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Two lignan dimers from bamboo stems (*Phyllostachys edulis*)

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Abstract

Phyllostadimers A and B, two bis-lignans in which the two lignan units are directly connected by a C–C bond, were isolated from stems of bamboo, *Phyllostachys edulis*. Their structures were determined on the basis of spectral evidence. In addition, 14 known compounds were also obtained throughout the investigation. Phyllostadimer A significantly inhibited liposomal lipid peroxidation.

Keywords: *Phyllostachys edulis*; Gramineae; Lignan dimers; Antioxidant activity

1. Introduction

Bamboos, which are large perennial grasses with woody stalks, comprise 45 genera, and are distributed widely in the tropics but extend also to sub-frigid zones. Bamboo is a very popular plant in Asia and its characteristic physical properties have made it very useful, such as a potential natural source of pulp. Bamboo has also been reported to contain antibacterial and medicinal substances (Okabe et al., 1975; Shibata et al., 1975; Chuyen et al., 1982; Nishina et al., 1991). In our continuing study of biologically active compounds from natural sources, we became interested in the constituents of bamboo (*Phyllostachys edulis* Makino; Gramineae). In this paper, we report the structures of two novel bis-lignans, phyllostadimers A (**1**) and B (**2**) and 14 known compounds, along with the antioxidant activity of compound **1**.

2. Results and discussion

Repeated column chromatography of a BuOH-soluble partition of the MeOH extract of stems of *Phyllostachys edulis* afforded two novel bis-lignans, which were named phyllostadimers A (**1**) and B (**2**), and further chromatographic purification of the EtOAc-soluble partition of the MeOH extract provided another 14 known compounds.

Compound **1** was obtained as an amorphous powder. Its IR spectrum showed hydroxy (3438 cm^{-1}) and aromatic (1591 cm^{-1}) bands. The ^1H NMR spectrum of **1** exhibited the presence of a 1,3,4,5-tetra-substituted benzene ring [δ_H 6.63 (2H, *s*)] and a 1,3,4-tri-substituted benzene ring [δ_H 6.96 (1H, *brs*), 6.73 (1H, *brd*, $J=8.1$ Hz), 6.85 (1H, d, $J=8.1$ Hz)]. In the ^1H–^1H COSY spectrum of **1**, the correlations of H-8 (δ_H 3.13) with H-7 (δ_H 4.78) and H-9 (δ_H 4.04), and H-8′ (δ_H 4.13) with H-7′ (δ_H 4.99) and 2H-9′ (δ_H 3.50 and 3.97) gave evidence for the partial structures I and II (Fig. 1).

The ^{13}C NMR spectrum of **1** also showed the presence of two aromatic rings (A and B) and partial structures I [δ_C 54.6 (CH), 72.1 (CH_2) and 86.0 (CH)] and II [δ_C 60.7 (CH_2), 72.7 (CH) and 87.2 (CH)]. Based on these data, compound **1** was assumed to be a lignan (Ward, 1999). In the HMBC spectrum, the proton signal at δ_H 6.63 (H-2 and H-6) was correlated with the carbon signals at δ_C 153.6 (C-3 and C-5), 137.7 (C-4), 134.5 (C-1) and 86.0 (C-7), and the proton signal at δ_H 4.78 (H-7) was correlated with the carbon signals at δ_C 102.9 (C-2 and C-6) and 72.1 (C-9). These results showed that partial structures A and I were connected. The observed HMBC correlations (Fig. 2) of H-2′ (δ_H 6.96) to C-1′ (δ_C 131.4), C-3′ (δ_C 146.8), C-4′ (δ_C 145.0),

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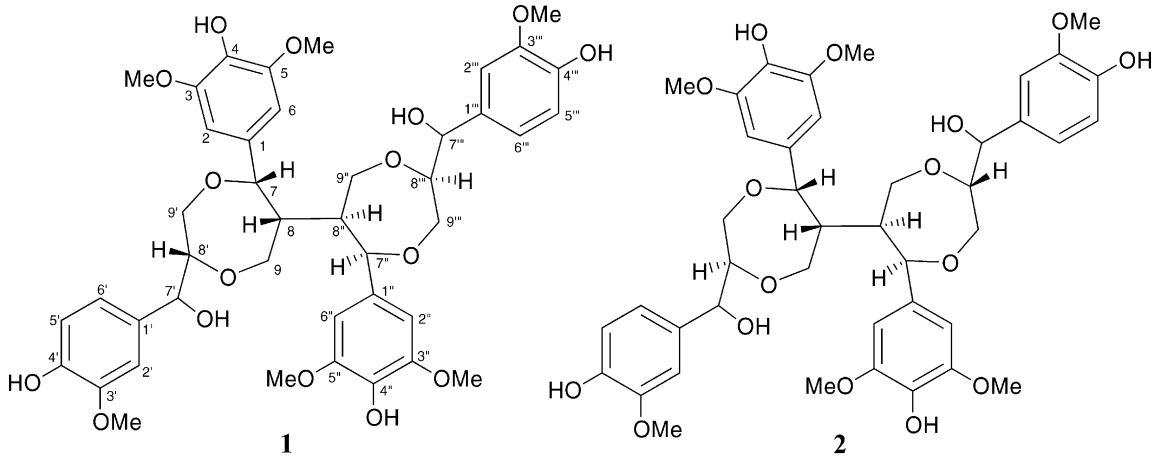

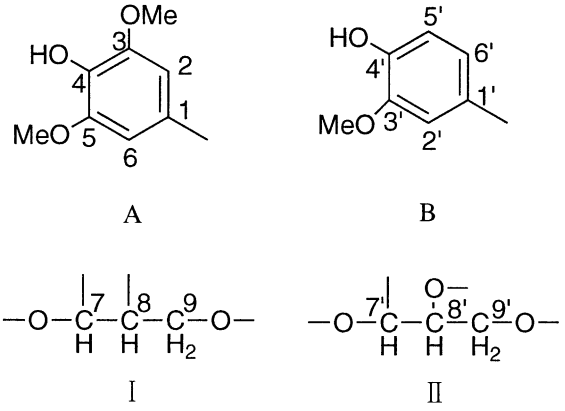

Fig. 1. Partial structures for compound **1**.

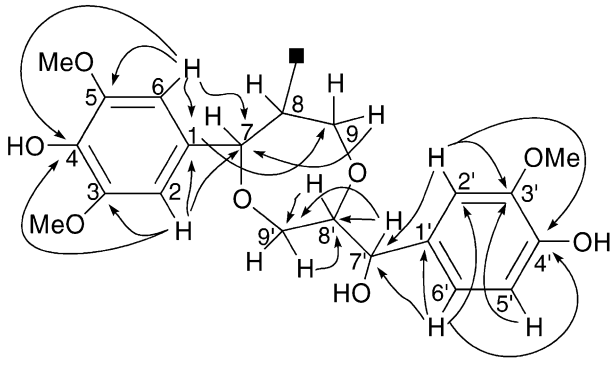

Fig. 2. Significant HMBC correlations observed for compound **1**.

C-7′ (δ_C 72.7) and C-8′ (δ_C 87.2), and H-8′ (δ_H 4.13) to C-1′, C-6′ (δ_C 118.9), C-7′ and C-9′ (δ_C 60.7) confirmed, in here, that partial structures B and II were connected.

Acetylation of compound **1** gave a triacetate (**1a**) [δ_H 1.98, 2.14 and 2.28 (each 3H, *s*)], for which the H-7′ signal in the ^{1}H NMR spectrum was shifted downfield from δ_H 4.99 to δ_H 6.09. This indicated that a hydroxy group occurred at C-7′ and that oxygen functions on C-7, C-9, C-8′ and C-9′ were connected by an ether ring. There were two possibilities for such an ether ring: between C-7 and C-9′, and C-9 and C-7′ or between C-7 and C-7′, and C-9 and C-9′ as well as C-7 and C-8′. In the NOESY spectrum of **1**, correlations were observed between H-7 and H-9′, and between H-9 and H-8′. This observation indicated that an ether ring was connected between C-7 and C-9′, and C-9 and C-7′. However, there was no connection to the C-8 methine. The FABMS of compound **1** showed a molecular ion peak at *m*/*z* 833.3047 $[M+Na]^+$ (calcd for $C_{42}H_{50}O_{16}Na$, 833.2987), which suggested that compound **1** may be a dimer. The acetate **1a** showed a molecular ion peak at *m*/*z* 1085.3636 $[M+Na]^+$ (calcd for $C_{54}H_{62}O_{22}Na$, 1085.3630) in the FABMS. Based on these observations and considering the ^{1}H NMR and ^{13}C NMR spectral data of **1**, the molecular formula of compound **1** was determined as $C_{42}H_{50}O_{16}$ and compound **1** was assigned as a dimer connected between C-8 and C-8″. The relative stereochemistry and the positions of the methoxyl groups were determined based on NOESY data, from correlations of H-7 with H-8 and H-9′β, H-9β with H-8, H-8′ and H-9′β, and H-8′ with H-9′β (Fig. 3).

Compound **2** showed a molecular ion peak at *m*/*z* 833.3010 $[M+Na]^+$ (calcd for $C_{42}H_{50}O_{16}Na$, 833.2994), similar to compound **1**, and its ^{1}H NMR spectrum showed almost the same chemical shifts and coupling patterns, except for H-8′ [**1**: δ_H 4.13 (*m*); **2**: 3.88 (1H, *m*)] and H-9′ [**1**: δ_H 3.50 (1H, brd, $J=8.0$ Hz) and 3.97 (1H, *brd*, $J=8.0$ Hz); **2**: δ_H 3.33 (1H, *brd*, $J=12.4$ Hz), 3.57 (1H, *brd*, $J=12.4$ Hz)]. The ^{13}C NMR spectrum of **2** was also similar to that of **1** except for C-7′ (**1**: 72.7; **2**: 74.2) and C-8′ (**1**: 87.2; **2**: 89.2). In the HMBC spectrum of **2**, the correlations of proton and carbon signals were almost same as those of compound **1** (Fig. 2). These results indicated that compounds **1** and **2** have the same structures, except for relative stereochemistry. The correlations of H-7 with H-8 and H-9′ β, and H-9β with H-8 and H-9′ β in the NOESY spectrum (Fig. 3) of **2** indicated that it had the same configuration as **1** except for that at C-8′. Thus, the structure of **2** was determined to be as shown.

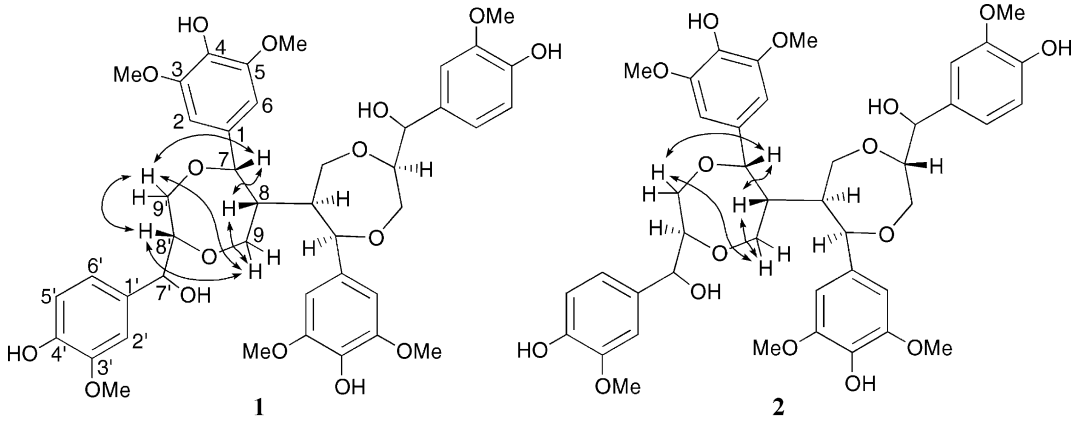

Fig. 3. Selected NOESY correlations of compounds **1** and **2**.

The following known compounds were identified in comparison with the literature data: stigmast-4-ene-3, 6-dione (**3**) and β-sitosterol (**4**) (Greca et al., 1990), friedelin (**5**) (Mahato and Kundu, 1994), glutinol (**6**) (Yuan and Sun, 1998), coniferaldehyde (**7**) (Sy and Brown, 1999), *p*-coumaric acid methyl ester (**8**), 3-(4-hydroxy-3-methoxyphenyl)-2-propenoic acid (**9**) (Kelley et al., 1976), 4-methoxybenzaldehyde (**10**) (Dhami and Stothers, 1966), 4-hydroxy-3-methoxy-propiophenone (**11**) (Ito et al., 2001), sinapaldehyde (**12**) (Gunhild and Roland, 1968), lyoniresinol (**13**) (Miyamura et al., 1983), *p*-coumaric acid (**14**), ferulic acid (**15**) (Massow and Smith, 1976), 4-hydroxybenzaldehyde (**16**) (Taguchi et al., 1981).

Structural stability of the compounds **1** and **2** was estimated by the molecular mechanics calculations with our developed computer program 504.exe. Because the crystallographic data for the compound were not obtained, the initial structures for the consequent calculations were constructed. First, 18 conformers were surveyed by the exhaustive conformational search for dioxepane moiety. Then, the most stable conformation of this moiety was duplicated, and substituted by phenyl and benzyl groups to derive two initial structures, "C1" and "C2", having different chirality for the phenyl group. Our program 504.exe generated seriate conformational validations and determined their steric energy using the AMBER (assisted model building with energy refinement) force field calculations. Neglecting the 100 kcal/mol energetically higher conformations than the temporally lowest energy conformation, the program surveyed more than 3000 of the optimized conformations. After this sequence, the most stable conformations of the model compounds C1 and C2 were extracted. The lowest energy conformation of the model compound C1 (steric energy = 34.19 kcal/mol, Fig. 4) shows its low Boltzmann-population (77.39%). It would be caused by the high steric hindrance of the benzyl groups of C1, inducing non-symmetric dioxepane dimeric moiety. The most stable conformation of

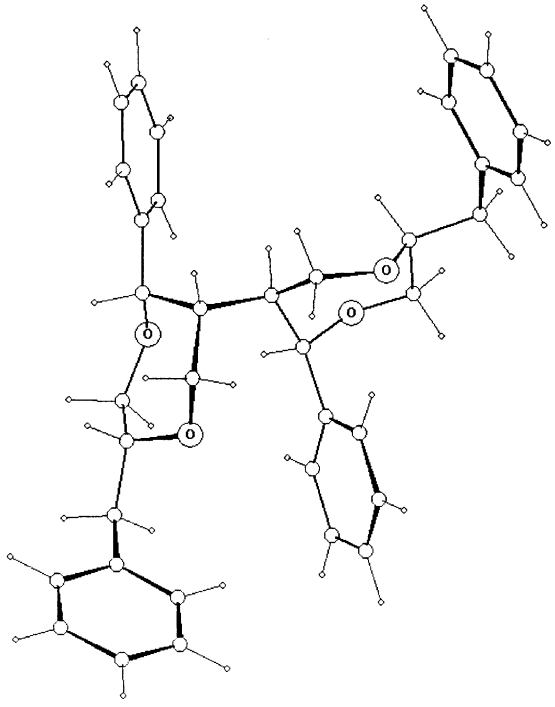

Fig. 4. The lowest energy conformation of the model compound C1.

the model compound C2 (steric energy = 30.35 kcal/mol, Fig. 5) is energetically isolated causing high Boltzmann-population of 97.10%. Its structure shows symmetric dioxepane dimeric moiety. It would indicate that the C2 compound is intramolecular-entropically stable.

The effects of compound **1** on ADP/Fe^{2+}-induced liposomal lipid peroxidation were compared with that of the well-known antioxidant α-tocopherol (Fig. 6). The liposomes were prepared by drying the chloroform solution of egg yolk phosphatidylcholine (EyPC) under a stream of N_2 gas. Then, the thin lipid film was hydrated with 10 mM Tris-HCl buffer (pH 7.4, 25 °C), and sonicated in a bath type sonicator. Both compound **1** and α-tocopherol inhibited lipid peroxidation in a concentration-dependent manner. However, compound **1**

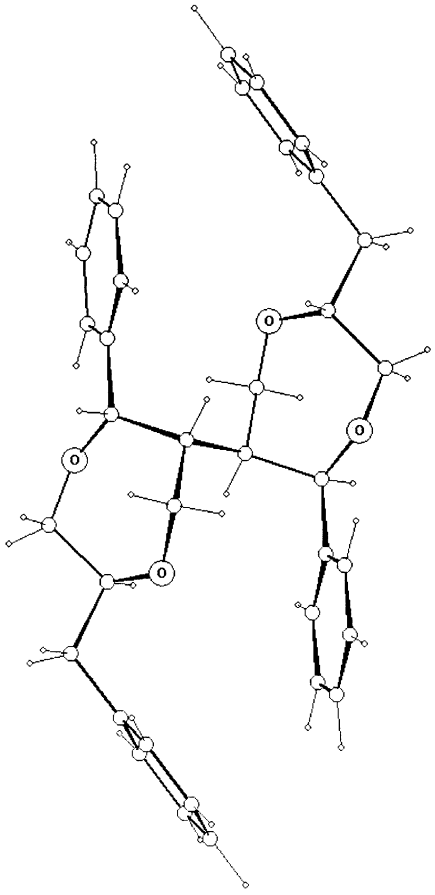

Fig. 5. The lowest energy conformation of the model compound C2.

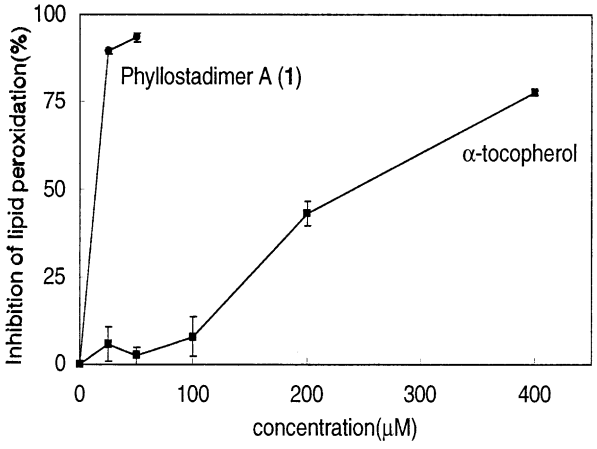

Fig. 6. Inhibitory effect of compound **1** and α-tocopherol on lipid peroxidation of EyPC liposomes induced by ADP/Fe^{2+}. The value relative to the amount of lipid peroxides in terms of TBARS without test compound is shown as the inhibition% on the ordinate. The values are means±S.D. in three runs.

was about 16 times more potent than α-tocopherol, i.e., the IC_{50} of compound **1** was about 15 μM, while that of α-tocopherol was 235 μM. Compound **1** may inhibit lipid peroxidation via radical scavenging like α-tocopherol, since compound **1** has four phenolic OH groups. However, the greater activity of compound **1** cannot be explained simply by the difference in the number of phenolic OH groups, and perhaps the unique structure of compound **1** may also contribute to its potent antioxidative effect.

3. Experimental

3.1. General

NMR (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR, both using TMS as internal standard) were measured on a Bruker AM-400 spectrometer. Mass spectra were measured on JEOL JMS-DX-303 and SX-102A instruments. Column chromatography: silica gel 60 (Merck), LH-20 (Pharmacia); HPLC: silica gel (YMC-pack SIL-06 SH-043-5-06, 250×20 mm, Hibar RT 250-25 Si 60), GPC (Shodex H-2001, 2002, $CHCl_3$), GPC (Asahipak GS-310 2G, MeOH), ODS (YMC-R-ODS-5, Yamamura). IR spectra were recorded on a JASCO Fourier transform infrared spectrometer (FT/IR-420). Optical rotations were recorded at room temperature on a JASCO DIP-370 polarimeter.

3.2. Plant material

The stems of bamboo, *Phyllostachys edulis* (23.8 kg) were collected May 1998 in Tokushima. The plant was identified by Dr. Kawazoe, and a voucher specimen (UTP98007) is held at the herbarium of Faculty of Pharmaceutical Sciences, University of Tokushima.

3.3. Extraction and isolation

The stems of *P. edulis* (23.8 kg) were crushed and extracted three times with MeOH at 60 °C. The MeOH extracts were concentrated in vacuo to give a residue (820 g), which was partitioned between EtOAc and H_2O. The EtOAc layer was concentrated to give a residue (39.5 g). The water layer was partitioned between *n*-BuOH and H_2O. The *n*-BuOH layer was concentrated to give a residue (163 g), which was loaded onto a silica gel column, and eluted with different solvents of increasing polarity (*n*-hexane–EtOAc; EtOAc–MeOH) to give 11 fractions (A–K). Fraction C (2.5 g) was applied to a Sephadex LH-20 column, eluted with MeOH to give eight further fractions (C1–C8). Fraction C4 (714 mg) was subjected to HPLC (ODS, MeOH–H_2O, 6:4), HPLC (silica gel, $CHCl_3$–MeOH, 95:5) to give **1** (14 mg) and **2** (8.8 mg). The EtOAc layer was subjected to silica gel cc, eluted with different solvents of increasing polarity (*n*-hexane–EtOAc; EtOAc–MeOH), and applied to a Sephadex LH-20 column (MeOH) to give 21 fractions (a–u). Fraction f (426 mg) was purified by HPLC (silica gel, $CHCl_3$), HPLC (GPC, $CHCl_3$) to

give **3** (6 mg) and **4** (3 mg), **5** (53 mg), **6** (33 mg). Fraction g (5.3 g) was separated by HPLC (GPC, $CHCl_3$) and HPLC (silica gel, $CHCl_3$–MeOH, 99:1) to give **7** (17 mg) and **8** (24 mg), **9** (70 mg) and **10** (10 mg) and **11** (11 mg), **12** (16 mg). Fraction k (8 g) was loaded on a silica gel column, eluted with different solvents of increasing polarity ($CHCl_3$–MeOH), and separated by HPLC (ODS, MeOH–H_2O, 8:2), HPLC (GPC, MeOH) to give **13** (35 mg), **14** (30 mg). Fraction j (6 g) was loaded onto a silica gel column, and eluted with different solvents of increasing polarity ($CHCl_3$–MeOH) to give 11 fractions. Fraction j5 (270 mg) was purified by HPLC (silica gel, $CHCl_3$–MeOH, 99:1) to give **16** (45 mg). Fraction j6 (500 mg) was separated by HPLC (GPC, $CHCl_3$), HPLC (silica gel, $CHCl_3$–MeOH, 99:1) and HPLC (silica gel, *n*-hexane–EtOAc, 1:3) to give **15** (19 mg).

3.3.1. Phyllostadimer A (1)

Amorphous powder; mp 117–119 °C; $[\alpha]_D$ −4.0° ($CHCl_3$; *c* 1.0); IR (KBr) ν_{max} 3438, 1591, 1518, 1459, 1230, 1127 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.96 (1H, brs, H-2′, 2‴), 6.85 (1H, d, J = 8.1 Hz, H-5′,5‴), 6.73 (1H, brd, J = 8.1 Hz, H-6′,6‴), 6.63 (2H, s, H-2,2″ and H-6,6″), 4.99 (1H, brs, H-7′,7‴), 4.78 (1H, brd, J = 6.0 Hz, H-7,7″), 4.34 (1H, t, J = 6.8, 12.8 Hz, H-9,9″), 4.13 (1H, m, H-8′,8‴), 4.04 (1H, m, H-9,9″), 3.97 and 3.50 (each 1H, brd, J = 8.0 Hz, H-9′,9‴), 3.13 (1H, m, H-8,8″), 3.92 (6H, s, OCH_3-3,3″ and OCH_3-5,5″), 3.88 (3H, s, OCH_3-3′,3‴); ^{13}C NMR data, see Table 1; HRFABMS *m*/*z* 833.3047 $[M+Na]^+$ (calcd for $C_{42}H_{50}O_{16}Na$, 833.2987).

Table 1
^{13}C NMR spectral data of compounds **1** and **2**

	1	2
C-1, 1″	134.5	134.9
C-2, 2″	102.9	102.9
C-3, 3″	153.6	153.3
C-4, 4″	137.7	137.8
C-5, 5″	153.6	153.3
C-6, 6″	102.9	102.9
C-7, 7″	86.0	85.9
C-8, 8″	54.6	54.6
C-9, 9″	72.1	72.1
C-1′, 1‴	131.4	132.0
C-2′, 2‴	108.5	109.9
C-3′, 3‴	146.8	146.6
C-4′, 4‴	145.0	145.6
C-5′, 5‴	114.3	114.4
C-6′, 6‴	118.9	120.5
C-7′, 7‴	72.7	74.2
C-8′, 8‴	87.2	89.2
C-9′, 9‴	60.7	60.8
OMe-3, 3″	56.4	56.4
OMe-5, 5″	56.4	56.4
OMe-3′, 3‴	56.1	56.1

3.3.2. Acetylation of 1

Compound **1** (3 mg) was subjected to acetylation with Ac_2O–pyridine overnight at room temperature to give **1a**. Compound **1a**: Amorphous powder; mp 78–80 °C; ^1H NMR ($CDCl_3$) δ 7.00 (1H, brs, H-2′, 2‴), 6.97 (1H, d, J = 8.0 Hz, H-5′,5‴), 6.92 (1H, d, J = 8.0 Hz, H-6′,6‴), 6.52 (2H, s, H-2,2″ and H-6,6″), 6.09 (1H, d, J = 4.2 Hz, H-7′,7‴), 4.71 (1H, brs, H-7,7″), 4.61 (1H, ddd, J = 2.8, 4.2, 5.2 Hz, H-8′,8‴), 4.47 (1H, dd, J = 5.2, 11.9 Hz, H-9,9″), 4.27 (1H, m, H-9′,9‴), 4.24 (1H, dd, J = 2.8, 11.9 Hz, H-9,9″), 3.91 (1H, dd, J = 2.8, 9.1 Hz, H-9′,9‴), 3.06 (1H, m, H-8,8″), 3.80 (3H, s, OCH_3-3′,3‴), 3.75 (6H, s, OCH_3-3,3″ and OCH_3-5,5″), 2.28 (3H, s, OAc-4,4″), 2.14 (3H, s, OAc-4′,4‴), 1.98 (3H, s, OAc-7′,7‴); HRFABMS *m*/*z* 1085.3636 $[M+Na]^+$ (calcd for $C_{54}H_{62}O_{22}Na$, 1085.3630).

3.3.3. Phyllostadimer B (2)

Amorphous powder; mp 118–120 °C; $[\alpha]_D$ + 19.0° ($CHCl_3$; *c* 1.0); IR (KBr) ν_{max} 3438, 2938, 1591, 1518, 1230, 1125 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.95 (2H, d, J = 8.0 Hz, H-2′,2‴), 6.88 (1H, d, J = 8.0 Hz, H-5′,5‴), 6.62 (2H, s, H-2,2″ and H-6,6″), 5.02 (1H, d, J = 8.4 Hz, H-7′,7‴), 4.77 (1H, d, J = 3.6 Hz, H-7,7″), 4.32 (1H, dd, J = 6.4, 8.8 Hz, H-9,9″), 3.96 (1H, dd, J = 2.8, 8.8 Hz, H-9,9″), 3.88 (1H, m, H-8′,8‴), 3.57 and 3.33 (each 1H, brd, J = 12.4 Hz, H-9′,9‴), 3.10 (1H, m, H-8,8″), 3.92 (6H, s, OCH_3-3,3″ and OCH_3-5,5″), 3.89 (3H, s, OCH_3-3′,3‴); ^{13}C NMR data, see Table 1; HR-FABMS *m*/*z* 833.3010 $[M+Na]^+$ (calcd for $C_{42}H_{50}O_{16}Na$, 833.2994).

3.4. Theoretical computations

We developed the FORTRAN95 program "504.exe" for the exhaustive conformation search for medicinal and phytochemical compounds based on the modified method of the corner-flapping/edge-flipping algorithm (Goto and Osawa, 1989; Goto and Osawa, 1993; Goto et al., 1998). In our program, the generated conformations were optimized by the molecular mechanics calculations with AMBER force fields (Weiner and Kollman, 1981; Weiner et al., 1986; Damm et al., 1997). Atomic charges of the computed molecule were estimated by the semi-empirical molecular orbital calculation with PM3 Hamiltonians in MOPAC program (Stewart, 1989).

3.5. Lipid oxidation assay

ADP was obtained from Oriental Yeast Co., Tokyo, Japan. EyPC was purchased from Nihon Seikagaku Co., Tokyo, Japan. EyPC liposomes (final concentration, 0.2 μmol lipid/ml) were suspended in 10 mM Tris-HCl buffer (pH 7.4, 25 °C). Test compounds dissolved in DMSO was added into the liposomal suspension, and incubated for 5 min. Peroxidation was initiated by addition of 1 mM ADP and 0.1 mM $FeSO_4$.

After incubation for 15 min, an ethanol solution of 4.5 mM butylated hydroxytoluene into the reaction mixture to terminate lipid peroxidation. The amount of lipid peroxides was determined in terms of thiobarbituric acid-reactive substances (TBARS) from the absorbance at 532 nm, with α-tocopherol as an external standard (Buege and Aust, 1978).

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