(3-methoxyl-4-hydroxyphenyl)-3-{4-[6-hydroxy-2-(3-methoxyl-4-hydroxyphenyl)-3-(3,5-dihydroxyphenyl)-2,3-dihydrobenzofuranyl]}-4-(*E*)-(3-methoxyl-4-hydroxystyryl)-2,3-dihydrobenzofuran (**2**): Yellowish amorphous powder. UV λ_{max} (EtOH) nm: 285, 330. IR (KBr) cm^{-1}: 3419, 1603, 1516, 1275, 1123, 960, 870. EI-MS *m*/*z*: 770 (M^+). HR-EI-MS *m*/*z*: 771.2445 $[M+H]^+$ (calcd for $C_{45}H_{38}O_{12}$: 771.2442). ^{1}H- and ^{13}C-NMR (acetone-d_6) see Table 2.

5,11-Bis(3-methoxy-4-hydroxyphenyl)-2,4,8,10-tetrahedroxydibenzo-[*a*,*e*]-tetrahedropentalene (**3**): Yellowish nubbly ctystal, mp 221 °C. UV λ_{max} (EtOH) nm: 205, 285. IR (KBr) cm^{-1}: 3424, 2918, 1611, 1513, 1464, 1265, 1128, 1034. EI-MS (*m*/*z*, %): 514 (M^+, 90), 390 (100), 135 (65), 84 (51), 66 (33), 44 (47), 32 (100). *Anal.* Calcd for $C_{30}H_{26}O_8$: C, 66.54; H, 5.49. Found: C, 66.35; H, 4.87. ^{1}H- and ^{13}C-NMR (acetone-d_6) see Table 1.

1-[6-Hydroxy-2-(3-methoxy-4-hydroxyphenyl)-3-(3,5-dihydroxyphenyl)-4-(*E*)-(3-methoxy-4-hydroxystyryl)-2,3-dihydrobenzofuranyl]-2,3-bis(3-methoxy-4-hydroxyphenyl)-4-(3,5-dihydroxyphenyl)-5,7-dihydroxy-1,2,3,4-tetrahedronaphthalene (**4**): Brown amorphous powder. UV (EtOH) λ_{max} nm (log ε): 280 (4.47), 310 (sh) (4.17). IR (KBr) cm^{-1}: 3398.4, 1602.8, 1514.0, 1463.9, 1272.9, 1153.4, 1029.9, 840.9. FT-MS (M^++H+K) *m*/*z*: 1068. ^{1}H- and ^{13}C-NMR (acetone-d_6) see Table 3.

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