Occurrence of Stilbene Glucosides in *Upuna borneensis*

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

[a]) Gifu Prefectural Institute of Health and Environmental Sciences, 1-1 Naka-fudogaoka, Kakamigahara 504-0838, Japan (phone: +81-583-80-2120; fax: +81-583-71-5016; e-mail: zvn00510@nifty.ne.jp)
[b]) Department of Pharmacognosy, Gifu Pharmaceutical University, 5-6-1, Mitahora-higashi, Gifu 502-8585, Japan
[c]) Microbial Chemistry Research Center, 3-14-23 Kamiosaki, Shinagawa-ku, Tokyo 141-0021, Japan
[d]) Botanical Gardens, Koishikawa, Graduate School of Science, University of Tokyo, 3-7-1, Hakusan, Bunkyo-Ku, Tokyo, 112-0001, Japan
[e]) Indonesian Institute of Sciences, Jalan Ir. H. Juanda 13, Bogor 16122, Indonesia

Four new stilbene glucosides, upunosides A (**1**), B (**5**), C (**6**), and D (**7**), were isolated from the stem of *Upuna borneensis* (Dipterocarpaceae) together with the three known glucosides **3**, **4**, and **8**. Upunoside A (**1**) is the first natural instance of a glucoside of a resveratrol pentamer, and its aglycone has a dibenzo-fused bicyclo[5.3.0]octadiene and two dihydrobenzofuran moieties. The relative structure of the aglycone was determined by spectral analysis including 1D and 2D NMR experiments.

Introduction. – The family Dipterocarpaceae is well known for its abundance of resveratrol (=5-[(*1E*)-2-(4-hydroxyphenyl)ethenyl]benzene-1,3-diol) oligomers [1][2]. Since the monomer (resveratrol) as well as its oligomers display multifunctional bioactivities, much attention has been paid to the structural variation of oligomers. In previous papers, we reported the isolation and structure elucidation of 27 phenolic compounds including new resveratrol oligomers (upunaphenols A–E), resveratrol *O*-glucosides, and acetophenone *C*-glucosides together with 13 known resveratrol oligomers that occur in the stem of *Upuna borneensis* (Dipterocarpaceae) [3–5]. In our further studies on the chemical constituents of this plant, four new resveratrol oligomers, named upunosides A (**1**), B (**5**), C (**6**), and D (**7**), were isolated together with the three known derivatives **3**, **4**, and **8** (*Fig. 1*). All the compounds were obtained as monoglucosides. We now report the structure elucidation of these compounds. The configuration of **1** is discussed in detail by comparison with vaticaphenol A (=vaticanol B; **2**).

Results and Discussion. – Upunosides A (**1**) and D (**7**), vaticasides B (**3**) and C (**4**), and paucifloroside A (**8**) were isolated from the MeOH extract and upunosides B (**5**) and C (**6**) from the acetone extract of the stem of *Upuna borneensis* by column chromatography (ODS, silica gel) and prep. TLC.

Upunosides A (**1**), a dark-yellow amorphous powder, showed a positive reaction with the *Gibbs* reagent. The molecular formula was $C_{76}H_{64}O_{20}$ as determined by the pseudomolecular ion $[M+Na]^+$ at *m/z* 1319.3866 in the HR-ESI-MS. The ^{1}H- and

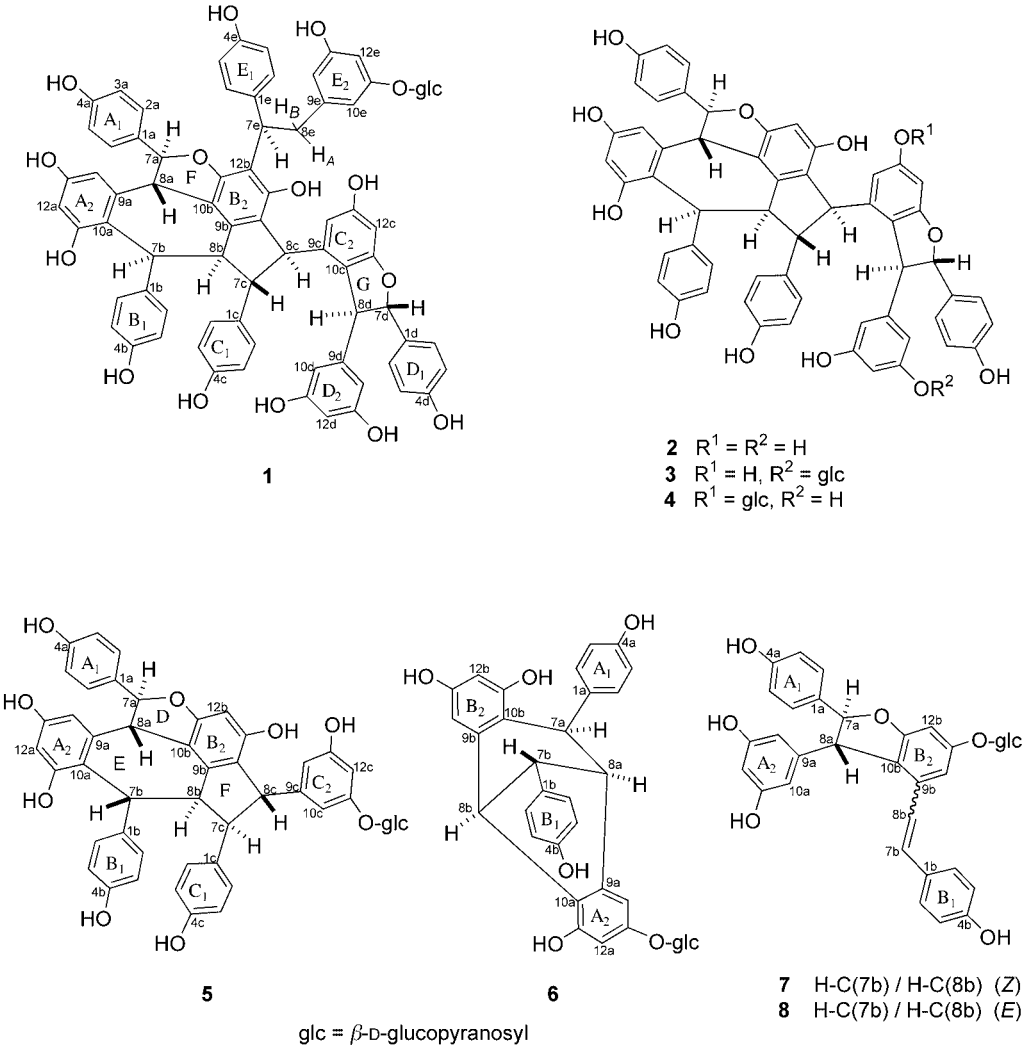

Fig. 1. *Structures of upunosides A* (**1**), *B* (**5**), *C* (**6**), *and D* (**7**), *vaticanol B* (**2**), *vaticasides B* (**3**) *and C* (**4**), *and paucifloroside A* (**8**)

^{13}C-NMR, ^{1}H,^{1}H- and, ^{13}C,^{1}H-COSY, and HMBC data of **1** (*Table 1* and *2*, and *Fig. 2*) revealed the presence of five 4-hydroxyphenyl groups (designated as A_1–E_1), a 3,5-dihydroxyphenyl group (D_2), a 3,5-dioxygenated benzene ring (E_2), two 3,5-dioxygenated-1,2-disubstituted benzene rings (A_2 and C_2), and a β-D-glucopyranose moiety.

The presence of mutually coupled aliphatic H-atoms (H–C(7a)/H–C(8a), H–C(7d)/H–C(8d), H–C(7e)/H–C(8e$_A$) and H–C(8e$_B$)), a sequence of four aliphatic H-atoms (H–C(7b), H–C(8b), H–C(7c), and H–C(8c)), and a β-D-glucopyranose moiety (δ(C) 101.5, 74.6, 77.3, 70.8, 77.8, and 62.1; anomeric H-atom at δ(H) 4.88) was supported by the NMR data, which led to the composition $C_{70}H_{54}O_{15}$ for the aglycone of **1**. The

Table 1. *NMR Data*[a]) *for Upunoside A* (**1**). Arbitrary numbering.

	δ(H)	δ(C)		δ(H)	δ(C)
C(1a)		131.1	C(1d)		133.7
H–C(2a,6a)	7.30 (*d*, *J* = 8.6)	130.1	H–C(2d,6d)	7.20 (*d*, *J* = 8.7)	127.4
H–C(3a,5a)	6.80 (*d*, *J* = 8.6)	116.0	H–C(3d,5d)	6.87 (*d*, *J* = 8.7)	116.1
C(4a)		158.3[b])	C(4d)		158.0[b])
H–C(7a)	5.78 (*d*, *J* = 11.9)	89.8	H–C(7d)	5.44 (*d*, *J* = 3.4)	94.0
H–C(8a)	4.38 (br. *d*, *J* = 11.9)	48.9	H–C(8d)	4.41 (*d*, *J* = 3.4)	57.0
C(9a)		141.6	C(9d)		146.9
C(10a)		124.6	H–C(10d,14d)	6.04 (*d*, *J* = 2.0)	106.9
C(11a)		155.4	C(11d,13d)		159.7[g])
H–C(12a)	6.27 (*d*, *J* = 2.0)	101.5[e])	H–C(12d)	6.26 (*t*, *J* = 2.1)	102.3
C(13a)		156.5[f])	C(1e)		136.7
H–C(14a)	6.13 (br. *d*, *J* = 2.0)	105.7	H–C(2e,6e)	7.24 (*d*, *J* = 8.6)	129.9
C(1b)		133.2	H–C(3e,5e)	6.71 (*d*, *J* = 8.6)	115.4
H–C(2b,6b)	7.08 (*d*, *J* = 8.6)	130.5	C(4e)		156.0
H–C(3b,5b)	6.72 (*d*, *J* = 8.6)	115.5	H–C(7e)	4.45 (*dd*, *J* = 8.8, 7.6)	42.5
C(4b)		155.7	H_A–C(8e)	3.21 (*dd*, *J* = 13.2, 7.6)	40.1
H–C(7b)	5.14 (*d*, *J* = 3.4)	36.8	H_B–C(8e)	3.34 (*dd*, *J* = 13.2, 8.8)	
H–C(8b)	3.11 (br. *d*, *J* = 11.0)	52.7	C(9e)		144.6
C(9b)		140.4[e])	H–C(10e)	6.18 (br. *s*)	110.0
C(10b)		116.8	C(11e)		159.1[h])
C(11b)		156.5[f])	H–C(12e)	6.41 (br. *s*)	101.7
C(12b)		114.0	C(13e)		159.1[h])
C(13b)		151.6	H–C(14e)	6.29 (br. *s*)	111.0
C(14b)		121.2[d])	H–C(glc-1)	4.88 (*d*, *J* = 7.1)	101.5[e])
C(1c)		130.4	H–C(glc-2)		74.6
H–C(2c,6c)	6.39 (*d*, *J* = 8.6)	129.0	H–C(glc-3)	3.48–3.53	77.3
H–C(3c,5c)	6.43 (*d*, *J* = 8.6)	115.7	H–C(glc-4)		70.8
C(4c)		156.3	H–C(glc-5)	3.46 (*m*)	77.8
H–C(7c)	4.04 (*t*, *J* = 11.0)	58.0	CH_2(glc-6)	3.78 (*dd*, *J* = 11.2, 4.1),	62.1
H–C(8c)	4.44 (*d*, *J* = 11.0)	49.9		3.87 (br. *d*, *J* = 11.2)	
C(9c)		139.6[e])	OH–C(13b)	5.02 (*s*)	
C(10c)		121.0[d])	OH-groups	7.86–8.60 (br. *s*)	
C(11c)		162.4			
H–C(12c)	6.34 (*d*, *J* = 1.8)	96.8			
C(13c)		159.7[g])			
H–C(14c)	6.57 (*d*, *J* = 1.8)	107.5			

[a]) In (D_6)acetone; at 300 (^{1}H) and 75 MHz (^{13}C); δ in ppm, *J* in Hz. [b])–[d]) Interchangeable. [e])–[h]) Overlapping.

^{1}H-NMR spectrum showed signals for phenolic OH groups (δ(H) 5.02 and 7.86–8.60), which disappeared upon addition of D_2O, but the exact number was ambiguous. In the HMBC spectrum, the significant ^3J correlations H–C(7a)/C(2a,6a), H–C(8a)/C(14a), H–C(7b)/C(2b,6b), H–C(7c)/C(2c,6c), H–C(8c)/C(14c), H–C(7d)/C(2d,6d), H–C(8d)/C(10d,14d), H–C(7e)/C(2e,6e), and H–C(8e)/C(10e) (*Fig. 2*) indicated that the rings A_1, A_2, B_1, C_1, C_2, D_1, D_2, E_1, and E_2 are attached at C(7a), C(8a), C(7b), C(7c), C(8c), C(7d), C(8d), C(7e), and C(8e), respectively. Further correlations, H–C(7b)/C(11a) and H–C(8d)/C(11c), supported the single bonds C(7b)–C(10a) and C(10c)–C(8d). After complete assignment of all the quaternary C-atoms in the rings A_1–E_1, A_2, and C_2–E_2, the remaining six quaternary aromatic C-atoms (C(9b), C(10b), C(11b), C(12b), C(13b), and C(14b)) in the ^{13}C-NMR spectrum (δ(C) 140.4, 116.8, 156.5, 114.0, 151.6, and 121.2) were assigned to those of a 1,3-dioxygenated fully substituted benzene ring (B_2). Two C–O signals (C(11b) and C(13b)) were correlated with H–C(7e), which indicated that C(7e) was linked to C(12b). The other C–C linkages to ring B_2 (C(8a)–C(10b), C(8b)–C(9b), and C(8c)–C(14b)) were substantiated by the correlations H–C(8a)/C(11b),

Table 2. *^{1}H,^{13}C-HMBC and ^{1}H,^{1}H-NOESY Spectral Data of* **1**

	^{1}H,^{13}C-HMBC	^{1}H,^{1}H-NOESY
H–C(2a,6a)	C(4a), C(7a)	H–C(7a), H–C(8a), H–C(14a)
H–C(3a,5a)	C(1a), C(4a)	
H–C(7a)	C(1a), C(2a,6a), C(8a), C(9a)	H–C(2a,6a), H–C(14a)
H–C(8a)	C(1a), C(7a), C(9a), C(11b)	H–C(2a,6a), H–C(14a), H–C(2b,6b)
H–C(12a)	C(10a), C(11a), C(13a), C(14a)	
H–C(14a)	C(8a), C(10a), C(12a), C(13a)	H–C(2a,6a), H–C(7a), H–C(8a)
H–C(2b,6b)	C(4b), C(7b)	H–C(8a), H–C(7b), H–C(7c), H–C(14c)
H–C(3b,5b)	C(1b), C(4b)	
H–C(7b)	C(9a), C(10a), C(11a), C(1b), C(2b,6b), C(8b), C(9b)	H–C(2b,6b), H–C(2c,6c)
H–C(8b)	C(10a), C(7b), C(8c)	H–C(2c,6c), H–C(8c)
H–C(2c,6c)	C(4c), C(7c)	H–C(7b), H–C(8b), H–C(7c), H–C(8c)
H–C(3c,5c)	C(1c), C(4c)	
H–C(7c)	C(7b), C(8b), C(1c), C(2c,6c), C(8c), C(9c)	H–C(2b,6b), H–C(2c,6c), H–C(14c)
H–C(8c)	C(13b), C(14b), C(1c), C(7c), C(9)c, C(14c)	H–C(8b), H–C(2c,6c), OH–C(13b)
H–C(12c)	C(10c), C(11c), C(13c), C(14c)	
H–C(14c)	C(8c), C(10c), C(12c), C(13c)	H–C(2b,6b), H–C(7c), OH–C(13b)
H–C(2d,6d)	C(4d), C(7d)	H–C(7d), H–C(8d), OH–C(13b)
H–C(3d,5d)	C(1d), C(4d)	H–C(12e)
H–C(7d)	C(10c), C(11c), C(1d), C(2d,6d),C(8d), C(9d)	H–C(2d,6d), H–C(10d,14d)
H–C(8d)	C(10c), C(7d), C(10d,14d)	H–C(2d,6d), H–C(10d,14d)
H–C(10d,14d)	C(9d), C(11d,13d), C(12d)	H–C(7d), H–C(8d)
H–C(12d)	C(10d,14d), C(11d,13d)	
H–C(2e,6e)	C(4e), C(7e)	H–C(7e), H–C(8e$_A$), H–C(8e$_B$)
H–C(3e,5e)	C(1e), C(4e)	
H–C(7e)	C(11b), C(12b), C(1e), C(2e,6e), C(8e)	H–C(2e,6e), H–C(10e), H–C(14e), OH–C(13b)
H–C(8e$_A$)	C(12b), C(7e), C(9e), C(10e)	H–C(2e,6e), H–C(10e)
H–C(8e$_B$)	C(1e), C(7e), C(9e), C(14e)	H–C(2e,6e), H–C(14e)
H–C(10e)	C(8e), C(11e), C(12e), C(14e)	H–C(7e), H–C(8e$_B$), H–C(glc-1)
H–C(12e)	C(10e), C(11e), C(13e), C(14e)	H–C(3d,5d), H–C(glc-1)
H–C(14e)	C(8e), C(10e), C(12e), C(13e)	H–C(7e), H–C(8e$_A$), H–C(8e$_B$)
H–C(glc-1)	C(11e)	H–C(10e), H–C(12e)
OH–C(13b)	C(12b), C(13b), C(14b)	H–C(8c), H–C(14c), H–C(2d,6d), H–C(7e)

H–C(7b)/C(9b), and H–C(8c)/C(13b), respectively. An additional cross-peak observed for H–C(7d)/C(11c) supported the presence of an ether linkage, C(7d)–O–C(11c), which is part of a dihydrobenzofuran moiety (C(7d)–C(8d)–C(10c)–C(11c)–O: ring G). Although no long-range correlation H–C(7a)/C(11b) was observed, the presence of another dihydrobenzofuran moiety (C(7a)–C(8a)–C(10b)–C(11b)–O: ring F) was deduced after considering the molecular formula of the aglycone. Long-range correlation between the anomeric H-atom (δ(H) 4.88) and C(11e) (δ(C) 159.1) in the HMBC spectrum confirmed that the glucosyloxy group was at C(11e).

These data established the planar structure of upunoside A (**1**) with two dihydrobenzofuran moieties, which was confirmed by other HMBC correlations. The aglycone is a resveratrol pentamer and can be regarded as a condensed product of a

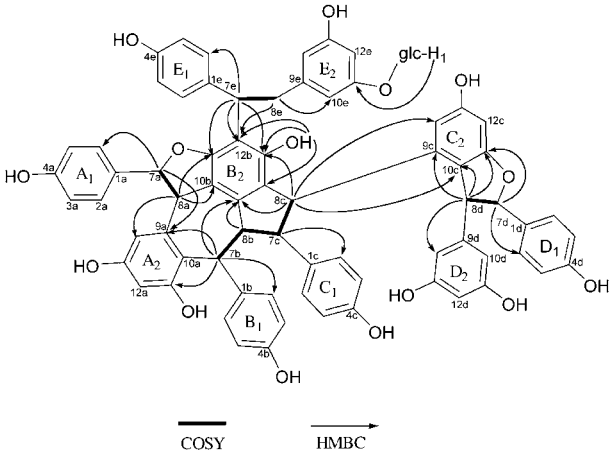

Fig. 2. *Selected correlations in 2D NMR of upunoside A* (**1**)

resveratrol tetramer (**1A** + **1B**) with a resveratrol monomer (**1C**) (*Fig. 3*). The planar structure of the tetramer is identical to that of the known resveratrol tetramer vaticaphenol A [6] (= vaticanol B [7][8]; **2**). The relative configuration of each substructure **1A** – **C** was deduced from coupling-constant values and from NOESY measurements.

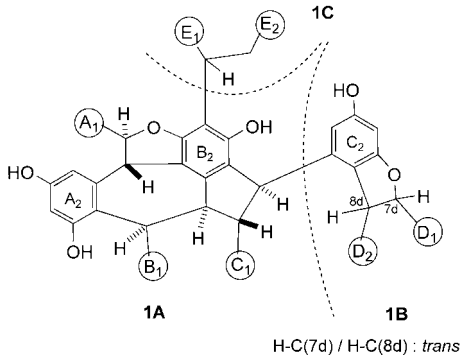

Fig. 3. *Partial structures* **1A** – **C** *of upunoside A* (**1**)

The coupling constant for H–C(7a)/H–C(8a) (11.9 Hz) of **1** was characteristic for their 1,2-*trans*-diaxial position at the 2,3-diaryl-dihydrobenzofuran moiety of the fused pentacyclic ring system [9]. The equatorial orientation of H–C(7b) and the axial orientation of H–C(8b), H–C(8c), and H–C(7c) were unambiguously evidenced by the J_{vic} values and confirmed by the NOESY experiment (*Fig. 4*). The *cis* relationship of H–C(8a) and ring B_1 was deduced from the NOE H–C(8a)/H–C(2b,6b). The coupling constant J(7d, 8d) = 3.4 Hz and the NOE interactions for H–C(7d)/H–C(10d,14d) and H–C(8d)/H–C(2d,6d) resulted from the *trans*-diequatorial orientation of H–C(7d) and H–C(8d). The relative configuration of the tetrameric unit (substructures **1A** + **1B**) was concluded to be the same as that of vaticaphenol A (= vaticanol B; **2**), which was corroborated by the similarity of their spectral data. However, the configurational relationship within the substructures **1A** and **1B** in *Fig. 3* has not been discussed yet [6–8], *i.e.*, it has not been established whether H–C(7d) or H–C(8d) is in the α-position. Thus, the configurational relationships within **1A** and **1B** including **1C** were determined as follows. Strong NOEs were generally observed between the aliphatic H-atom and those

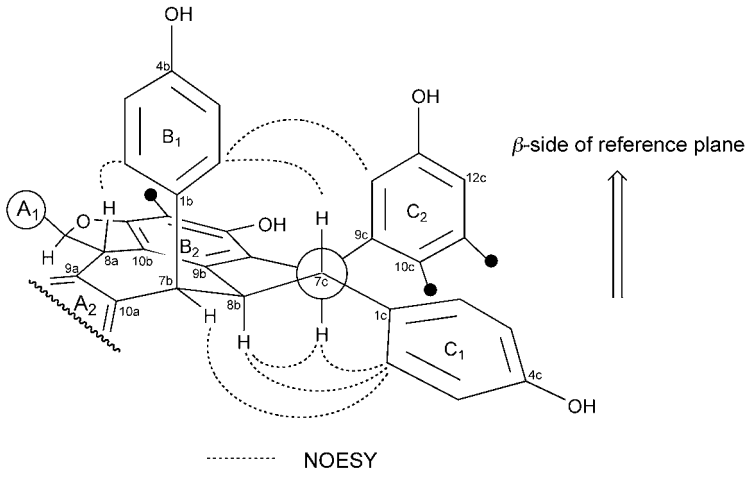

Fig. 4. *NOEs observed for the partial structure* (resveratrols A–C) *of* **1**

at the aromatic ring, as found for H–C(2a,6a)/H–C(7a), H–C(8a)/H–C(14a), and so on (see *Table 2*). But no NOE was observed for H–C(8c)/H–C(14c). This phenomenon strongly indicated that ring C_2 is not allowed to rotate freely due to steric hindrance around **1B**, which is probably caused by the aromatic rings C_1 and B_2. An NOE was further observed for H–C(2b,6b)/H–C(14c), suggesting that the aromatic H-atom of ring C_2 (H–C(14c)) is positioned restrictively on the β-side of the reference plane (*Fig. 4*). Another distinct NOE was observed for H–C(2d,6d)/OH–C(13b), supporting the relative (*S*) configuration at C(7d) (*Fig. 5*). Therefore, the orientation of H–C(7d) and H–C(8d) at ring G was determined to be β and α, respectively. Further NOEs were observed for H–C(7e)/OH–C(13b) and H–C(12e)/H–C(3d,5d), while no NOE was observed for H–C(2e,6e)/OH–C(13b) (*Fig. 5*). These results indicated that C(7e) has the *rel*-(*R*)-configuration, and the C(12b)–C(7e) bond is not allowed to rotate freely. The C(7e)–C(8e) bond, is β-oriented with respect to the reference plane (*Fig. 5*). Because no NOE was observed for H–C(2e,6e)/H–C(10e) and H–C(2e,6e)/H–C(14e), the two rings E_1 and E_2 must be in *anti*-periplanar position, and the rotation about C(7e)–C(8e) is also restrained. This results in a different environment for H_A–C(8e) and H_B–C(8e), as shown by their

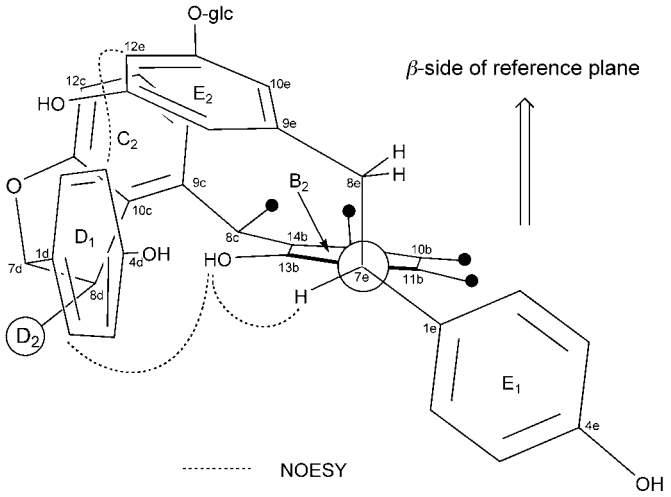

Fig. 5. *NOEs observed for the partial structure* (resveratrols B–E) *of* **1**

different δ(H). These data confirmed the relative configuration of **1**, and restricted rotation of ring C_2 allowed us to establish the configurational relationship within the partial structures **1A**–**C**.

In the ^{1}H-NMR spectrum, OH–C(13b) of **1** was observed at δ(H) 5.02, while that of **2** was at 7.61 [6]. A similar behavior of the OH signals have also been observed for vaticanol J (δ(H) 5.30)[10] and pauciflorol D (δ(H) 4.70)[11], both of which bear the same partial structure composed of resveratrol units A–E. These data and the configuration of **1** described above explain reasonably well the anisotropy effect of ring E_2 on OH–C(13b). The upper-field shift of H–C(2c,6c) (δ(H) 6.39) and H–C(3c,5c) (δ(H) 6.43) at ring C_1 can be caused by the anisotropy. Supporting evidence for the effect was obtained by the spectral comparison of vaticaphenol A (**2**) with pauciflorol B (*Fig. 6*) [8]. Although the trimeric unit of both compounds is identical, the chemical shifts of the H-atoms at ring C_1 are quite different (**2**): δ(H) 6.40 for H–C(2c,6c) and 6.50 for H–C(3c,5c); pauciflorol B: δ(H) 7.02 for H–C(2c,6c) and 6.74 for H–C(3c,5c)), indicating that ring C_1 of **2** is influenced by the anisotropy effect of the resveratrol D unit.

If **2** and the tetrameric unit of **1** are assumed to have identical configuration, ring D_2 of **2** is located in the vicinity of ring C_1 (*Fig. 6*) and the configurational relationship between **2A** and **2B** is also clarified. In [8], we suggested the restricted free rotation of ring D_2 of **2** by reason of separated signals of H–C(10d) (δ(H) 6.13) and H–C(14d) (5.94) at $-60°$, due to the contribution of the large substituent (resveratrol units A–C) to the important steric hindrance around ring D_2. The present discussion suggests that the hindrance is caused by two factors, the restriction of free rotation about C(8c)–C(9c) and the steric hindrance due to ring C_1. Consequently, the protons at ring C_1 (H–C(2c,6c); H–C(3c,5c)) were shielded by the anisotropy effect of ring D_2. The anisotropy effects observed in **1** were an important clue confirming the proposed configuration; thus, consideration of anisotropy effects is essential to determine the configuration of stilbene oligomers, especially when dealing with highly condensed and structurally complex cognates.

Upunoside A (**1**) is the first instance of a glucoside of a resveratrol pentamer. The occurrence of vaticaphenol A (=vaticanol B; (**2**) and piceid as major constituents of *Upuna borneensis* [3][4] suggested that **1** would be biologically synthesized by coupling of these derivatives. This biogenetic consideration and the configuration of **1** supported the configuration of **2**. In addition, the *rel*-(*S*)-configuration of all the methine H-atoms

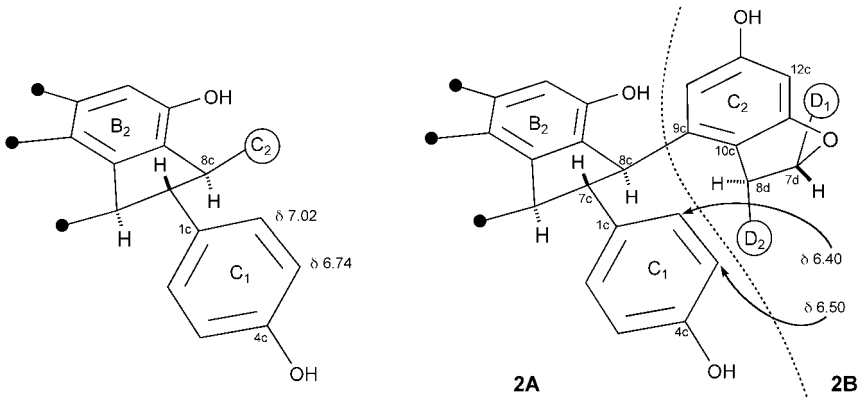

Fig. 6. *Structures and ^{1}H-NMR data* ((D$_6$)acetone) *of pauciflorol B and vaticaphenol A* (**2**)

at the rings F and G (C(7a), C(8a), C(7d), and C(8d)) suggested the possibility that **2** is biogenetically formed by two molecules of (−)-ε-viniferin (= 5-{2,3-dihydro-6-hydroxy-2-(4-hydroxyphenyl)-4-[(*1E*)-2-(4-hydroxyphenyl)ethenyl]benzofuran-3-yl}benzene-1,3-diol), which is a major constituent of this plant [5].

Upunoside B (**5**) was obtained as a yellow amorphous powder and showed a positive reaction to *Gibbs* reagent. The HR-FAB-MS ($[M-H]^-$ at *m/z* 841.2504) established the molecular formula $C_{48}H_{42}O_{14}$, corresponding to a monoglucoside of a resveratrol trimer [8]. The NMR data of **5** (*Table 3*) analyzed in 2D experiments exhibited the signals of β-D-glycosyloxy and three resveratrol units. The HMBC spectrum (*Table 4*) confirmed the presence of a planar structure similar to that of **1**.

The important correlations in the HMBC spectrum of **5** were H−C(8a)/C(10b), H−C(7b)/C(11a), and H−C(8c)/C(13b), which confirmed the C(8a)−C(10b), C(7b)−C(10a), and C(8c)−C(14b) bonds. The location of the glucosyloxy group was C(11c) as determined by the HMBC cross-peak between the anomeric H-atom (δ(H) 4.92) and the aromatic C-atoms at δ(C) 159.5 (C(11c)). Complete HMBC correlations are listed in *Table 4*. The planar structure of the aglycone of **5** is identical to those of some known resveratrol trimers, *i.e.*, of vaticanols A and E and pauciflorols A and B, all of which have been isolated from some dipterocarpaceaous plants [7][8], and of suffruticosols A and B from *Paeonia suffruticosa* (Paeoniaceae) [12]. The relative configuration of **5** was determined as follows. The same arguments obtained from the J_{vic} values establishing the configuration of **1** were used to confirm the *trans*-diaxial position of H−C(7a)/H−C(8a) and H−C(7b)/H−C(8b) of **5**. In the NOESY experiment (*Table 4*; selected data in *Fig. 7*), the significant NOEs, H−C(8a)/H−C(7b), H−C(8a)/H−C(2c,6c), and H−C(2c,6c)/H−C(7b), suggested that H−C(8a), H−C(7b), and ring C_1 are on the same side of a reference plane (β-side). When the conformation of two five membered rings D and F are considered, the flaps of the envelope must be C(8a) and C(7c), respectively. Considering the forms of the rigid pentacyclic system and the NOEs H−C(10c)/H−C(8b) and H−C(14c)/H−C(8b), H−C(8b) and ring C_2 must be α-positioned, thus confirming the relative configuration of **5**.

The signals of H−C(2c,6c) and H−C(3c,5c) appeared at higher field (δ(H) 6.41 and 6.34) than those of H−C(2a,6a) and H−C(3a,5a) (δ(H) 7.64 and 6.95), because these H-atoms are located above ring B_2 and thus affected by the anisotropy effect of the π system. The shift to higher field of the signal of OH−C(11a) (δ(H) 6.80) can be similarly explained by the anisotropy effect of ring A_2. Anisotropy effects are frequently observed for stilbene oligomers in solution [8].

Upunosides C (**6**) and D (**7**) were obtained as yellow amorphous powders. Their compositions were deduced to be $C_{34}H_{32}O_{11}$ from the $[M-H]^-$ ions at *m/z* 615.1862 (**6**) and 615.1876 (**7**) in the negative-ion HR-FAB-MS. The presence of a β-D-glucopyranosyloxy group was supported by the NMR spectra of both compounds. The ^{1}H- and ^{13}C-NMR data of **6** (*Table 3*), except for the β-D-glucopyranosyloxy group, showed close similarity to those of ampelopsin F [13]. The HMBC and NOESY spectra (see *Exper. Part*) confirmed that the aglycone of **6** is ampelopsin F. The position of the glucosyloxy group was determined to be at C(13a) by NOEs of the aromeric proton of **6** (*Table 4*). The ^{1}H- and ^{13}C-NMR data for the aglycone of **7** (see *Exper. Part*) closely resembled those of *cis*-ε-viniferin [14]. By the same reasons as described for **6**, the structure of **7** was elucidated as *cis*-ε-viniferin 13b-*O*-β-D-glucopyranoside.

In addition to the four new *O*-glucosides of stilbene oligomer, **1** and **5**–**7**, three known glucosides were isolated and identified as vaticasides B (**3**), C (**4**) [15], and paucifloroside A (**8**) [8].

The authors are grateful to Mr. *Y. Doke*, Gifu Prefectural Institute of Industrial Product Technology, for his constant technical support for NMR spectra. They also express their appreciation to Mrs. *M. Hosokawa* and Mrs. *M. Hayashi* of Gifu Pharmaceutical University for measurement of FAB-MS data.

Table 3. *NMR Data for Upunoside B* (**5**) *and C* (**6**)[a])

5 (in (D_6)acetone)			**6** (in CD_3OD)		
	δ(H)	δ(C)		δ(H)	δ(C)
C(1a)		130.5	C(1a)		138.9
H–C(2a,6a)	7.64 (*d*, *J* = 8.4)	130.2	H–C(2a,6a)	7.03 (*d*, *J* = 8.4)	130.1
H–C(3a,5a)	6.95 (*d*, *J* = 8.4)	116.0	H–C(3a,5a)	6.72 (*d*, *J* = 8.4)	116.2
OH–C(4a)	8.56 (br. *s*)	158.5	C(4a)		156.2
H–C(7a)	5.96 (*d*, *J* = 11.5)	90.2	H–C(7a)	4.10 (*s*)	47.5
H–C(8a)	5.28 (br. *d*, *J* = 11.5)	48.4	H–C(8a)	3.31 (*s*)	59.4
C(9a)		142.0	C(9a)		147.3[c])
C(10a)		122.2[b])	C(10a)		131.4
OH–C(11a)	6.80 (br. *s*)	157.9	C(11a)		153.0
H–C(12a)	6.04 (*d*, *J* = 2.2)	103.4	H–C(12a)	6.30 (*d*, *J* = 2.2)	103.5
OH–C(13a)	8.12 (br. *s*)	157.1	C(13a)		159.3
H–C(14a)	6.29 (*d*, *J* = 2.2)	104.9	H–C(14a)	6.68 (*d*, *J* = 2.2)	105.7
C(1b)		132.8	C(1b)		135.8
H–C(2b,6b)	7.07 (*d*, *J* = 8.4)	132.2	H–C(2b,6b)	6.67 (*d*, *J* = 8.6)	129.0
H–C(3b,5b)	6.57 (*d*, *J* = 8.4)	114.8	H–C(3b,5b)	6.49 (*d*, *J* = 8.6)	115.8
OH–C(4b)	8.06 (br. *s*)	156.1	C(4b)		156.1
H–C(7b)	4.46 (*d*, *J* = 11.5)	45.5	H–C(7b)	3.58 (br. *s*)	50.8
H–C(8b)	4.10 (br. *dd*, *J* = 11.5, 6.0)	47.1	H–C(8b)	4.08 (br. *s*)	49.7
C(9b)		146.7	C(9b)		147.3[c])
C(10b)		117.9	C(10b)		114.0
C(11b)		159.9	C(11b)		158.1
H–C(12b)	6.26 (*s*)	96.1	H–C(12b)	6.07 (*d*, *J* = 2.4)	102.1
OH–C(13b)	8.09 (br. *s*)	155.4	C(13b)		157.2
C(14b)		122.2[b])	H–C(14b)	6.36 (*d*, *J* = 2.4)	105.8
C(1c)		134.6	H–C(glc-1)	4.82[d])	102.4
H–C(2c,6c)	6.41 (*d*, *J* = 8.4)	129.0	H–C(glc-2)	3.38 (*m*) [e])	74.9
H–C(3c,5c)	6.34 (*d*, *J* = 8.4)	114.9	H–C(glc-3)	3.44 (*m*) [e])	78.0
OH–C(4c)	7.86 (br. *s*)	155.9	H–C(glc-4)	3.36 (*m*) [e])	71.0
H–C(7c)	3.95 (*d*, *J* = 6.0)	62.2	H–C(glc-5)	3.41 (*m*) [e])	78.1
H–C(8c)	4.17 (*s*)	56.5	CH_2(glc-6)	3.66 (*dd*, *J* = 11.9, 5.8),	62.6
C(9c)		146.8		3.89 (*dd*, *J* = 11.9, 1.7)	
H–C(10c)	6.45 (br. *s*)	107.8			
C(11c)		159.5			
H–C(12c)	6.42 (br. *s*)	101.9			
OH–C(13c)	8.28 (br. *s*)	159.5			
H–C(14c)	6.33 (br. *s*)	107.8			
C(1d)		158.9			
C(2d,6d)		108.9			
H–C(glc-1)	4.92 (*d*, *J* = 7.5)	101.0			
H–C(glc-2)	3.42 (*m*) [f])	74.4			
H–C(glc-3)	3.44 (*m*) [f])	77.3			
H–C(glc-4)	3.49 (*m*) [f])	71.0			
H–C(glc-5)	3.50 (*m*) [f])	77.7			
CH_2(glc-6)	3.74 (*dd*, *J* = 1.7, 5.1),	62.4			
	3.89 (br. *dd*, J = 11.7)				

[a]) At 300 (^{1}H) and 75 MHz (^{13}C); δ in ppm, *J* in Hz. [b]), [c]) Overlapping. [d]) Masked by the broad H_2O peak, obtained from ^{1}H,^{1}H-COSY correlation. [e]), [f]) Obscured by overlapping each other, obtained from ^{13}C,^{1}H-COSY correlation.

Table 4. *^{1}H,^{13}C-HMBC and ^{1}H,^{1}H-NOESY Data of* **5**

	^{1}H,^{13}C-HMBC	^{1}H,^{1}H-NOESY
H–C(2a,6a)	C(4a), C(7a)	H–C(7a), H–C(8a), H–C(14a)
H–C(3a,5a)	C(1a), C(4a)	OH–C(4a)
H–C(7a)	C(1a), C(2a,6a), C(8a), C(9a)	H–C(2a,6a), H–C(14a)
H–C(8a)	C(1a), C(7a), C(9a), C(11b)	H–C(2a,6a), H–C(14a), H–C(7b), H–C(2c,6c)
H–C(12a)	C(10a), C(11a), C(13a), C(14a)	OH–C(11a), OH–C(13a)
H–C(14a)	C(8a), C(10a), C(12a), C(13a)	H–C(2a,6a), H–C(7a), H–C(8a), OH–C(13a)
H–C(2b,6b)	C(4b)	H–C(7b), H–C(8b), H–C(7c)
H–C(3b,5b)	C(1b), C(4b)	OH–C(11a), OH–C(4b)
H–C(7b)	C(9a), C(10a), C(11a), C(1b), C(2b,6b), C(8b), C(9b)	H–C(8a), H–C(2b,6b), H–C(2c,6c), OH–C(11a)
H–C(8b)	C(9b), C(10a), C(1c), C(7c)	H–C(2b,6b), H–C(10c), H-C(14c)
H–C(12b)	C(10b), C(11b), C(13b), C(14b)	OH–C(13b)
H–C(2c,6c)	C(4c), C(7c)	H–C(8a), H–C(7b), H–C(7c), H–C(8c)
H–C(3c,5c)	C(1c), C(4c)	OH–C(4c)
H–C(7c)	C(8b), C(9b), C(14b), C(1c), C(2c,6c), C(8c), C(9c)	H–C(2b,6b), H–C(2c,6c), H–C(10c), H–C(14c)
H–C(8c)	C(8b), C(9b), C(13b), C(14b), C(1c), C(7c), C(9c), C(10c), C(14c)	H–C(2c,6c), OH–C(13b), H–C(10c), H–C(14c)
H–C(10c)	C(8c), C(11c), C(12c), C(14c)	H–C(8b), H–C(7c), H–C(8c), H–C(glc-1)
H–C(12c)	C(10c), C(11c), C(13c), C(14c)	H–C(glc-1), OH–C(13c)
H–C(14c)	C(8c), C(10c), C(12c), C(13c)	H–C(8b), H–C(7c), H–C(8c), OH–C(13c)
H–C(glc-1)	C(11e), C(glc-6)	H–C(10c), H–C(12c)
OH–C(4a)	C(3a,5a), C(4a)	H–C(3a,5a)
OH–C(11a)	C(10a), C(11a), C(12a)	H–C(12a), H–C(7b), H–C(3b,5b)
OH–C(13a)	C(12a), C(13a), C(14a)	H–C(12a), H–C(14a)
OH–C(4b)	C(3b,5b), C(4b)	H–C(3b,5b)
OH–C(13b)	C(12b), C(13b), C(14b)	H–C(12b), H–C(8c)
OH–C(4c)	C(3c,5c), C(4c)	H–C(3c,5c)
OH–C(13c)	C(12c), C(13c), C(14c)	H–C(12c), H–C(14c)

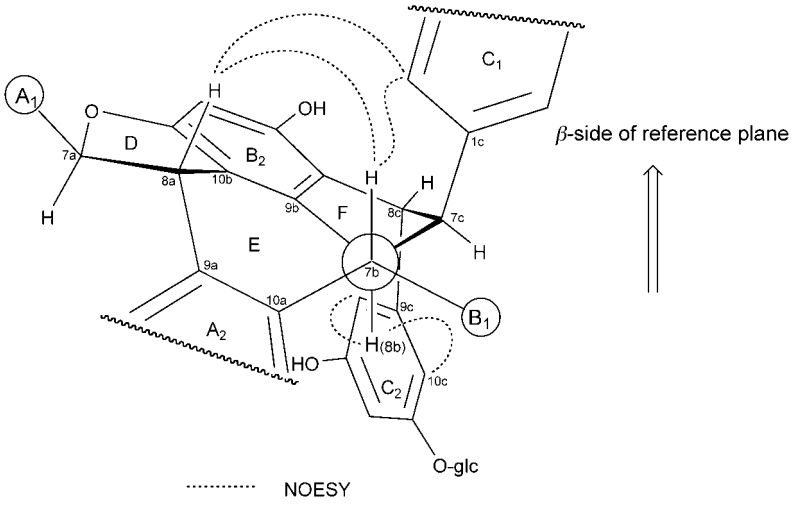

Fig. 7. *Conformation of the dihydrobenzofuran moiety* (rings D and E) *and the dibenzo-fused bicyclo[5.3.0]-decadiene moiety* (rings E and F) *of* **5**

Experimental Part

General. Anal. TLC: *Merck* silica gel F_{254} (0.25 mm). Prep. TLC: *Merck* silica gel F_{254} (0.5 mm). Column chromatography (CC): *Merck* silica gel *60* (70–230 mesh), *Sephadex LH-20*. Optical rotation: *Jasco P-1020* polarimeter. UV Spectra: *Shimadzu UV-2200* spectrophotometer; λ_{max} (log ε) in nm. ^{1}H- and ^{13}C-NMR Spectra: *Jeol JNM-LA-300* spectrometer; (D_6)acetone soln.; δ(H) in ppm rel. to Me_4Si (=0 ppm) as internal ref., δ(C) in ppm rel. to solvent (carbonyl C-atom, 206.0 ppm), coupling constants *J* in Hz. ESI-MS: *Jeol JMS-T100LC* mass spectrometer; in *m/z*. FAB-MS: *Jeol JMS-DX-300* spectrometer; in *m/z*.

Plant Material. *Upuna borneensis* SYM. was cultivated at Bogor Botanical Garden, Bogor, Indonesia, from which its stem was collected and identified by one of us (*D.D.*) in May 2000. A voucher specimen is deposited at the Gifu Prefectural Institute of Health and Environmental Sciences, Gifu, Japan.

Extraction and Isolation. The dried and ground stem of *U. borneensis* (820 g) was successively extracted with acetone (2 l, 3 ×), MeOH (2 l, 3 ×), and 70% MeOH (2 l, 2 ×) at r.t., and the extracts were evaporated: 175 g (acetone), 17 g (MeOH), and 18 g (70% MeOH). A part (172 g) of the acetone extract was subjected to CC (silica gel, $CHCl_3$/MeOH of increasing polarity): *Fractions 1-63*. After checking by TLC (*Gibbs* test), the fractions were combined as follows: *Fr. 1–10* (= *Fr. A*; $CHCl_3$/MeOH 20:1; 8.2 g), *Fr. 11–15* (= *Fr. B*; $CHCl_3$/MeOH 15:1; 820 mg), *Fr. 16–19* (= *Fr. C*; $CHCl_3$/MeOH 15:1; 2.4 g), *Fr. 20–26* (= *Fr. D*; $CHCl_3$/MeOH 10:1; 4.2 g), *Fr. 27–30* (= *Fr. E*; $CHCl_3$/MeOH 10:1; 6.5 g), *Fr. 31–34* (= *Fr. F*; $CHCl_3$/MeOH 10:1; 1.9 g), *Fr. 35–39* (= *Fr. G*; $CHCl_3$/MeOH 9:1; 3.6 g), *Fr. 40–43* (= *Fr. H*; $CHCl_3$/MeOH 8:1; 2.0 g), *Fr. 44–51* (= *Fr. I*; $CHCl_3$/MeOH 7:1; 62 g), *Fr. 52–60* (= *Fr. J*; $CHCl_3$/MeOH 6:1; 44 g), *Fr. 61–62* (= *Fr. K*; $CHCl_3$/MeOH 5:1; 6.8 g), *Fr. 63* (= *Fr. L*; acetone/MeOH 1:1; 23 g). *Fr. K* was further subjected to CC (*Sephadex LH-20,* MeOH); *Fr. K.1–K.7*. Compound **6** (8 mg) was obtained from *Fr. K.3* after purification by CC (reversed-phase, 50% MeOH) and prep. TLC (AcOEt/$CHCl_3$/MeOH/H_2O 35:18:16:5). Compound **5** (11 mg) was obtained from *Fr. K.4* after purification by repeated CC (*Sephadex LH-20,* MeOH) and prep. TLC (AcOEt/$CHCl_3$/MeOH/H_2O 35:18:16:5). A part (16 g) of the MeOH extract and a part (17 g) of the 70% MeOH extract were combined, and the MeOH-soluble part (30 g) was subjected to CC (reversed-phase, 10 → 70% MeOH/H_2O): *Fractions 1–21*. The fractions were combined as follows: *Fr. 1–10* (= *Fr. MA*; 10 → 20% MeOH; 2.2 g), *Fr. 11–15* (= *Fr. MB*; 25 → 35% MeOH; 8.6 g), *Fr. 16–19* (= *Fr. MC*; 40 → 50% MeOH; 16 g), *Fr. 20–21* (= *Fr. MD*; 60 → 70% MeOH; 1.2 g). *Fr. MC* was further subjected to CC (silica gel, AcOEt/$CHCl_3$/MeOH/H_2O 80:40:11:2); *Fr. MC.1–MC.17*. Compounds **7** (6 mg) and **8** (6 mg) were obtained from the combined *Fr. MC.5–MC.6* after purification by prep. TLC (AcOEt/$CHCl_3$/MeOH/H_2O 75:75:45:10) and repeated CC (reversed-phase, 50% MeOH). Compounds **1** (8 mg), **3** (6 mg), and **4** (6 mg) were obtained from the combined *Fr. MC.9–MC.12* after purification by CC (reversed-phase, 40% MeOH) and prep. TLC (AcOEt/$CHCl_3$/MeOH/H_2O 35:18:16:5).

Upunoside A (= rel-*(3*R*,4*R*,4a*S*,5*S*,9b*S*,10*S*)-3-[(2*S*,3*S*)-3-(3,5-dihydroxyphenyl)-2,3-dihydro-6-hydroxy-2-(4-hydroxyphenyl)benzofuran-4-yl]-1-[(1*R*)-2-[3-(β-*D*-glucopyransoyloxy)-5-hydroxyphenyl]-1-(4-hydroxyphenyl)ethyl]-3,4,4a,5,9b,10-hexahydro-4,5,10-tris(4-hydroxyphenyl)benzo[5,6]azulens[7,8,1-*cde*]benzofuran-2,6,8-triol*; **1**). Dark yellow amorphous powder. $[\alpha]_D = -18$ ($c = 0.2$, MeOH). UV: 224 (4.7), 282 (4.2). ^{1}H- and ^{13}C-NMR: *Table 1*. ^{1}H,^{13}C-HMBC, ^{1}H,^{1}H-NOESY: *Table 2*. ESI-MS: 1319 ($[M+Na]^+$). HR-ESI-MS 1319.3866 ($[M+Na]^+$; $C_{76}H_{64}NaO_{20}^+$; calc. 1319.3889).

Upunoside B (rel-*(3*S*,4*S*,4a*S*,5*R*,9b*S*,10*S*)-3-[3-(β-*D*-Glucopyranosyloxy)-5-hydroxyphenyl]-3,4,4a,5,9b,10-hexahydro-4,5,10-tris(4-hydroxyphenyl)benz[5,6]azuleno[7,8,1-*cde*]benzofuran-2,6,8-triol*; **5**). Yellow amorphous powder. $[\alpha]_D = -116$ ($c = 0.2$, MeOH). UV: 225 (4.8), 282 (4.2). ^{1}H- and ^{13}C-NMR: *Table 3*. ^{1}H,^{13}C-HMBC, ^{1}H,^{1}H-NOESY: *Table 4*. FAB-MS (neg.): 841 ($[M-H]^-$). HR-FAB-MS (neg.): 841.2504 ($[M-H]^-$, $C_{48}H_{41}O_{14}^-$; calc. 841.2496) .

Upunoside C (= rel-*(5*S*,10*R*,11*R*,12*S*)-8-(β-*D*-Glucopyranosyloxy)-10,11-dihydro-11,12-bis(4-hydroxyphenyl)-5,10-methano-5*H*-dibenzo[a,d]cycloheptene-1,3,6-triol*; **6**). Yellow amorphous powder. $[\alpha]_D = -68$ ($c = 0.18$, MeOH). UV: 225 (4.7), 281 (4.1). ^{1}H- and ^{13}C-NMR: *Table 3*. ^{1}H,^{13}C-HMBC: H–C(2a,6a)/C(4a) and C(7a); H–C(3a,5a)/C(1a) and C(4a); H–C(7a)/C(1a), C(2a,6a), C(8a), C(9a), C(9b), C(10b), and C(11b); H–C(8a)/C(1a), C(7a), C(9a), C(10a), C(14a), C(1b), C(7b), C(8b), and C(10b); H–C(12a)/C(10a), C(11a), C(13a), and C(14a); H–C(14a)/C(8a), C(10a), C(12a), and C(13a); H–C(2b,6b)/C(4b) and C(7b); H–C(3b,5b)/C(1b) and C(4b); H–C(7b)/C(7a), C(8a), C(9a), C(10a), C(1b), C(2b,6b), C(8b), and C(9b); H–C(8b)/C(8a), C(9a), C(10a), C(11a), C(1b), C(7b), C(9b), C(10b), and (14b); H–C(12b)/C(10b), C(11b), C(13b), and C(14b); H–C(14b)/C(8b), C(10b), C(12b), and C(13b); H–C(glc-1)/C(13a). ^{1}H,^{1}H-NOESY: H–C(2a,6a)/H–C(7a), H–C(8a), and H–C(7b); H–C(7a)/H–C(2a,6a) and H–C(8a); H–C(8a)/H–C(2a,6a), H–C(7a), H–C(14a), H–C(2b,6b), and H–C(7b); H–C(12a)/H–C(glc-1); H–C(14a)/H–C(8a) and H–C(glc-1); H–C(2b,6b)/H–C(8a), H–C(7b), and H–C(8b); H–C(7b)/H–C(2a,6a),

H–C(8a), H–C(2b,6b), and H–C(8b); H–C(8b)/H–C(2b,6b), H–C(7b), and H–C(14b); H–C(14b)/H–C(8b); H–C(glc-1)/H–C(12a) and H–C(14a). FAB-MS (neg.): 615 ($[M-H]^-$). HR-FAB-MS (neg.): 615.1862 ($[M-H]^-$, $C_{34}H_{31}O_{11}^-$; calc. 615.1866).

Upunoside D (= rel-*5-[(2*R*,3*R*)-6-(β*-D-*Glucopyranosyloxy)-2,3-dihydro-2-(4-hydroxyphenly)-4-[2-(4-hydroxyphenyl)ethenyl]benzofuran-3-yl]benzene-1,3-diol*; **7**). Yellow amorphous powder. $[\alpha]_D = -72$ ($c = 0.2$, MeOH). UV: 213 (4.4), 283 (4.2). ^{1}H-NMR ((D$_6$)acetone, 300 MHz; * = obscured by overlapping each other, obtained from ^{13}C,^{1}H-COSY correlation): 7.06 (*d*, *J* = 8.6, H–C(2a,6a)); 6.80 (*d*, *J* = 8.6, H–C(3a,5a)); 5.30 (*d*, *J* = 5.5, H–C(7a)); 4.02 (*d*, *J* = 5.5, H–C(8a)); 6.02 (*d*, *J* = 2.2, H–C(10a,14a)); 6.22 (*t*, *J* = 2.2, H–C(12a)); 7.01 (*d*, *J* = 8.6, H–C(2b,6b)); 6.70 (*d*, *J* = 8.6, H–C(3b,5b)); 6.30 (*d*, *J* = 12.1, H–C(7b)); 6.03 (*d*, *J* = 12.1, H–C(8b)); 6.50 (*d*, *J* = 2.0, H–C(12b)); 6.52 (*d*, *J* = 2.0, H–C(14a)); 4.78 (*d*, *J* = 7.5, H–C(glc-1)); 3.44 (*m*, H–C(glc-2))*; 3.49 (*m*, H–C(glc-3))*; 3.48 (*m*, H–C(glc-4))*; 3.39 (*m*, H–C(glc-5))*; 3.71 (*dd*, *J* = 11.8, 4.5, H–C(glc-6)); 3.81 (*dd*, *J* = 11.8, 2.3, H–C(glc-6)). ^{13}C–NMR ((D$_6$)acetone, 75 MHz): 133.8 (C(1a)); 128.6 (C(2a,6a)); 116.5 (C(3a,5a)); 158.6 (C(4a)); 94.6 (C(7a)); 57.2 (C(8a)); 146.9 (C(9a)); 107.2 (C(10a,14a)); 160.0 (C(11a,13a)); 102.3 (C(12a)); 129.7 (C(1b)); 131.3 (C(2b,6b)); 116.3 (C(3b,5b)); 158.1 (C(4b)); 132.1 (C(7b)); 126.2 (C(8b)); 137.1 (C(9b)); 123.0 (C(10b)); 162.5 (C(11b)); 98.2 (C(12b)); 160.4 (C(13b)); 110.0 (C(14b)); 102.8 (C(glc-1)); 75.0 (C(glc-2)); 78.1 (C(glc-3)); 71.4 (C(glc-4)); 77.8 (C(glc-5)); 62.8 (C(glc-6)). ^{1}H,^{13}C-HMBC: H–C(2a,6a)/C(4a) and C(7a); H–C(3a,5a)/C(1a) and C(4a); H–C(7a)/C(1a), C(2a,6a), C(8a), C(9a), and C(11b); H–C(8a)/C(1a), C(7a), C(9a), C(10a,14a), C(10b), and C(11b); H–C(10a,14a)/C(8a), C(11a,13a), and C(12a); H–C(12a)/C(10a,14a) and C(11a,13a); H–C(2b,6b)/C(4b) and C(7b); H–C(3b,5b)/C(1b) and C(4b); H–C(7b)/C(1b), C(2b,6b), and C(9b); H–C(8b)/C(1b), C(9b), C(10b), and (14b); H–C(12b)/C(10b), C(11b), C(13b), and C(14b); H–C(14b)/C(8b), C(10b), C(12b), and C(13b); H–C(glc-1)/C(13a). ^{1}H,^{1}H-NOESY: H–C(2a,6a)/H–C(7a) and H–C(8a); H–C(7a)/H–C(2a,6a) and H–C(10a,14a); H–C(8a)/H–C(2a,6a), H–C(10a,14a), H–C(2b,6b), and H–C(8b); H–C(10a,14a)/H–C(7a), H–C(8a), and H–C(2b,6b); H–C(2b,6b)/H–C(8a), H–C(10a,14a), H–C(7b), and H–C(14b); H–C(7b)/H–C(2b,6b); H–C(8b)/H–C(8a) and H–C(14b); H–C(12b)/H–C(glc-1); H–C(14b)/H–C(2b,6b), H–C(8b), and H–C(glc-1). FAB-MS (neg.): 615 ($[M-H]^-$). HR-FAB-MS (neg.): 615.1876 ($[M-H]^-$, $C_{34}H_{31}O_{11}^-$; calc. 615.1866).

REFERENCES

[1] S. Sotheeswaran, V. Pasupathy, *Phytochemistry* **1993**, *32*, 1083.
[2] J. Gorham, M. Tori, Y. Asakawa, 'The Biochemistry of the Stilbenoids', Chapman & Hall, London, 1995.
[3] T. Ito, T. Tanaka, Z. Ali, Y. Akao, Y. Nozawa, Y. Takahashi, R. Sawa, K. Nakaya, J. Murata, D. Darnaedi, M. Iinuma, *Heterocycles* **2004**, *63*, 129.
[4] Z. Ali, T. Ito, T. Tanaka, K. Nakaya, M. Iinuma, J. Murata, D. Darnaedi, *Phytochemistry* **2004**, *65*, 2141.
[5] T. Ito, M. Furusawa, T. Tanaka, Z. Ali, I. Iliya, K. Nakaya, J. Murata, D. Darnaedi, M. Iinuma, *Chem. Pharm. Bull.* **2005**, *53*, in press.
[6] E.-K. Seo, H. Chai, H. L. Constant, T. Santisul, V. Reutrakul, C. W. W. Beecher, N. R. Farnsworth, G. A. Cordell, J. M. Pezzuto, A. D. Kinghorn, *J. Org. Chem.* **1999**, *64*, 6976.
[7] T. Tanaka, T. Ito, K. Nakaya, M. Iinuma, S. Riswan, *Phytochemistry* **2000**, *54*, 63.
[8] T. Ito, T. Tanaka, M. Iinuma, I. Iliya, K. Nakaya, Z. Ali, Y. Takahashi, R. Sawa, Y. Shirataki, J. Murata, D. Darnaedi, *Tetrahedron* **2003**, *59*, 5347.
[9] J. Ito, M. Niwa, Y. Oshima, *Heterocycles* **1997**, *45*, 1809.
[10] T. Ito, T. Tanaka, K. Nakaya, M. Iinuma, Y. Takahashi, H. Naganawa, M. Ohyama, Y. Nakanishi, K. F. Bastow, K.-H. Lee, *Tetrahedron* **2001**, *57*, 7309.
[11] T. Ito, T. Tanaka, M. Iinuma, K. Nakaya, Y. Takahashi, R Sawa, J. Murata, D. Darnaedi, *J. Nat. Prod.* **2004**, *67*, 932.
[12] S. D. Sarker, P. Whiting, L. Dinan, V. Sik, H. H. Rees, *Tetrahedron* **1999**, *55*, 513.
[13] Y. Oshima, Y. Ueno, K. Hisamichi, M. Takeshita, *Tetrahedron* **1993**, *49*, 5801
[14] H. J. Kim, E. J. Chang, S. J. Bae, S. M. Shim, H. D. Park, C. H. Rhee, J. H. Park, S. W. Choi, *Arch. Pharm. Res.* **2002**, *25*, 293.
[15] T. Ito, T. Tanaka, Y. Ido, K. Nakaya, M. Iinuma, Y, Takahashi, H. Naganawa, S. Riswan, *Heterocycles* **2001**, *55*, 557.

Received July 13, 2004