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New resveratrol oligomers in the stem bark of *Vatica pauciflora*

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Abstract—Five new resveratrol oligomers; pauciflorols A–C (**1**–**3**), isovaticanols B (**6**) and C (**8**), and three new oligostilbene glucosides; pauciflorosides A (**11**), B (**13**), C (**14**), were isolated from the stem bark of *Vatica pauciflora* (Dipterocarpaceae) together with known 17 resveratrol oligomers (**4**, **5**, **7**, **9**, **10**, **12** and **15**–**25**) and bergenin (**26**). The structures of isolates were established on the basis of detailed spectroscopic analysis. The typical and characteristic spectral properties of some resveratrol oligomers were also discussed.

1. Introduction

Stilbene and its oligomers including their glucosides are occurring in the particular families such as Dipterocarpaceae,[1–22] Vitaceae,[23–30] Cyperaceae,[31,32] Leguminosae[33–36] and Gnetaceae.[37–39] Resveratrol (*tran*-3,5,4′-trihydroxystilbene), one of the stilbenes, has recently been drawn to attentions because of its various biological properties such as anti-oxidative, antimutagenic, and an inducer of phase II drug-metabolizing enzymes.[40] The further wide-ranged biological activities like antifungal,[8] cytotoxicic[5,6,41,42] anti-inflammatory,[26,43] antivirus[6] and antibacterial[16,44] have been still more examined. Dipterocarpaceaeous plants are well known to rich resource of various resveratrol oligomers. A genus *Vatica* comprising 65 species belongs to the largest subfamily Dipterocarpoideae in Dipterocarpaceae, most of which distributes in Southeast Asia.[45] Although some phytochemicals in a few of families were disclosed, the systematical phenolic compositions have not been discussed yet. The structural elucidation of resveratrol oligomers in some Dipterocarpaceous plants [*Vateria*,[46,47] *Hopea*,[48,49] *Vatica*,[50–53] and *Shorea*[54–56]] and some biological properties of the characterized oligomers[41,42,44] were discussed in our previous papers. The different oxidative condensation of resveratrol admitted the oligomers to a variety of frameworks in the family like dihydrobenzofuran ring, benzocyclopentane ring, dibenzo[2.1]octadiene, dibenzobicyclo[3.2.1]octadiene, dibenzobicyclo[3.3.0]octadiene and tribenzobicyclo[3.3.2]octatriene system.[1,5,50] The unusual spectroscopic properties have been observed in the complex stereo structures of some stilbene oligomers caused by anisotropy and fixation of phenyl group and so on.[26,47,50] The phytochemical and biologically active interest in resveratrol oligomers in the family led us the current study of *V. pauciflora* (Korth.). This paper deals with the isolation and structure elucidation of new resveratrol oligomers [pauciflorols A–C (**1**–**3**), and isovaticanols B (**6**) and C (**8**)] (Scheme 1) and the glucosides [pauciflorosides A (**11**), B (**13**) and C (**14**)] (Scheme 2) along with 17 known resveratrol cognates (**4**, **5**, **7**, **9**, **10**, **12** and **15**–**25**) (Schemes 1–3) and bergenin (**26**). Some unusual spectroscopic properties observed in isovaticanol B (**6**), vaticanol B (**7**) and isovaticanol C (**8**) in NMR spectrum are also comprehensively discussed.

2. Results and discussion

An acetone extract of the stem bark of *V. pauciflora* was subjected to open column chromatography on silica gel. Further repeated purification by Sephadex LH-20 column chromatography, preparative TLC and reversed-phase column chromatography resulted in the isolation of new resveratrol oligomers, pauciflorols A (**1**–**3**), isovaticanols B

Keywords: *Vatica pauciflora*; resveratrol oligomer; dipterocarpaceae; structure elucidation; spectral property.

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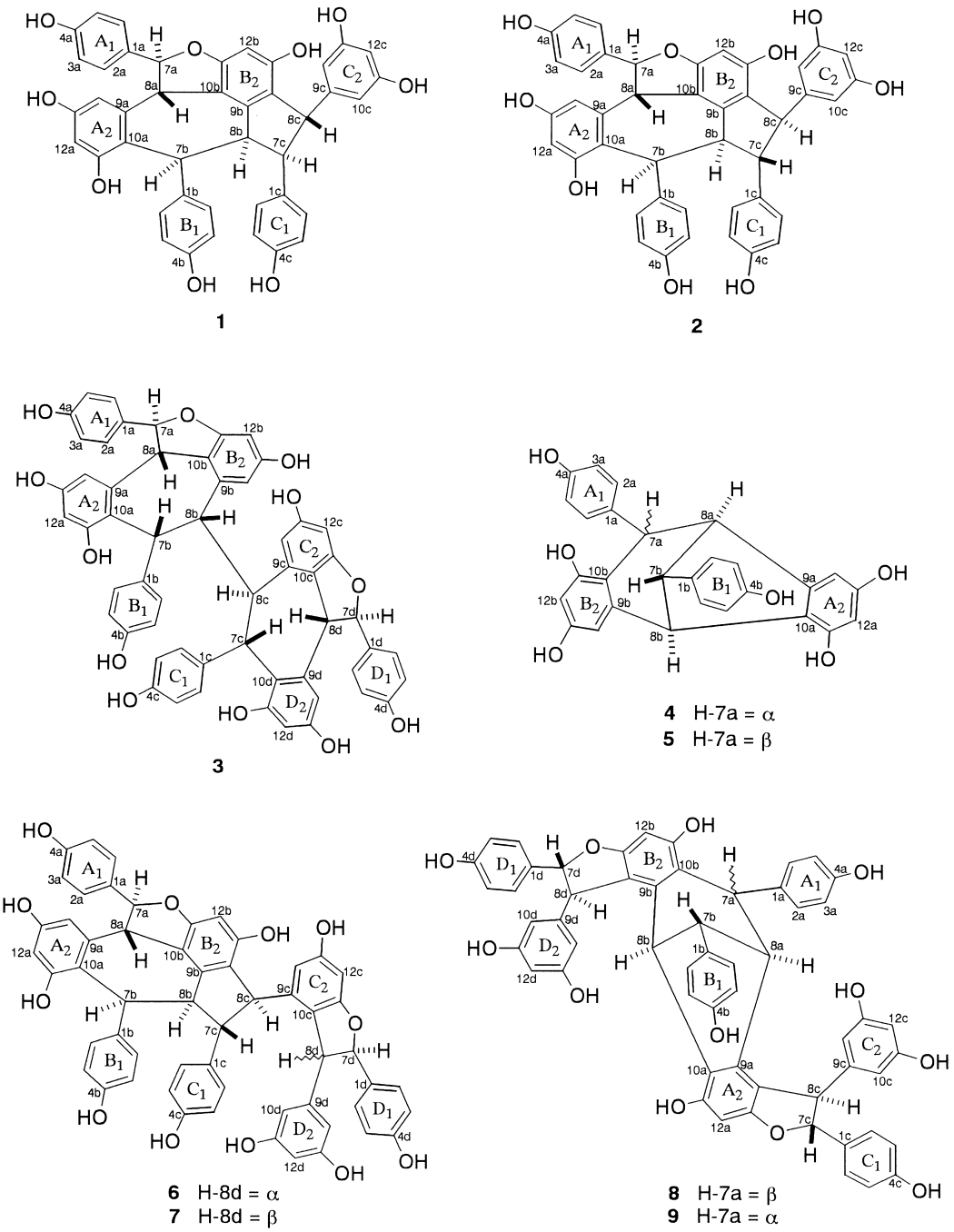
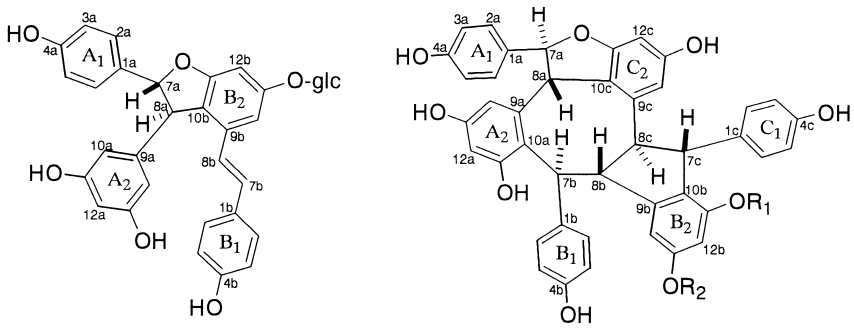


Scheme 1.

(**6**) and C (**8**) and pauciflorosides A (**11**), B (**13**) and C (**14**), along with 17 known resveratrol cognates (**4**, **5**, **7**, **9**, **10**, **12** and **15**–**25**) (Schemes 1–3) and bergenin (**26**). All the isolates (**1**–**26**) showed a positive reaction to the Gibbs reagent on TLC. The new compounds (**1**–**3**, **6**, **8**, **11**, **13** and **14**) displayed absorption maximun between at 283–287 nm, which is consistent with the presence of one or more nonconjugated phenyl rings.

Pauciflorol A (**1**) was obtained as a pale yellow amorphous powder. The molecular weight was determined to be 680 by a peak of $[M-H]^-$ ion at *m/z* 679 in the negative ion FAB-MS and the molecular formula of $C_{42}H_{32}O_9$ was confirmed by negative ion high resolution (HR) FABMS (*m/z* $[M-H]^-$ 679.1960). In the ^{13}C NMR spectrum 42 carbon signals were observed. The ^1H NMR spectrum in CD_3COCD_3 (Table 1) exhibited signals for eight phenolic hydroxyl groups (δ 7.63–8.46) which were clearly disappeared by addition of D_2O. Considering the molecular formula, the remaining oxygen would contribute to the ether linkage. The spectrum coupled with ^{13}C NMR, ^1H–^1H COSY, ^{13}C–^1H COSY and HMBC spectra (Fig. 1 and Table 1) exhibited signals due to six aromatic rings as follows; three *p*-hydroxyphenyl groups (rings A_1–C_1), a 1,2,3,5-tetra-substituted aromatic ring (ring A_2), a 1,2,3,5,6-penta-substituted aromatic ring (ring B_2) and a 3,5-dihydroxyphenyl group (ring C_2). The presence of a set of mutually coupled aliphatic protons (H-7a/H-8a) and a



10 R = H
11 R = glc

12 $R_1 = R_2 = H$
13 $R_1 = H$, R_2 = glc
14 R_1 = glc, $R_2 = H$

Scheme 2.

sequence of four aliphatic protons (H-7b/H-8b/H-7c/H-8c) were also shown. The $^1H-^1H$ coupling pattern of the former (H-7a/H-8a) was characteristic of a dihydrobenzofuran ring[23], and of the latter (H-7b/H-8b/H-7c/H-8c) was similar to a partial structure of vaticanol A (**19**),[53] which suggested that a bicyclo[5,2,0]decadiene ring system (C-8a/C-9a/C-10a/C-7b/C-8b/C-7c/C-8c/C-14b/C-9b/C-10b) was present and that **1** is an oxidative trimer of resveratrol and the planar structure is as same as that of vaticanols A (**19**), E (**20**)[51] and suffruticosol B.[57] The planar structure was confirmed by the following evidence. The correlations in the HMBC spectrum (Fig. 1) were observed between H-7a/C-2a(6a), H-7b/C-2b(6b), H-7c/C-2c(6c), H-8a/C-14a, H-7b,8b/C-9b and H-8c/C-10c(14c), which indicated that three resveratrols A–C [(resveratrol A: ring $A_1-7a-8a-$ ring A_2)] were composed by six rings (A_1-C_1 and A_2-C_2) and six methine units. The J^3 long range correlations observed between H-8a/C-11b, H-7b/C-9a, H-7b/11a, H-8c/C-9b and H-8c/C-13b in the spectrum supported the C–C bonds between C-8a/C-10b, C-7b/C-10a and C-8c/C-14b. Although no long-range correlation between H-7a/C-11b was observed, the presence of the dihydrobenzofuran ring [C-7a/C-8a/C-10b/C-11b/O] was clear after consideration of an ether linkage existence. The planar structure of pauciflorol A was then determined to be **1** as shown in Figure 1.

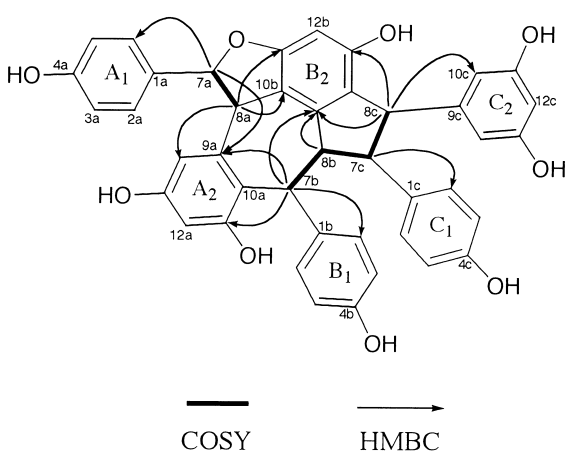
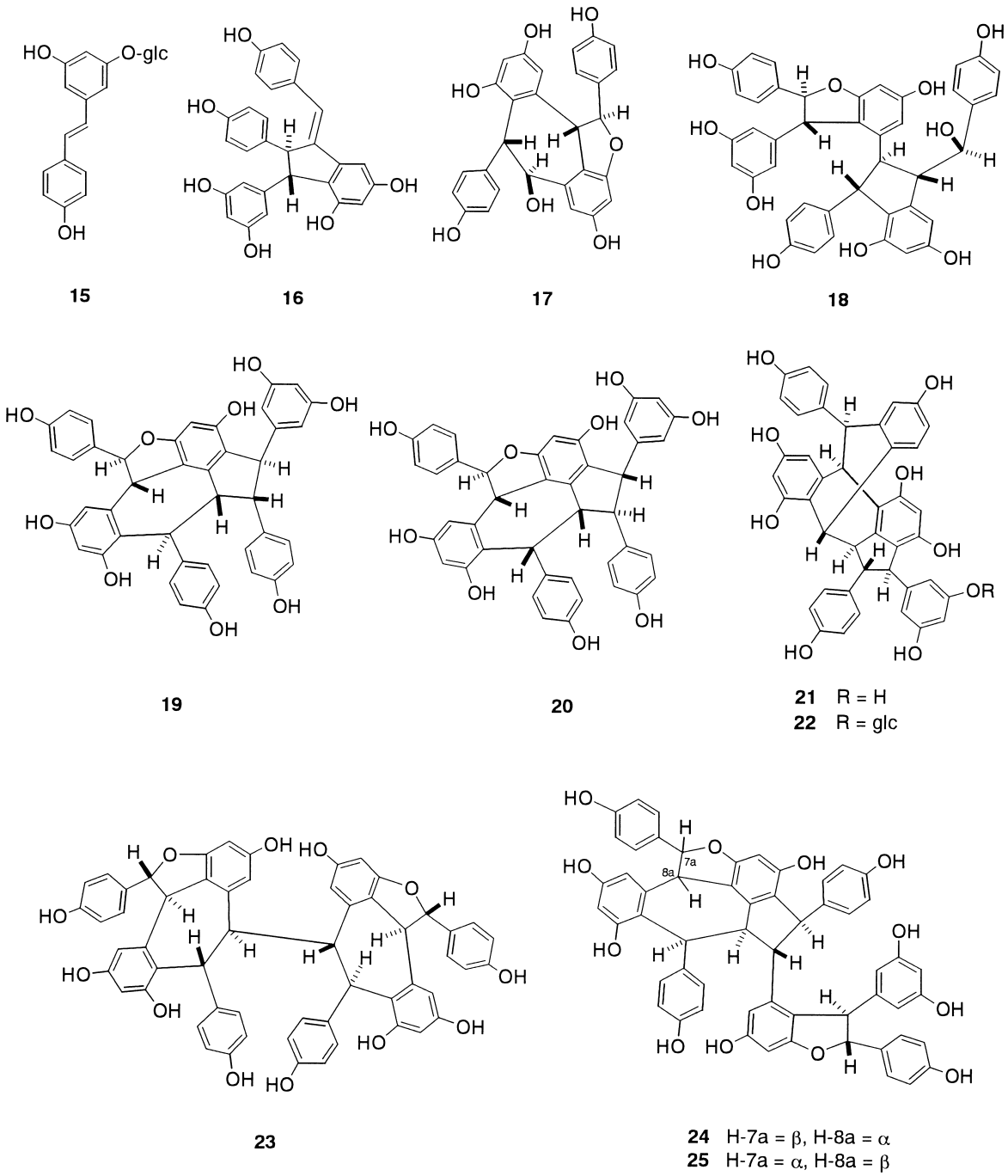


Figure 1. Selected correlations in 2D NMR of **1**.

To confirm the relative stereochemistry, NOESY experiments were conducted (Fig. 2, left). In there the clear cross peaks between H-7a/H-14a, H-8a/H-2a(6a) and H-2a(6a)/H-14a were observed. These cross peaks substantiated that the relative stereochemistry of the methine protons is *trans*. The relationship between four methine protons (H-7b, H-8b, H-8c and H-7c) and the dihydrobenzofuran ring was determined as follows. NOE interactions between H-8a/H-2b(6b) indicated that the ring B_1 is oriented in β-configuration (H-7b: α-configuration). The significant NOEs observed between H-2c(6c)/H-7b, H-2c(6c)/H-8c, H-10c(14c)/H-8b and H-10c(14c)/H-7c also indicated that the relative configuration of methine protons at C-7b, C-8b, C-7c and C-8c were α, α, α and β (Fig. 2, left) or α, β, β and α (Fig. 2, right **19**). Although the ring C_1 and H-7b in the former case (Fig. 2, left) are situated in the opposite orientation, both are located in near position. This contradiction will be resolved by the following consideration. The conformation of dibenzobicyclo[5,3,0]decadiene system (C-8a/C-9a/C-10a/C-7b/C-8b/C-7c/C-8c/C-14b/C-9b/C-10b) and β orientation of H-8a and the ring B_1 drawn in Figure 3 can well explain the results of NOE [H-2c(6c)/H-7b]. When the ring B_1 and the ring C_1 were situated in the same orientation as **1**, NOEs were observed between H-2b(6b)/H-2c(6c) and H-2b(6b)/H-3c(5c) (Fig. 2, left). But such NOE were not observed in **19** (Fig. 2, right). On the basis of these results, the relative stereo structure, in paticular, on the decadiene system was confirmed. The chemical shifts of H-2b(6b) and H-3b(5b) were observed in upper field (δ 6.56 and 6.14) compared to those of H-2a(6a) and H-3a(5a) (δ 7.21 and 6.76), because these protons are located above the ring B_2 and affected by anisotropy of the π system. The upper field shift of H-3c(5c) (δ 6.40) can be similarly explained by anisotropy of the ring B_1.

The planar structure of **1** is identical to those of known resveratrol trimers such as vaticanols A (**19**),[53] E (**20**)[51] isolated from this plant (Scheme 3) and suffruticosol.[57] Although **1** and **19** have similar $^1H-^1H$ coupling constants in the sequence of four aliphatic protons (H-7b/H-8b/H-7c/H-8c) except for H-7b/H-8b moiety [**19**: δ 5.17 (br s, H-7b); 4.52 (d, J=7.3 Hz, H-8b); 3.74 (d, 3.65, J=7.3 Hz, H-7c); 4.20 (s, H-8c)], the orientation is quite different. When the conformational differences based on a dibenzo[2,1]heptadiene ring in the decadiene system (C-8a/C-9a/C-10a/C-7b/C-8b/C-9b/C-10b) between **1** and **19** were considered as



Scheme 3.

shown in Figure 4. The dihedral angle of 90° is unsatisfactory with *cis* H-7b/H8b in **1**, to the contrary, almost 90° angle is satisfied with *trans* H-7b/H8b in **19**. Detail analysis of NOE reflected on the differences of anisotropy and conformation as found **1** and **19** enables the determination and discrimination of diastereomeric structures.

Pauciflorol B (**2**), a pale yellow amorphous powder, had the molecular formula of $C_{42}H_{32}O_9$ supported by the HR-FABMS ([M−H]$^-$: *m/z* 679.1970). Analysis of the ^{1}H and ^{13}C NMR, ^{1}H–^{1}H COSY, ^{13}C–^{1}H COSY and HMBC spectrum (Table 1) confirmed that **2** had the same planar structure as **1**.

The stereo structure of **2** was determined by the result of NOESY experiment. In this experiment (Fig. 5), the NOEs [H-7a/H-14a, H-14a/H-2a(6a), H-8a/H-2a(6a), H-8a/H-2b(6b)], which are similar to those of **1**, suggested that the orientation of the protons (H-7a/H-8a) on the dihydrobenzofuran ring is *trans* and that the ring B_1 has a same orientation as H-8a (β-configuration). The aromatic protons on the ring C_1 [H-2c(6c)] showed NOEs with four methine protons (H-7b, H-8b, H-7c and H-8c), which can be observed only when H-7b, H-8b and H-8c are situated in *cis* toward the ring C_1 (α-configuration). The correlations between H-2b(6b)/H-7c, H-2b(6b)/H-10c(14c) and H-7c/H-10c(14c) supported the same configuration of the rings B_1 and C_2. On the basis of these results, the relative structure of

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

No.	1			2		
	δH	δC	HMBC	δH	δC	HMBC
1a		130.94			130.15	
2a, 6a	7.21 (d, 8.6)	130.22	4a, 7a	7.26 (d, 8.6)	129.58	4a, 7a
3a, 5a	6.76 (d, 8.6)	116.02	1a, 4a	6.81 (d, 8.6)	115.45	1a, 4a
4a (OH)	8.46 (br s)	158.56	3a(5a), 4a	8.50 (br s)	157.93	
7a	5.79 (d, 11.5)	90.80	1a, 2a(6a), 8a, 9a	5.84 (d, 11.7)	89.93	1a, 2a(6a), 8a, 9a
8a	4.48 (br d, 11.5)	49.04	1a, 7a, 9a, 10a, 9b, 10b, 11b	4.47 (br d, 11.7)	48.19	1a, 7a, 9a, 10a, 9b, 10b, 11b
9a		141.57			141.04	
10a		126.17			124.14	
11a (OH)	8.44 (br s)	154.80	10a, 11a, 12a	8.29 (br s)	155.18[a]	10a, 11a, 12a
12a	6.37 (d, 2.2)	101.89	10a, 11a, 13a, 14a	6.35 (d, 2.2)	101.05	10a, 13a, 14a
13a (OH)	8.05 (br s)	156.67	12a, 13a, 14a	8.11 (br s)	156.12[b]	
14a	6.13 (d, 2.2)	106.01	8a, 10a, 12a, 13a	6.17 (br d, 2.2)	105.31	8a, 10a, 12a
1b		133.11			132.70	
2b, 6b	6.56 (d, 8.5)	130.27	4b, 7b	7.19 (d, 8.5)	129.89	4b, 7b
3b, 5b	6.14 (d, 8.5)	113.97	1b, 4b	6.69 (d, 8.5)	114.85	1b, 4b
4b (OH)	7.63 (br s)	154.60	3b(5b), 4b	8.09 (br s)	155.18[a]	
7b	5.51 (br d, 3.3)	39.33	9a, 10a, 11a, 1b, 2b(6b), 8b, 9b, 7c	5.28 (d, 3.3)	36.86	9a, 10a, 11a, 1b, 2b(6b), 8b, 9b
8b	3.97 (m)	48.67	10a, 1b, 9b, 10b, 14b, 1c, 7c	3.66 (m)	51.81	1b, 1c
9b		144.17			143.49	
10b		116.55			115.37	
11b		160.12			158.83	
12b	6.26 (s)	96.07	10b, 11b, 13b, 14b	6.15 (s)	96.01	10b, 11b, 13b, 14b
13b (OH)	8.19 (br s)	154.93	12b, 13b, 14b	6.75 (br s)	154.09	12b, 13b, 14b
14b		121.90			120.39	
1c		134.75			132.14	
2c, 6c	6.97 (d, 8.5)	130.49	4c, 7c	7.02 (d, 8.5)	129.32	4c, 7c
3c, 5c	6.40 (d, 8.5)	115.30	1c, 4c	6.74 (d, 8.5)	115.22	1c, 4c
4c (OH)	7.80 (br s)	156.51	3c(5c), 4c	8.15 (br s)	156.12[b]	
7c	3.74 (d, 7.7)	60.68	9b, 14b, 8b, 1c, 2c(6c), 8c, 9c	3.76 (dd, 11.6, 9.3)	61.40	7b, 8b, 1c, 2c(6c), 8c, 9c
8c	4.78 (s)	54.23	8b, 9b, 13b, 14b, 1c, 7c, 9c, 10c(14c)	4.25 (d, 9.3)	56.69	9b, 13b, 14b, 1c, 7c, 9c, 10c(14c)
9c		147.99			146.17	
10c, 14c	6.00 (d, 2.0)	106.50	8c, 12c	6.20 (s)	106.78	8c, 11c(13c), 12c
11c, 13c (OH)	8.00 (br s)	159.34	10c(14c), 11c(13c), 12c	8.05 (br s)	158.56	10c(14c), 11c(13c), 12c
12c	6.15 (t, 2.0)	101.31	10c(14c), 11c(13c)	6.19 (s)	101.10	10c(14c), 11c(13c)

Measured in CD_3COCD_3. 300 MHz (^{1}H) and 75 MHz (^{13}C).
[a] Overlapping.

pauciflorol B was characterized as shown in Figure 5. The ^{1}H and ^{13}C NMR spectral data of **2** is similar to those of **1** except for their partial structures of the ring B_1 and resveratrol C. The conspicuous differences in the spectrum between them are the *J* values of H-8b/H-7c and H-7c/H-8c (Table 1), which can well support that their structural differences are configuration of H-7c and H-8c. The stereo structure of **2** is identical to those of trimeric unit (resveratrols A–C) of vaticanol B (**7**)[53] (Scheme 1). The similarity of spectral data between them further approved to the structure of **2**. The stereo structure of **2** can well explain the anisotropic effect of the ring C_2, which causes the upper field shift of OH-13b (δ 6.75). This type of anisotropy is also observed in the case of hemsleyanol C (**24**)[54] [δ 6.46 (OH-13b)], the stereo structure of benzocyclopentane ring of which is as same as **2**. Such discussion of tendencies in the anisotropic effect can be applicable to the confirmation of stereo structures.

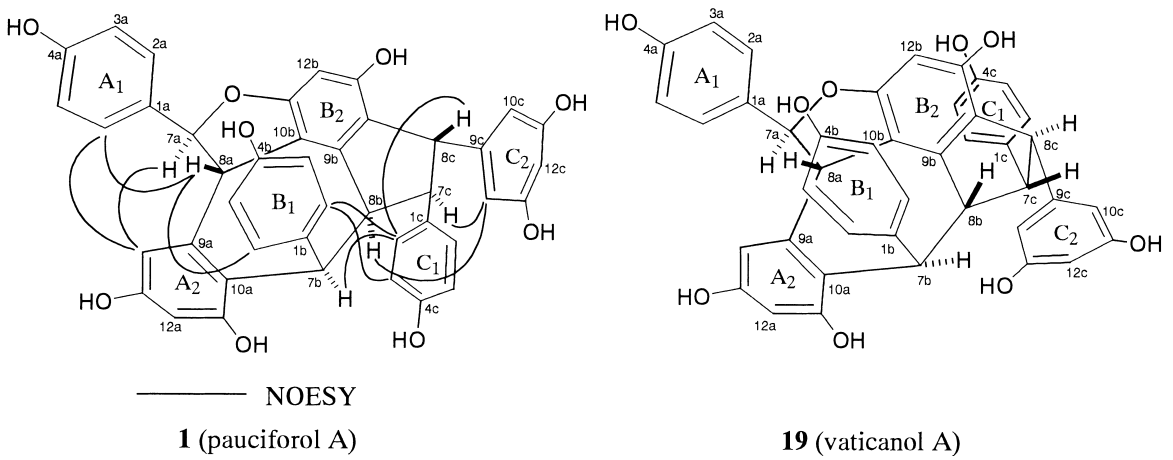


Figure 2. Selected NOESY correlations in **1** and stereo structures of **1** and **19**.

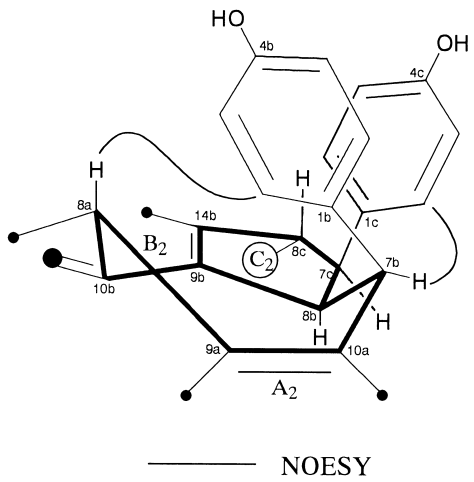


Figure 3. Dibenzobicyclo[5,3,0]decadiene system in **1**.

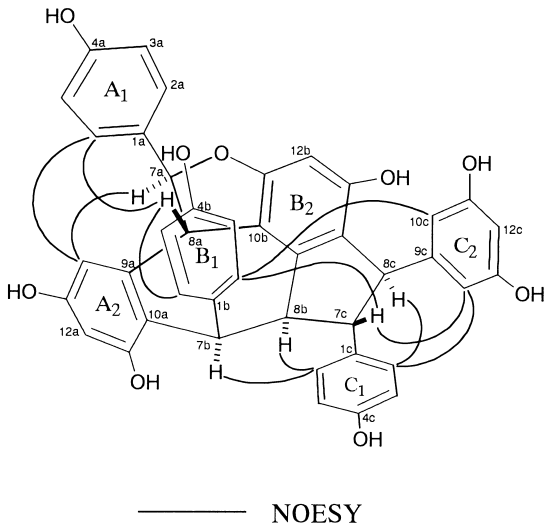
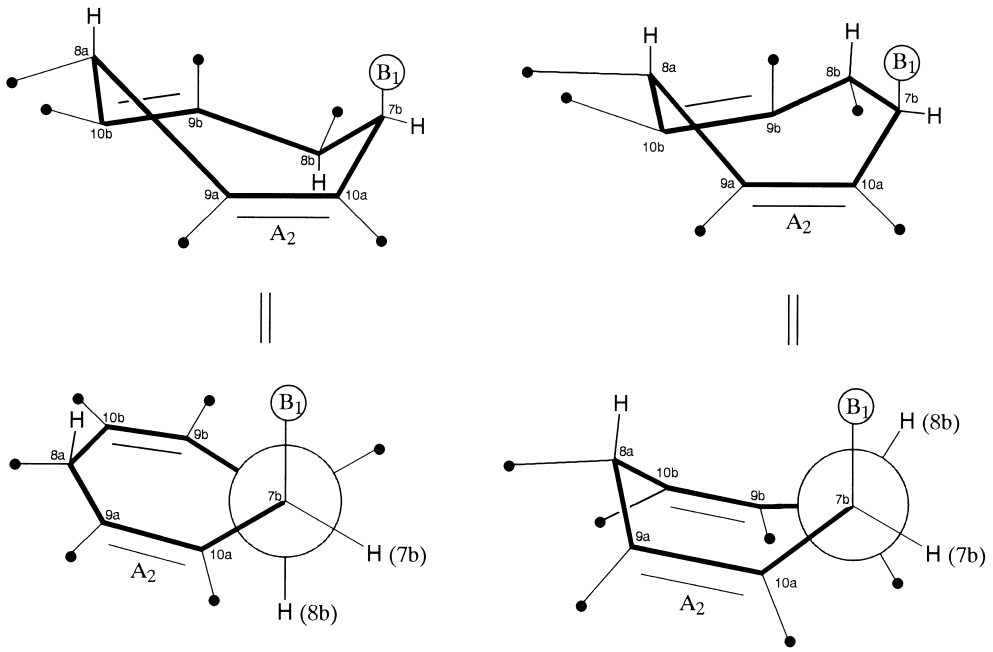


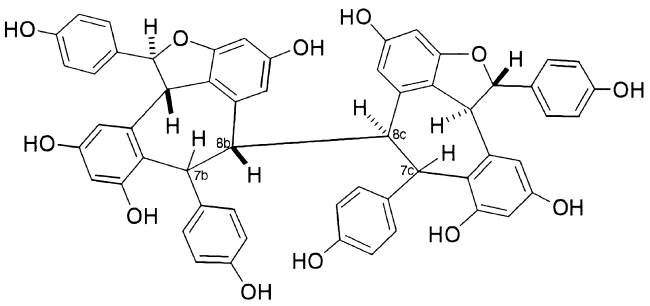
Figure 5. Selected NOESY correlations in **2**.

Pauciflorol C (**3**), a brown amorphous powder, the molecular formula of $C_{56}H_{42}O_{12}$ was established by the HR-FABMS ([M−H]$^-$ ion at *m/z* 905.2596). The ^{13}C NMR spectrum showed 56 carbon signals. The analysis of ^{1}H, ^{13}C NMR (Table 2) and ^{1}H–^{1}H COSY (Fig. 6) spectral data indicated the presence of eight oxygenated aromatic rings which form four 4-hydroxyphenyl groups (rings A_1–D_1) and four 1,2,3,5-tetrasubstituted benzene rings (rings A_2–D_2). The spectrum also exhibited two sets of mutually coupled aliphatic protons (H-7a/H-8a and H-7d/H-8d) and a sequence of four aliphatic protons (H-7b/H-8b/H-8c/H-7c) as drawn with bold line in Figure 6. The presence of 10 hydroxyl groups and two ether linkages was deduced after considering the molecular formula and 10 broad signals due to hydroxyl groups in the ^{1}H NMR spectrum (δ 7.59–8.40). All carbon signals attributed to eight methine carbons and 48 aromatic carbons in the ^{13}C NMR spectral data were assigned by analysis of the HMQC and HMBC spectrum (Table 2). The significant ^3J long range correlations were observed between H-7a/C-2a(6a), H-7b/C-2b(6b), H-7c/C-2c(6c), H-7d/C-2d(6d), H-8a/C-14a, H-8b/C-14b, H-8c/C-14c and H-8d/C-14d in the HMBC spectrum (Fig. 6), which indicated that eight rings (A_1–D_1 and A_2–D_2) and eight methine units formed four resveratrols A–D. Long range correlations were further observed between the aliphatic methine protons and the quaternary carbons on the four tetra-substituted benzene rings (rings A_2–D_2) as follows; H-8a/C-11b, H-7b/C-9a, H-7c/C-9d and H-8d/C-11c, which indicated the connection between C-8a/C-10b, C-7b/C-10a, C-7c/C-10d and C-8d/C-10c, respectively. Further cross peaks observed between H-7a/C-11b



1 **19**

Figure 4. Stereo structure of **1** and **19**.



Scheme 4.

and H-7d/C-11c supported the presence of two ether linkages (C-7a/O/C-11b and C-7d/O/C-11c), both of which formed dihydrobenzofuran rings (C-7a/C-8a/C-10b/C-11b/O and C-7d/C-8d/C-10c/C-11c/O). The planar structure of pauciflorol C was then concluded to be **3** as shown in Figure 6. Pauciflorol C (**3**) seems to be one of stereo isomers of hopeaphenol (**27**),[22,27] isohopeaphenol (**28**)[27] (Scheme 4) and vateriaphenol B (**23**)[47] (Scheme 3).

For confirmation of the relative stereochemistry of **3**, NOESY experiments among the stereo isomers (**23**, **27** and **28**) were conducted (Fig. 7). The clear cross peaks were observed between H-7a/H-14a, H-8a/H-2a(6a), H-7d/H-14d and H-8d/H-2d(6d). These NOEs indicated that the relative stereochemistry of the two dihydrobenzofuran rings (H-7a/H-8a and H-7d/H-8d) is *trans*. The relationship between four methine protons (H-7b, H-8b, H-8c and H-7c) and the two dihydrobenzofuran rings was determined as follows. NOEs between H-8a/H-7b and H-8a/H-8b indicated that two methine protons (H-7b and H-8b) on the dibenzocycloheptadiene ring (C-8a/C-9a/C-10a/C-7b/C-8b/C-9b/C-10b) were oriented in the same configuration as H-8a (β-configuration). The relationship between H-8b and H-8c is *trans* diaxial on the basis of *J* value (12.0 Hz).[23,58,59] Furthermore the configuration of H-7c and H-8d was confirmed to be β by the following distinct NOEs: H-7b/H-7c, H-7b/H-8d, H-8b/H-7c and H-8b/H-8d. The relative stereo structure of **3** was then drawn as in Figure 7. This

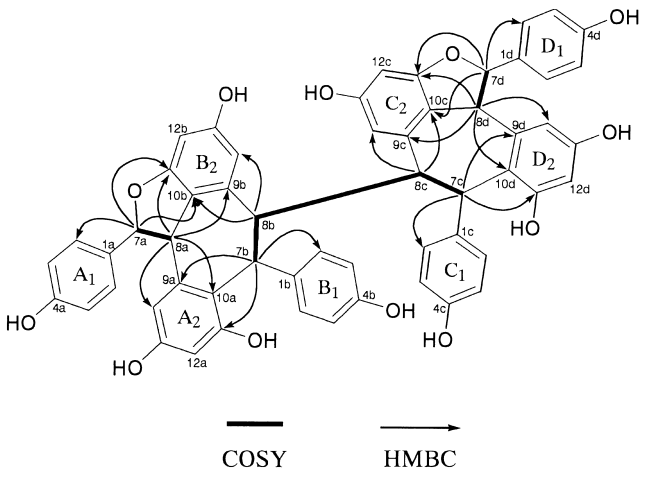


Figure 6. Selected correlations in 2D NMR of **3**.

Table 2. ^{1}H and ^{13}C NMR spectral data of **3**

No.	δH	δC	HMBC
1a		133.85	
2a, 6a	7.18 (d, 8.6)	130.14	3a(5a), 4a, 7a
3a, 5a	6.82 (d, 8.6)	116.72	1a, 4a
4a		158.39	
7a	5.63 (d, 8.5)	93.34	1a, 2a(6a), 8a, 9a, 10b, 11b
8a	4.65 (d, 8.5)	52.66	1a, 7a, 9a, 10a, 14a, 9b, 10b, 11b
9a		140.90	
10a		124.00	
11a (OH)	7.68 (br s)	157.17	10a, 11a, 12a
12a	6.30 (d, 2.3)	101.77	10a, 11a, 13a, 14a
13a		156.57	
14a	6.07 (d, 2.3)	106.91	9a, 10a, 12a, 13a
1b		135.07	
2b, 6b	6.65 (d, 8.6)	130.74	3b(5b), 4b, 7b
3b, 5b	6.42 (d, 8.6)	114.35	1b, 4b
4b		155.45	
7b	4.91 (s)	43.41	10a, 11a, 1b, 2b(6b), 8b, 9b, 8c
8b	4.46 (d, 12.0)	47.70	10a, 1b, 7b, 9b, 10b, 14b, 7c, 8c
9b		140.70	
10b		118.73	
11b		159.65	
12b	5.92 (d, 1.8)	94.74	10b, 11b, 13b, 14b
13b (OH)	7.92 (br s)	159.41	12b, 13b, 14b
14b	6.19 (d, 1.8)	105.21	8b, 10b, 12b, 13b
1c		138.19	
2c, 6c	6.74 (d, 8.6)	129.87	3c(5c), 4c, 7c
3c, 5c	6.49 (d, 8.6)	114.85	1c, 4c
4c		155.33	
7c	5.28 (d, 4.7)	44.61	8b, 1c, 2c(6c), 8c, 9c, 10d, 11d
8c	3.54 (dd, 12.0. 4.7)	51.47	7b, 8b, 1c, 7c, 9c, 10c, 14c, 10d
9c		141.24	
10c		117.74	
11c		160.89	
12c	5.98 (d, 2.1)	95.41	10c, 11c, 13c, 14c
13c (OH)	7.96 (br s)	158.76	12c
14c	6.02 (d, 2.1)	111.47	8c, 10c, 12c, 13c
1d		133.48	
2d, 6d	7.08 (d, 8.6)	130.51	3d(5d), 4d, 7d
3d, 5d	6.75 (d, 8.6)	116.45	1d, 4d
4d		158.36	
7d	5.62 (d, 9.5)	93.43	1d, 2d(6d), 8d, 9d, 10c, 11c
8d	5.01 (d, 9.5)	52.42	1d, 7d, 9d, 10d, 14d, 9c, 10c, 11c
9d		141.36	
10d		118.66	
11d (OH)	7.59 (br s)	158.30	10d, 11d, 12d
12d	6.16 (d, 2.3)	102.17	10d, 11d, 13d, 14d
13d		156.65	
14d	5.96 (d, 2.3)	106.48	9d, 11d, 12d, 13d
OH	7.74 (br s, 2H), 7.94 (br s, 1H) 8.01 (br s, 1H), 8.40 (br s, 2H)		

Measured in CD_3COCD_3. 500 MHz (^{1}H) and 125 MHz (^{13}C).

stereo structure also well explains the following results of NOEs: H-14b/H-14c, H-2b(6b)/H-2c(6c) and H-2b(6b)/H-3c(5c).

The planar structure of **3** is identical to three known diastereomeric resveratrol tetramers (**23**, **27** and **28**) which are composed of two resveratrol dimers (Schemes 3 and 4).[25,30,47] In case of **27** and **28**, two identical dimers (dimer 1:two ampelopsin A's[30] in **27**, dimer 2: two balanocarpols[14] in **28**) are coupled through a linkage of C-8b/C-8c. Half

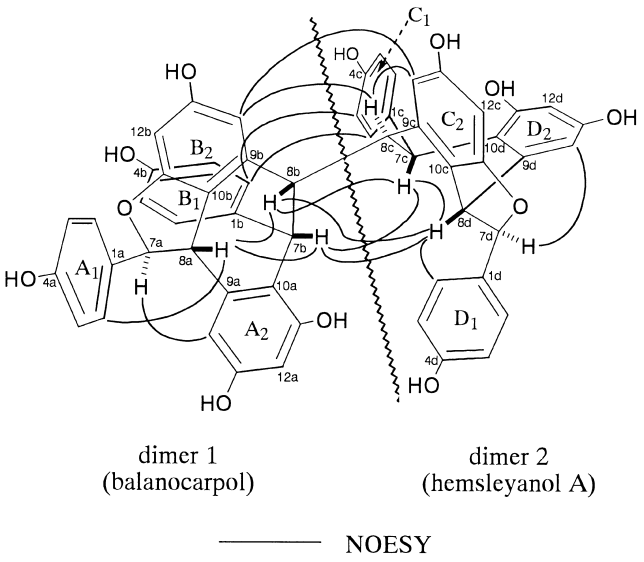


Figure 7. Selected NOESY correlations in **3**.

signals of the total atom numbers are observed in the ^{1}H and ^{13}C NMR spectrum of **27** and **28** because of symmetrical structure.[27] Two heterogenic dimeric units [dimer 1: balanocarpol, dimer 2: hemsleyanol A (**17**)[56]] are the components of **3** (Fig. 7). Then **3** losses the symmetrical plane and the full signal numbers were observed in the ^{1}H and ^{13}C NMR spectrum, which enabled the detail analysis of stereochemistry by NOESY experiment. H-8a and H-8d on dihydrobenzofuran rings in **27** appeared in higher field (δ 4.12) due to anisotropic effect of the rings B_1 and C_1.[27] The chemical shift of the same protons in **3** appeared at lower field [δ 4.65 (H-8a) and 5.01 (H-8d)] as same as **28** [δ 5.37 (H-8a and H-8d)],[27] which supported that the stereo relationship between H-8a/ring B_1 and H-8d/ring C_1 is opposite orientation in **3** as same as **28**. Furthermore, the signals of H-14b and H-14c in **27** and **28** appeared respectively at δ 5.07 and 5.42, but the same protons of **3** appeared at δ 6.19 and 6.02. The differences can be considered as follows: due to the orientation of four aliphatic protons sequence (H-7b/H-8b/H-8c/H-7c) of α/β/α/β in **27** and β/β/α/α in **28**, the aromatic protons (H-14b and H-14c) are located very above the rings C_2 and B_2, respectively. The rings cause anisotropic effects on the protons. The molecular model of **27** is shown in Figure 8. The orientation of protons (H-7b/H-8b/H-8c/H-7c: β/β/α/β) in **3** does not cause such effects. These facts confirmed further the proposed stereo structure of pauciflorol C (**3**).

Compound **4**, yellow amorphous powder, had same relative structure as (−)-ampelopsin F isolated from *Caragana sinica* (Leguminosae).[36] The optical rotation showed opposite values to that isolated from *Ampelopsis brevipedunculata* (Vitaceae).[28] The detail NMR spectral data assigned by the aid of 2D-NMR are superimposed to literature values. The enantiomer of (+)-ampelopsin A[49] and (+)-ampelopsin H[54] have been previously isolated from *Hopea parviflora* and *Shorea hemsleyana* (Dipterocarpaceae), and the enantiomer of (−)-isohopeaphenol from *S. hemsleyana*,[56] *Hopea utilis*[48] and *Vateria indica*[47] have been also reported. Resveratrol dimers (for example: ampelopsins A, D[29] and F) and tetramers (for example: viniferols B and C[23]) may biosynthesized through (+)-ε-viniferin (**10**) in Vitaceous plants, which well agrees to the aspect of their absolute configurations.[60,61] (−)-ε-Viniferin is occurring in Dipterocarpaceae, Cyperaceae, Gnetaceae and Leguminosae, but (+)-ε-viniferin is only in Vitaceae. From the viewpoint of biosynthetic pathway, the relationship of enantiomers that exist in some plants of Dipterocarpaceae and Vitaceae (ampelopsins A, F, and H, hopeaphenol and isohopeaphenol) can be reasonably explained.

Isovaticanol B (**6**) was obtained as a brown amorphous powder. The $[M-H]^-$ ion peak at *m/z* 905.2605 in the HR-FABMS in negative ion mode corresponds to the molecular formula of $C_{56}H_{42}O_{12}$. By usual methylation or acetylation, **6** afforded a decamethyl ether (**6a**) or a deca-acetate (**6b**), suggesting that isovaticanol B has ten phenolic hydroxyl groups. The ^{1}H or ^{13}C NMR spectrum analyzed with $^{1}H-^{1}H$ COSY, HMQC and HMBC spectra [measured at room temperature (rt)] (Table 3, Figs. 9 and 11) exhibited the existence of four 4-hydroxyphenyl groups (rings A_1-D_1), two 1,2,3,5-tetrasubstituted benzene rings (rings A_2 and C_2), a pentasubstituted benzene ring (ring B_2). The spectrum further showed the signals due to a sequence of four aliphatic methine protons coupled successively (H-7b/H-8b/H-7c/H-8c) and two sets of mutually coupled aliphatic protons (H-7a/H-8a and H-7d/H-8d). The position of eight phenolic hydroxyl groups on the seven aromatic rings (A_1-D_1 and A_2-C_2) and assignment of quaternary carbon atoms on these rings were established by means of the correlations in the HMBC spectra (Table 3). Considering the molecular formula ($C_{56}H_{42}O_{12}$), the remaining moiety is $C_6H_5O_2$. In the ^{1}H NMR spectrum, the other signals of a *meta* coupled aromatic proton [δ 6.01 (1H, t, J=2.1 Hz, H-12d)], a broad singlet [δ 5.74 (H-10d and H-14d)], and two hydroxyl groups [δ 7.66 (OH-11d and H-13d)] were assignable to the rest benzene ring (ring D_2). The six carbons on the ring D_2

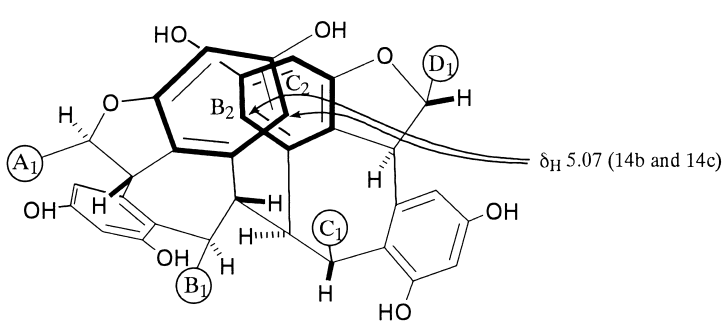


Figure 8. Upper field shift of aromatic protons in **27** caused by anisotropy.

were observed at δ 142.74 (C-9d), 109.06 [C-10d(14d)], 158.80 [C-11d(13d)] and 101.95 (C-12c). The behaviors of chemical shift values are closely resembled those of a 3,5-dihydroxyphenyl group as found in the ring C_2 of **1** (except for C-9c of **1**: δ 147.99). These results indicated that the ring C_1 formed the 3,5-dihydroxyphenyl group and a steric hindrance in the molecule may cause high field shifts of H-10d(14d) and C-9d, which suggested that **6** was a stilbene tetramer composed of four resveratrol units (resveratrols A–D). In the HMBC spectrum (Fig. 9), distinct cross peaks were observed between the methine protons and the aromatic carbons as follows; H-7a/C-2a(6a), H-8a/C-14a, H-7b/C-2b(6b), H-8b/C-9b, H-7c/C-2c(6c), H-8c/C-14c, H-7d/C-2d(6d) and H-8d/C-10d(14d), which indicated the respective connections of C-1a/C-7a, C-8a/C-9a, C-1b/ C-7b, C-8b/C-9b, C-1c/C-7c, C-8c/C-9c, C-1d/C-7d and C-8d/C-9d. The spectrum also displayed significant correlations of H-8a/C-11b, H-7b/C-11a, H-8c/C-13b and H-8d/C-11c, which confirmed the linkages between C-8a/C-10b, C-7b/C-10a, C-8c/C-14b and C-8d/C-10, respectively. The planar structure of **6** is one of stereo isomers of vaticanol B (**7**),[53] viniferols B and C,[23] and characterized as isovaticanol B shown in Figure 9.

Table 3. NMR spectral data of **6**, **6a** and **6b**

No.	**6**[a]			**6a**[b]	**6b**[b]
	δH	δC	HMBC	δH	δH
1a		130.84			
2a, 6a	7.23 (d, 8.6)	130.19	3a(5a), 4a, 7a	7.39 (d, 8.6)	7.44 (d, 8.5)
3a, 5a	6.78 (d, 8.6)	116.08	1a, 4a	6.91 (d, 8.6)	7.13 (d, 8.5)
4a	8.45 (br s)	158.61	3a(5a), 4a		
7a	5.78 (d, 11.3)	90.46[c]	1a, 2a(6a), 8a, 9a	5.96 (d, 10.7)	6.11 (d, 11.8)
8a	4.44 (br d, 11.3)	48.88	1a, 7a, 9a, 10a, 14a, 10b, 11b	4.40 (br d, 10.7)	4.36 (br d, 11.8)
9a		141.81			
10a		124.55			
11a (OH)	8.14 (s)	155.74	10a, 11a, 12a		
12a	6.27 (d, 2.3)	101.73	10a, 11a, 13a, 14a	6.48 (d, 2.2)	7.14 (br s)
13a	8.01 (br s)	156.79	12a, 13a, 14a		
14a	6.12 (br d, 2.3)	105.83	8a, 9a, 10a, 12a, 13a	6.27 (br d, 2.2)	6.87 (br s)
1b		133.56			
2b, 6b	7.16 (d, 8.6)	130.73	3b(5b), 4b, 7b	7.22 (d, 8.6)	7.23 (d, 8.6)
3b, 5b	6.70 (d, 8.6)	115.59	1b, 4b	6.81 (d, 8.6)	7.01 (d, 8.6)
4b	8.13 (br s)	155.97	3b(5b), 4b		
7b	5.26 (d, 3.7)	37.10	9a, 10a, 11a, 1b, 2b(6b), 8b, 9b, 7c	5.20 (d, 3.5)	4.58 (d, 3.0)
8b	3.13 (br d, 11.0)	53.31	1b, 7b, 9b, 7c	3.36 (br d, 10.7)	3.64 (br d, 11.2)
9b		143.22			
10b		116.19			
11b		159.00			
12b	6.14 (d, 0.9)	96.72	10b, 11b, 13b, 14b	6.34 (s)	6.46 (s)
13b (OH)	7.19 (s)	155.20	12b, 13b, 14b		
14b		121.76			
1c		131.27			
2c, 6c	6.37 (d, 8.6)	129.12	3c(5c), 4c, 7c	6.42 (d, 8.6)	6.70 (d, 8.6)
3c, 5c	6.40 (d, 8.6)	115.82	1c, 4c	6.57 (d, 8.6)	6.73 (d, 8.6)
4c	7.80 (br s)	156.34	3c(5c), 4c		
7c	4.11 (t, 11.0)	56.99	7b, 8b, 1c, 2c(6c), 8c, 9c	4.12 (t, 10.7)	4.20 (t, 11.2)
8c	4.56 (d, 11.0)	49.56	9b, 13b, 14b, 1c, 7c, 9c, 10c, 14c	4.47 (d, 10.7)	4.49 (d, 11.2)
9c		140.94			
10c		125.57			
11c		161.49			
12c	6.29 (d, 2.1)	96.65	10c, 11c, 13c, 14c	6.43 (d, 2.2)	6.85 (d, 2.0)
13c (OH)	8.24 (br s)	159.34	12c, 13c, 14c		
14c	6.48 (d, 2.1)	107.24	8c, 10c, 12c, 13c	6.53 (d, 2.2)	6.74 (d, 2.0)
1d		129.34			
2d, 6d	7.05 (d, 8.7)	128.76	3d(5d), 4d, 7d	7.10 (d, 8.8)	7.16 (d, 8.8)
3d, 5d	6.60 (d, 8.7)	115.10	1d, 4d	6.66 (d, 8.8)	6.83 (d, 8.8)
4d	8.07 (br s)	157.13	3d(5d), 4d		
7d	5.82 (d, 7.9)	90.48[c]	1d, 2d(6d), 8d, 9d	5.96 (d, 7.9)	6.10 (d, 7.7)
8d	4.75 (d, 7.9)	53.45	9c, 10c, 11c, 7d, 9d, 10d(14d)	4.80 (d, 7.9)	4.91 (d, 7.7)
9d		142.74			
10d	5.74 (br s)	109.06		5.70 (br s)	5.54 (br s)
11d (OH)	7.66 (br s)	158.80	10d, 11d, 12d		
12d	6.01 (t, 2.1)	101.95	10d(14d), 11d(13d)	6.00 (t, 2.1)	6.69 (t, 2.1)
13d (OH)	7.66 (br s)	158.80			
14d	5.74 (br s)	109.06		5.70 (br s)	6.45 (br s)
OMe (**6a**)				3.42 (×2), 3.62, 3.63	1.77, 1.88, 2.14
[OAc (**6b**)]				3.68 (×2), 3.71, 3.76	2.15, 2.18 (×2), 2.23
				3.77 (br, ×2)	2.24, 2.25,2.28

Measured in CD_3COCD_3.
[a] 500 MHz (^{1}H) and 125 MHz (^{13}C).
[b] 300 MHz (^{1}H).
[c] Interchangeable.

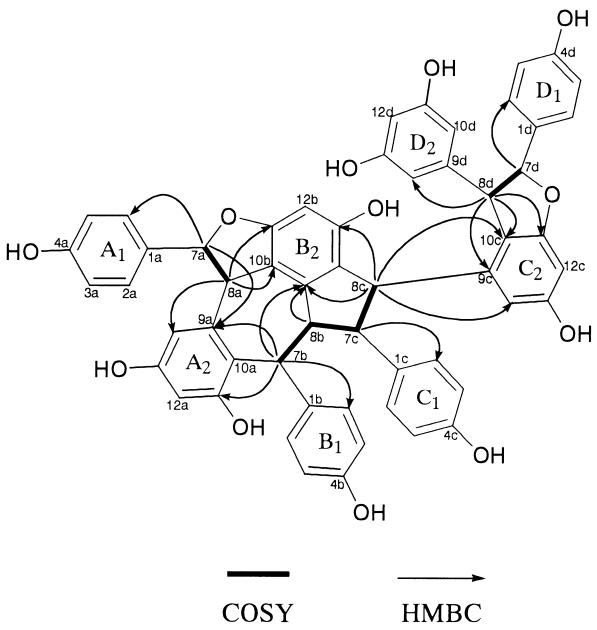


Figure 9. Selected correlations in 2D NMR of **6**.

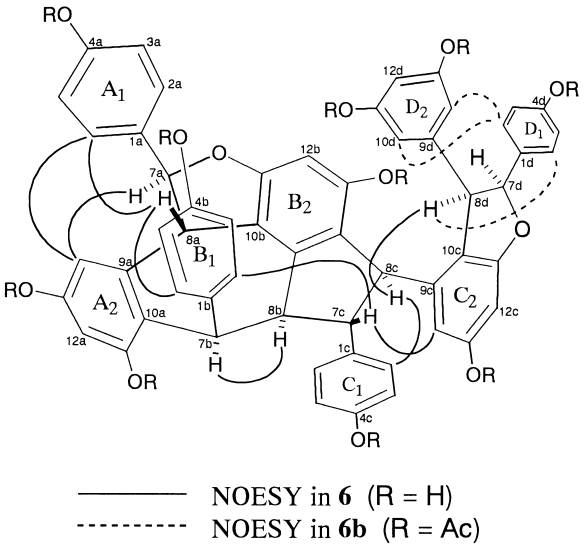


Figure 10. Selected NOESY correlations in **6** and **6b**.

In the NOESY experiment (Fig. 10), the results of NOE [H-7a/H-14a, H-8a/H-2a(6a), H-8a/H-2b(6b), H-7c/H-2b(6b), H-7c/H-14c and H-8c/H-2c(6c)], which are similar to those of **7**,[53] suggested that the orientation of the protons (H-7a/H-8a) on the dihydrobenzofuran rings is *trans* and that the sequence of four methine protons (H-7b/H-8b/H-7c/H-8c) has a same orientation as **7**. In addition, the signal patterns assigned to resveratrols A–C in **6** were similar to those of **7**. In the ^{1}H NMR spectrum of **6b** (Table 3) signals assigned to H-10d and H-14d became to separate into two peaks. This fact strongly indicated that the free rotation of ring D_2 in **6b** was disturbed by the steric hindrance, and two protons were located in different environment. To confirm the relative stereochemistry of resveratrol D moiety, NOESY experiment of **6b** was conducted (Fig. 10). Through this experiment, significant NOEs such as H-8d/H-2d(6d), H-2d(6d)/H-10d and H-2d(6d)/H-14d were observed, but no effect between H-7d and H-10d was observed, which suggested that the orientation of methine protons (H-7d and H-8d) was *cis*. If H-7d and H-8d were located in *trans* and the free rotation of the ring D_2 was disturbed, both NOEs of H-2d(6d)/H-10d and H-2d(6d)/H-14d cannot be explained. In addition, the chemical shift values of H-10d(14d) in **6** changed in higher field (δ 5.74) than that of **7** (δ 6.10). The higher field shift could be explained by anisotropic effect of the ring D_1. The spectral differences in a pair of epimeric tetramers, vaticanols C (**9**)[53] and F,[51] had been reported. The structural differences of *trans* or *cis* orientation of the dihydrobenzofuran ring are as same as **6** and **7**. The distinct differences in the ^{13}C NMR spectral data also have been reported as follows: the methine carbons on one of dihydrobenzofuran rings appeared at δ 94.3 (C-7c) and 57.9 (C-8c) in **9** (*trans*), while those of vaticanol F (*cis*) appeared at δ 90.0 (C-7c) and 53.1 (C-8c). These data suggested that *cis* orientation of dihydrobenzofuran ring is likely to cause a high field shift of two methine carbons. The present case (H-7d and H-8d of **6**: see Table 3; H-7d and H-8d of **7**:[53] δ 94.6 and 57.5) is superimposed to these observations. Therefore, isovaticanol B (**6**) was elucidated to be an epimer of vaticanol B (**7**) due to C-7d.

The similar behaviors of aromatic rings in ^{1}H NMR spectrum of some related stilbene oligomers (vaticanols G and H,[50] vateriaphenol A[47] and amurensins D–F[26]) had been reported. In their ^{1}H NMR spectra, one of 4-hydroxyphenyl groups had been observed as four doublet of doublets at −20°C (or −40°C). In the ^{1}H NMR spectral measurement of **6** at different temperatures, the signals (H-10d, OH-11d, OH-13d and H-14d) gradually separated and became independent signals in accordance with low temperature [Fig. 11, **a** (rt)–**d** (−40°C)], the inclination of which was observed in the ^{1}H NMR spectrum of **6b** at rt (Table 3). These phenomena were for the first time found in the 3,5-dihydroxylphenyl group in **6**. The signal of H-10d(14d) or OH-11d(13d) of **7** appeared as a broad singlet or a singlet, respectively [Fig. 12, **a** (rt)], which indicated that the ring D_2 of **7** rotates more freely than that of **6** at rt. In **7** at lower temperatures [Fig. 11, **b** (0°C)–**e** (−60°C)], the signals gradually became separating as observed in **6**. The signals of H-10d and H-14d in **6** began to separate around −20°C, while those of **7** did around −40°C. The differences can be explained as follows: in the relative stereo structure of **6**, the ring D_2 is situated between two bulky substituents of a trimeric unit (resveratrols A–C) and the ring D_1, then the strong steric hindrance caused by them extensively inhibits the free rotation of the ring D_2, which resulted in separation of signals around −20°. On the other hand, the steric hindrance in **7** was weaker than that of **6** because the methine protons (H-7d and H-8d) are *trans* orientation. Then the ring D_2 in **7** can rotate much freely and H-10d and H-14d can be observed as one signal (broad singlet) even around 0°C. On the basis of these experiments, the structures of **6** and **7** were exclusively explained and the effects of stereo structures on the spectroscopic properties were characterized. These results can be useful for examination of a stereochemistry of cognates.

Isovaticanol C (**8**), a pale yellow amorphous powder, had the molecular formula of $C_{56}H_{42}O_{12}$ supported by the HR-FABMS ([M−H]$^-$: *m/z* 905.2606). Analysis of the ^{1}H and ^{13}C NMR, ^{1}H–^{1}H COSY, HMQC and HMBC spectrum (Table 4 and Fig. 13) indicated that **8** had the following

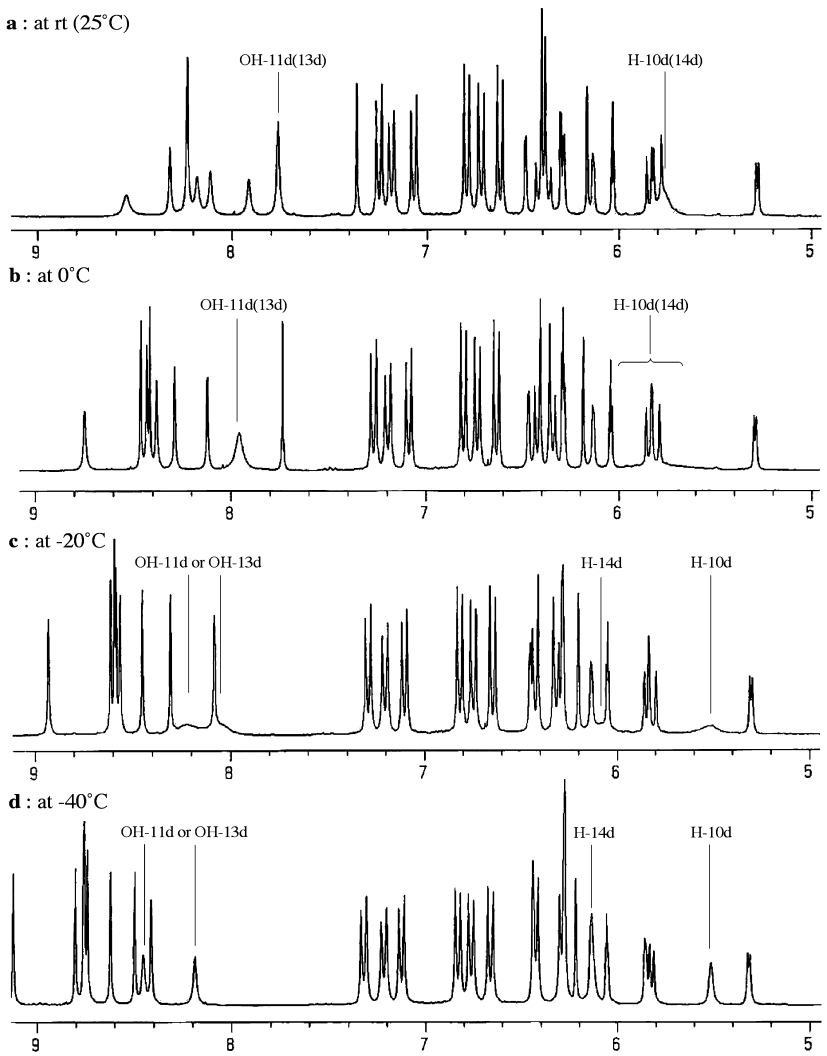


Figure 11. ^{1}H NMR spectra at variable temperatures of **6** (Measured in CD_3COCD_3, 300 MHz).

partial structures; four 4-hydroxyphenyl groups (rings A_1–D_1), two 3,5-dihydroxyphenyl groups (rings C_2 and D_2), two aromatic protons on pentasubstituted benzene rings (rings A_2 and B_2), four sequence of aliphatic methine protons (H-7a/H-8a/H-7b/H-8b) and two sets of mutually coupled aliphatic protons assignable to two dihydrobenzofuran rings (H-7c/H-8c and H-7d/H-8d). These results showed that **8** was a resveratrol tetramer with two dihydrobenzofuran units. Among the aromatic rings, the signals attributed to the ring A_1 were observed as four doublet of doublets in the ^{1}H NMR spectrum, the behavior of which was also observed in a 4-hydroxyphenyl group (ring A_1) in isoampelopsin F (**5**) (Scheme 1).[62] In the HMBC spectrum (Fig. 13), significant ^{3}J long range correlations were observed between H-7a/C-2a(6a) and H-7b/C-2b(6b), indicating that the rings A_1 and B_1 were connected at C-7a and C-7b, respectively. Other ^{3}J long range correlations observed between H-8a/C-1a, H-8b/C-8a, H-8a/C-1b and H-8b/C-1b suggested that the methine protons were connected in this order, H-7a, H-8a, H-7b and H-8b. Long range correlations between the aliphatic methine protons and the quaternary carbons on the two pentasubstituted benzene rings (rings A_2 and B_2) were H-7a/C-11b, H-8a/C-10a, H-8a/C-14a, H-8b/C-11a, H-8b/C-10b and H-8b/C-14b, which indicated that **8** had a dibenzobicyclo[3.2.1]octadiene system. On the basis of HMBC spectral analysis, the two dihydrobenzofuran units were joined at the rings A_2 and B_2 as shown in Figure 13. The planar structure of **8** was then determined to be the same as vaticanols C (**9**)[53] and F.[51]

In the NOESY experiment of **8** (Fig. 14, 8A–8C), the NOEs, which were also observed in **9**,[53] were observed between H-7c/H-10c(14c), H-8c/H-2c(6c), H-7d/H-10d(14d) and H-8d/H-2d(6d), respectively. The results suggested that the orientation of protons on the two dihydrobenzofuran rings was *trans*. Considering the NOEs [H-2b(6b)/H-8a and H-2b(6b)/H-8b] (Fig. 14, 8A), the orientation of H-8a, H-7b and H-8b on the dibenzobicyclo[3.2.1]octadiene system was determined to be α, β and α, respectively. In addition, the signal patterns attributed to the four sequence of protons on the skeleton [H-7a (d, J=5.5 Hz)/H-8a (d, J=5.5 Hz)/H-7b (s)/H-8b (s)] had similar to those of isoampelopsin F (**5**)[62] which is an epimer of ampelopsin F (**4**)[28] due to C-7a. The ^{1}H NMR spectrum was closely similar to those of **8** and **9**. Then the relationship of **4** and **5** was equal to that of **8** and **9**. Finally the relative stereochemistry of the ring system of **8** was concluded to be the same as **5**. The relationship between the

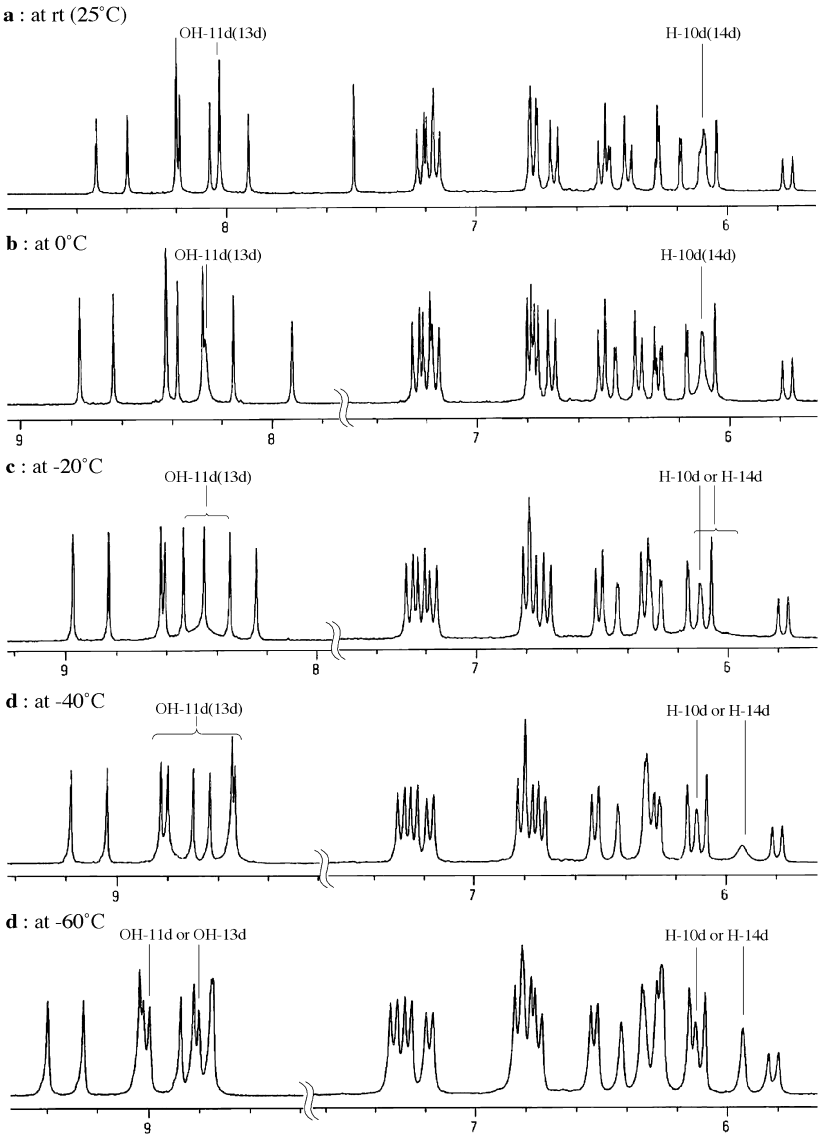


Figure 12. ^{1}H NMR spectra at variable temperatures of **7** (Measured in CD_3COCD_3, 300 MHz).

ring system and the two dihydrobenzofuran rings was determined as follows: distinct cross peaks in the NOEs of **8** between H-8d/H-8b and H-10d(14d)/H-7b (Fig. 14, 8B) suggested that H-8d was situated in α configuration. Considering the NOE between H-3a/H-2c(6c) (Fig. 14, 8C), which could be observed only when the rings A_1 and C_1 are located in the same orientation, β configuration of H-7c was deduced. The differences between **8** and **9** were attributed to the configuration of H-7a which was situated in β configuration in **8**. Thus the relative stereo structure of **8** was confirmed. In the stereo structure of **8**, the ring A_1 is situated above the ring A_2, which would disturb the free rotation of the ring A_1 by strong steric hindrance. As the result, four aromatic protons appeared independently as doublet of doublets. The high field shift of H-2a (δ 5.85), H-3a (δ 6.45) and H-8c (δ 2.57) can reasonably explained by the anisotropic effects of the rings A_2 (to H-2a and H-3a) and A_1 (to H-8c). Such spectral behaviors of 4-hydroxyphenyl groups had been observed in several above-mentioned stilbene oligomers. In isovaticanol C (**8**) and

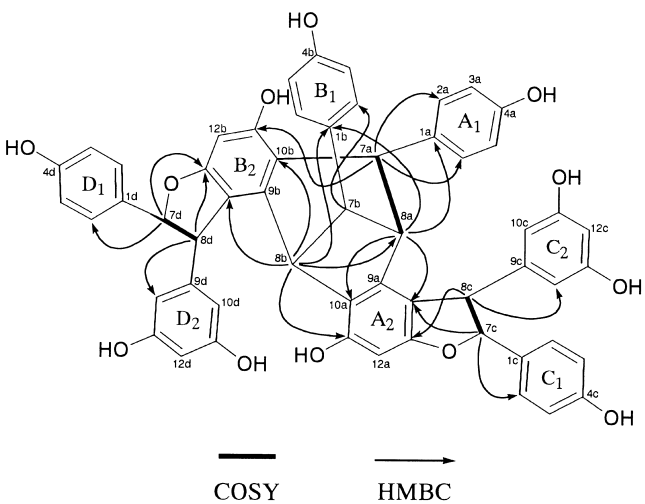


Figure 13. Selected correlations in 2D NMR of **8**.

Table 4. ^{1}H and ^{13}C NMR spectral data of **8**

No.	δH	δC	HMBC
1a		135.10	
2a	5.85 (d, 8.3, 2.2)	129.65	6a, 4a, 7a
3a	6.45 (d, 8.3, 2.2)	115.96[a]	1a, 4a
4a		156.67	
5a	6.81 (d, 8.3, 2.2)	115.28	1a, 4a
6a	7.34 (d, 8.3, 2.2)	131.72	2a, 4a, 7a
7a	4.37 (d, 5.5)	47.03	1a, 2a, 6a, 8a, 9a, 9b, 10b, 11b
8a	3.31 (d, 5.5)	49.48	7a, 9a, 10a, 14a, 1b, 7b, 8b, 10b
9a		141.68	
10a		126.46	
11a (OH)	8.15 (br s)	152.93	10a, 11a, 12a
12a	6.05 (s)	95.78	10a, 11a, 13a, 14a
13a		160.27	
14a		121.19	
1b		133.96	
2b, 6b	6.33 (d, 8.8)	129.48	3b(5b), 4b, 7b
3b, 5b	6.52 (d, 8.8)	115.50	1b, 4b
4b		155.83	
7b	3.28 (s)	58.31	7a, 8a, 9a, 10a, 1b, 2b(6b), 8b, 9b
8b	3.91 (s)	47.43	8a, 9a, 10a, 11a, 1b, 7b, 9b, 10b, 14b
9b		143.44	
10b		116.45	
11b (OH)	6.71 (br s)	157.57	10b, 11b, 12b
12b	6.11 (s)	95.85	10b, 11b, 13b, 14b
13b		159.58	
14b		117.71	
1c		132.48	
2c, 6c	7.00 (d, 8.8)	128.99	3c(5c), 4c, 7c
3c, 5c	6.80 (d, 8.8)	115.96[a]	1c, 4c
4c		157.97	
7c	5.16 (d, 8.6)	94.74	1c, 2c(6c), 8c, 9c, 13b
8c	2.57 (d, 8.6)	55.63	9b, 13b, 14b, 1c, 7c, 9c, 10c(14c)
9c		146.22	
10c, 14c	6.08 (d, 2.2)	108.60	8c, 11c(13c), 12c
11c, 13c		159.24	
12c	6.23 (t, 2.2)	101.73	10c(14c), 11c(13c)
1d		134.46	
2d, 6d	7.24 (d, 8.8)	128.19	3d(5d), 4d, 7d
3d, 5d	6.83 (d, 8.8)	116.07	1d, 4d
4d		158.08	
7d	5.43 (d, 5.7)	94.02	13b, 14b, 1d, 2d(6d), 8b, 9b
8d	4.88 (d, 5.7)	56.07	9b, 13b, 14b, 1d, 7d, 9d, 10d(14d)
9d		148.79	
10d, 14d	6.30 (d, 2.2)	107.33	8d, 11d(13d), 12d
11d, 13d (OH)	8.25 (br s)	159.95	10d(14d)
12d	6.35 (t, 2.2)	101.81	10d(14d), 11d(13d)
OH	7.84, 7.99, 8.15, 8.32, 8.32, 8.46		

Measured in CD3COCD3. 500 MHz (^{1}H) and 125 MHz (^{13}C).
[a] Overlapping.

isoampelopsin F (**5**), four signals were observed as clear doublet of doublets under rt, while the signals of vaticanols G (**21**) and H,[50] vateriaphenol A[47] and amurensins A–D[26] displayed the same behavior only under lower temperature. These differences suggested that the 4-hydroxyphenyl group (ring A_1) in **5** or **8** was much fixed than those of the others. We once proposed that the separation of signals was due to a steric hindrance(s) of the molecular skeleton[50] (vaticanol G) or the large substituent in the vicinity of the 4-hydroxyphenyl group[47] (vateriaphenol A). Amurensins A–D were also explained by the same manners as vateriaphenol A.[26] The fixed ring A_1 in **5** or **8**, especially in the simple skeleton of **5**, can not be discussed exactly only by the steric hindrance. Other strong attractive force, for example CH–π and(or) OH–π interaction,[63,64] might exist between a π-system and a proton in such molecules.

Paucifloroside A (**11**) was isolated as a yellow amorphous powder. Its molecular formula was established as $C_{34}H_{31}O_{11}$ by the results of the HR-FABMS ($[M-H]^-$: *m/z* 615.1873) and ^{13}C NMR spectral data. The presence of an *O*-β-glucopyranosyl moiety was supported by the NMR spectra which showed six carbon signals at δ 102.5, 78.1, 78.0, 74.8, 71.5, 62.8 and an anomeric proton at δ 4.99 (1H, d, *J*=7.3 Hz). The ^{1}H and ^{13}C NMR spectral data except for the β-glucopyranosyl moiety showed close similarity to those of ε-viniferin.[14] These results indicated that **11** was an *O*-β-glucopyranoside of ε-viniferin. To confirm the position of the glucosidic linkage, the ^{1}H and ^{13}C NMR spectral signals were assigned by $^{1}H-^{1}H$ COSY spectra and by comparison with those of ε-viniferin. In the NOE experiment, the aromatic protons (δ 6.53 and δ 7.01) assignable to H-12b and H-14b were enhanced when the anomeric proton (δ 4.99) was irradiated. Therefore, the glucosyl moiety was attached at C-13b of ε-viniferin. Consequently, the structure of paucifloroside A (**11**) was characterized as ε-viniferin-13b-*O*-β-glucopyranoside.[65]

Paucifloroside B (**13**), a yellow amorphous powder, had the molecular formula of $C_{48}H_{42}O_{14}$ supported by the result of HR-FABMS (*m/z* 841.2486). The ^{1}H and ^{13}C NMR spectral data closely resembled those of stenophyllol B[35,66] except for the presence of an *O*-glucopyranosyl moiety [δ 4.73 (1H, d, *J*=7.7 Hz); δ 101.8, 78.1, 77.5, 74.4, 71.3, 62.6] (Table 5). Acid hydrolysis of **13** gave stenophyllol B. The position of *O*-glucosyl moiety was determined to be at C-11b by NOE in the DIFNOE experiment which exhibited the effect between the anomeric proton (δ 4.73) and the aromatic proton at H-12b (δ 6.38). Therefore, the structure of paucifloroside A (**13**) was concluded to be stenophyllol B-11b-*O*-β-glucopyranoside.[65]

Paucifloroside C (**14**), a yellow amorphous powder, gave a molecular ion peak at *m/z* 841.2487 in the HR-FABMS corresponding to the molecular formula $C_{48}H_{42}O_{14}$. The pattern of the ^{1}H and ^{13}C NMR spectral data was similar to that of **13**. The difference was the position of *O*-glucosidic linkage. In the DIFNOE experiment, irradiation of the anomeric proton (δ 4.65) caused enhancement of two aromatic protons of H-12b (δ 6.29) and H-14b (δ 6.35). The structure of paucifloroside C (**14**) was then determined to be stenophyllol B-13b-*O*-β-glucopyranoside.[65]

In addition to these nine compounds (**1**–**4**, **6**, **8**, **11**, **13** and **14**), 17 known resveratrol oligomers were isolated and their structures were identified as (+)-ampelopsin D (**16**),[29] davidiol B (**18**),[34] hemsleyanols A (**17**),[56] C (**24**) and D (**25**),[54] isoampelopsin F (**5**),[62] piceid (**15**), stenophyllol B (**12**),[35] vateriaphenol B (**23**),[47] vaticanols A (**19**), B (**7**), C (**9**),[53] E (**20**)[51] and G (**21**), vaticaside D (**22**),[50] (−)-ε-viniferin (**10**),[14] and bergenin (**26**),[5] respectively, by spectral analysis and comparison with respective authentic samples.

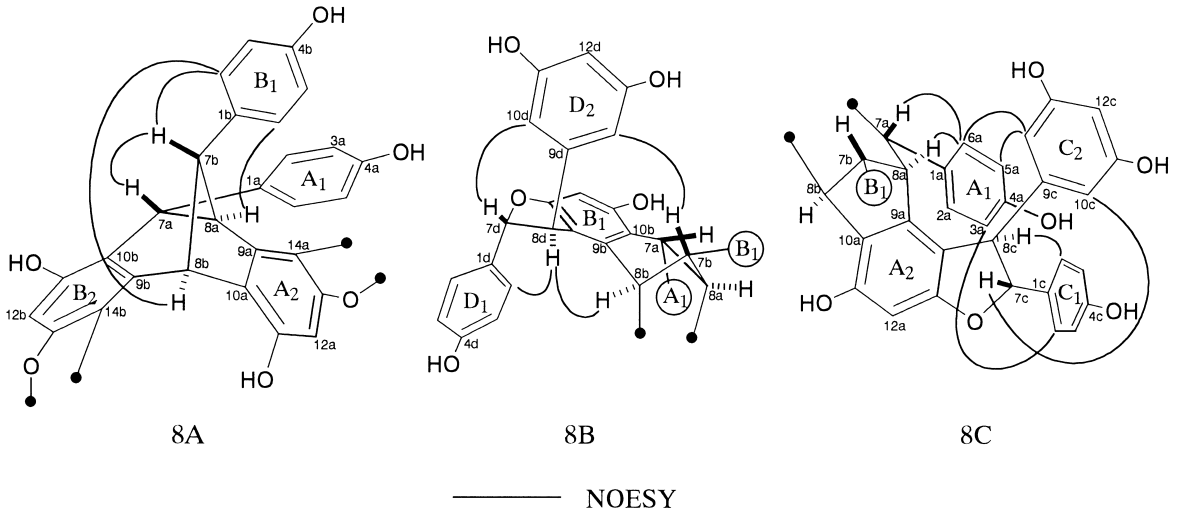


Figure 14. Selected NOESY correlations in partial structures of **8** (8A–8C).

Table 5. ^{1}H and ^{13}C NMR spectral data of **12**–**14**

No.	**12**[66]		**13**		**14**	
	δH	δC	δH	δC	δH	δC
1a		134.6		134.6		134.5
2a, 6a	6.89 (d, 8.8)	127.2	6.90 (d, 8.8)	127.2	6.84 (d, 8.8)	127.1
3a, 5a	6.76 (d, 8.8)	116.0	6.75 (d, 8.8)	115.9	6.73 (d, 8.8)	116.0
4a (OH)	8.29 (br s)	157.6	8.37 (br s)	157.6	8.35 (br s)	157.6
7a	5.84 (d, 3.9)	88.0	5.85 (d, 3.8)	88.1	5.84 (d, 3.9)	87.9
8a	5.09 (d, 3.9)	52.5	5.10 (d, 3.8)	52.6	5.03 (d, 3.9)	52.5
9a		141.4		141.3		141.5
10a		123.4		123.4		123.4
11a (OH)	8.59 (br s)	156.5	8.70 (br s)	156.5	8.67 (br s)	156.5
12a	6.33 (d, 1.9)	101.3	6.36 (d, 1.9)	101.4	6.35 (d, 1.9)	101.3
13a (OH)	7.94 (br s)	158.1	8.01 (br s)	158.1	8.01 (br s)	158.2
14a	6.26 (d, 1.9)	105.0	6.26 (d, 1.9)	105.0	6.26 (d, 1.9)	105.0
1b		136.9		137.0		136.7
2b, 6b	7.31 (d, 8.5)	129.9	7.32 (d, 8.5)	130.0	7.33 (d, 8.5)	130.0
3b, 5b	6.70 (d, 8.5)	115.8	6.71 (d, 8.5)	115.9	6.75 (d, 8.5)	115.9
4b (OH)	8.02 (br s)	156.2	8.02 (br s)	156.1	8.07 (br s)	156.3
7b	5.37 (d, 9.8)	47.2	5.40 (d, 9.9)	47.2	5.40 (d, 9.9)	46.9
8b	4.34 (dd, 9.8, 7.8)	53.5	4.34 (dd, 9.9, 7.8)	53.5	4.37 (dd, 9.9, 7.8)	53.6
9b		150.8		150.1		150.6
10b		123.4		125.9		126.0
11b (OH)	7.01 (br s)	154.6		155.6	7.43 (br s)	154.5
12b	6.08 (br s)	102.3	6.38 (d, 1.9)	104.8	6.29 (d, 1.8)	103.1
13b (OH)	7.96 (br s)	159.1	8.21 (br s)	159.1		159.6
14b	6.08 (br s)	103.1	6.18 (d, 1.9)	101.9	6.35 (d, 1.8)	103.5
1c		139.5		140.0		139.4
2c, 6c	7.21 (d, 8.5)	130.0	7.28 (d, 8.5)	130.0	7.20 (d, 8.5)	130.1
3c, 5c	6.68 (d, 8.5)	115.8	6.66 (d, 8.5)	116.0	6.67 (d, 8.5)	115.8
4c (OH)	8.18 (br s)	156.1	8.26 (br s)	156.0	8.26 (br s)	156.2
7c	4.73 (d, 6.3)	51.9	4.83 (d, 6.7)	52.0	4.77 (d, 6.6)	52.0
8c	3.43 (dd, 6.3, 7.8)	56.4	3.51 (dd, 6.7, 7.8)	55.9	3.46 (dd, 6.6, 7.8)	56.4
9c		144.1		144.0		144.0
10c		120.6		120.0		120.6
11c		160.4		160.0		160.4
12c	6.24 (d, 1.9)	95.9	6.23 (d, 1.6)	95.8	6.25 (d, 1.9)	95.9
13c (OH)	8.20 (br s)	158.7	8.29 (br s)	159.0	8.30 (br s)	158.8
14c	6.80 (br s)	106.8	6.73 (br s)	107.0	6.80 (br s)	106.9
glc-1			4.73 (d, 7.7)	101.8	4.65 (d, 7.5)	101.5
glc-2			3.22–3.76 (m)	74.4	3.29–3.60 (m)	74.4
glc-3			[glc-H-2–H-6]	77.5	[glc-H-2–H-6]	77.1
glc-4				71.3		70.6
glc-5				78.1		77.9
glc-6				62.6		61.9

Measured in CD_3COCD_3. 300 MHz (^{1}H) and 75 MHz (^{13}C).

3. Experimental

3.1. General procedures

The following instruments were used: FABMS spectra, JEOL JMS-DX-300 instrument; ^{1}H and ^{13}C NMR spectra, JEOL JNM A-500, EX-400 and LA-300 (Chemical shift values are presented as δ values with TMS as internal standard); UV spectra, Shimadzu UV-2200 spectrophotometer (in methanol solution); optical rotations, JASCO P-1020 polarimeter. The following adsorbents were used for purification: analytical TLC, Merck Kieselgel 60 F_{254} (0.25 mm); preparative TLC, Merck Kieselgel 60 F_{254} (0.5 mm); column chromatography, Merck Kieselgel 60, Pharmacia Fine Chemicals AB Sephadex LH-20 and Fuji Silysia Chemical Chromatorex, Waters Sep-Pak C_{18} cartridges; vacuum liquid chromatography (VLC), Merck Kieselgel 60.

3.2. Plant material

V. pauciflora (Korth.) was cultivated at Bogor Botanical Garden, Bogor, Indonesia, from where its stem bark was collected and identified in May 2000 by one of the co-authors (D. D.), and a voucher specimen is deposited in Gifu Prefectural Institute of Health and Environmental Sciences, Gifu, Japan.

3.3. Extraction and isolation

Dried and ground stem bark (500 g) of *V. pauciflora* was extracted successively with acetone (2 L×24 h×3), MeOH (2 L×24 h×3) and 70% MeOH (2 L×24 h×2) at rt. The extract was concentrated to yield respective residues; 38 g (acetone), 23 g (MeOH) and 15 g (70% MeOH). The acetone extract (37 g) was subjected to column chromatography (CC) on silica gel eluted with a mixture of $CHCl_3$–MeOH increasing in the polarity to give 60 fractions (Fr. 1–60). A part (30 mg) of Fr. 10 [$CHCl_3$–MeOH (10:1), 300 mg] was purified by PTLC [EtOAc–$CHCl_3$–MeOH–H_2O (80:40:11:2)] to give **10** (20 mg). An acetone insoluble part (500 mg) of Fr. 12 [$CHCl_3$–MeOH (10:1), 860 mg] was dissolved in acetone–$CHCl_3$ (2:1) mixture (100 mL) and gave **26** (420 mg) as powder. Compound **5** (4 mg) was obtained from Fr. 13 [$CHCl_3$–MeOH (10:1), 90 mg] after separation by VLC [EtOAc–$CHCl_3$–MeOH–H_2O (240:60:11:2) and PTLC [EtOAc–$CHCl_3$–MeOH–H_2O (80:40:11:2)]. The combined fractions of Fr. 18–Fr. 21 (Fr. 18–21) [$CHCl_3$–MeOH (8:1), 1.5 g] was further subjected to reversed-phase CC (H_2O–MeOH gradient system, 20%–60% MeOH) to give 16 fractions (Fr. 18–21A–Fr. 18–21P). Compounds **17** (9 mg), **4** (5 mg) and **16** (2 mg) were obtained from Fr. 18–21E, 18–21H and 18–21J, respectively, after purification by PTLC [EtOAc–$CHCl_3$–MeOH–H_2O (80:40:11:2)]. Fr. 24 [$CHCl_3$–MeOH (8:1), 2.5 g] was further purified by Sephadex LH-20 CC eluted with MeOH to give three fractions (Fr. 24A–Fr. 24C). Fr. 24A and Fr. 24B were purified by PTLC [EtOAc–$CHCl_3$–MeOH–H_2O (15:8:4:1)] to give **15** (52 mg) and **19** (80 mg), respectively. The third fraction (Fr. 24C) was further purified by reversed-phase CC (H_2O–MeOH) to give **12** (480 mg) and **20** (18 mg). Further purification of Fr. 29–32 [$CHCl_3$–MeOH (8:1), 3.2 g] by repeated Sephadex LH-20 CC (MeOH) and PTLC [EtOAc–$CHCl_3$–MeOH–H_2O (15:8:4:1)] achieved the isolation of **1** (10 mg), **2** (12 mg), **8** (8 mg), **18** (8 mg), **24** (12 mg) and **25** (25 mg). Compounds **7** (1.8 g), **9** (86 mg) and **23** (26 mg) were obtained from Fr. 33–36 [$CHCl_3$–MeOH (6:1), 3.4 g] after purification by repeated Sephadex LH-20 CC (MeOH). Fr. 37–40 [$CHCl_3$–MeOH (6:1), 2.7 g] was further purified by Sephadex LH-20 CC (MeOH) and reversed-phase CC through Sep-Pak cartridges (H_2O–MeOH) to give **3** (60 mg), **6** (12 mg), **11** (5 mg) and **21** (31 mg) Compounds **13** (4 mg) and **14** (3 mg) were obtained from Fr. 42-46 [$CHCl_3$–MeOH (4:1), 910 mg] after purification by Sephadex LH-20 CC (MeOH), reversed-phase CC through Sep-Pak cartridges (H_2O–MeOH) and VLC [EtOAc–$CHCl_3$–MeOH–H_2O (80:40:11:2)]. Purification of the 50th–58th fraction [$CHCl_3$–MeOH (4:1), 1.1 g] by Sephadex LH-20 CC (MeOH) achieved the isolation of **22** (9 mg).

3.3.1. Pauciflorol A (1). A pale yellow amorphous powder; $[\alpha]_D^{25}=-148°$ (c=0.1, MeOH); UV (MeOH) λ_{max} (log ε): 224 (4.7), 283 (3.6) nm; negative ion FAB-MS m/z: 679 $[M-H]^-$; negative ion HR-FABMS m/z: 679.1960 $[M-H]^-$ (calcd 679.1968 for $C_{42}H_{31}O_9$); The ^{1}H and ^{13}C NMR spectral data and HMBC correlations: see Table 1; NOESY correlations*: H-2a(6a)/H-7a, H-8a, H-14a, H-3a(5a)/OH-4a, H-2b(6b), H-7a/H-14a, H-8a/H-14a, H-2b(6b), H-12a/OH-11a, OH-13a, H-14a/OH-13a, H-2b(6b)/H-7b, H-2c(6c), H-3c(5c), H-3b(5b)/OH-4b, H-7b/OH-11a, H-2c(6c), H-7c, H-8b/H-10c(14c), H-12b/OH-13b, H-2c(6c)/H-7c, H-8c, H-3c(5c)/OH-4c, H-7c/H-10c(14c), H-8c/OH-13b, H-10c(14c), H-10c(14c)/ OH-11c(13c), H-12c/OH-11c(13c). *Selected correlations are designated in Figure 2.

3.3.2. Pauciflorol B (2). A pale yellow amorphous powder; $[\alpha]_D^{25}=-28°$ (c=0.1, MeOH); UV (MeOH) λ_{max} (log ε): 223 (4.9), 282 (3.9) nm; negative ion FAB-MS m/z: 679 $[M-H]^-$; negative ion HR-FABMS m/z: 679.1970 $[M-H]^-$ (calcd 679.1968 for $C_{42}H_{31}O_9$). The ^{1}H and ^{13}C NMR spectral data and HMBC correlations: see Table 1; NOESY correlations*: H-2a(6a)/H-7a, H-8a, H-14a, H-3a(5a)/OH-4a, H-7a/H-14a, H-8a/H-14a, H-2b(6b), H-12a/OH-11a, OH-13a, H-14a/OH-13a, H-2b(6b)/H-7b, H-7c, H-10c(14c), H-3b(5b)/OH-4b, H-7b/OH-11a, H-2c(6c), H-7c, H-8b/H-2c(6c), H-12b/OH-13b, H-2c(6c)/H-7c, H-8c, H-10c(14c), H-3c(5c)/OH-4c, H-7c/H-10c(14c), H-8c/H-10c(14c), H-10c(14c)/OH-11c(13c), H-12c/OH-11c(13c). *Selected correlations are designated in Figure 5.

3.3.3. Pauciflorol C (3). A brown amorphous powder; $[\alpha]_D^{25}=+20°$ (c=0.1, MeOH); UV (MeOH) λ_{max} (log ε): 224 (4.8), 283 (3.4) nm; negative ion FAB-MS m/z: 905 $[M-H]^-$; negative ion HR-FABMS m/z: 905.2596 (calcd 905.2598 for $C_{56}H_{41}O_{12}$); The ^{1}H and ^{13}C NMR spectral data and HMBC correlations: see Table 2; NOESY correlations*: H-2a(6a)/H-7a, H-8a, H-14a, H-7a/H-14a, H-8a/H-14a, H-7b, H-8b, H-12a/OH-11a, H-2b(6b)/H-7b, H-2c(6c), H-3c(5c), H-7b/H-7c, H-8d, H-8b/H-7c, H-8d, H-14b/H-8c, H-14c, H-2c(6c)/H-7c, H-7c/H-8d, H-8c/H-14c, H-2d(6d)/H-7d, H-8d, H-7d/H-14d, H-8d/H-14d. *Selected correlations are designated in Figure 7.

3.3.4. Isovaticanol B (6). A brown amorphous powder; $[\alpha]_D^{25}=+35°$ (c=0.1, MeOH); UV (MeOH) λ_{max} (log ε):

224 (4.9), 283 (3.9) nm; negative ion FAB-MS *m/z*: 905 $[M-H]^-$; negative ion HRFAB-MS *m/z*: 905.2605 (calcd 905.2598 for $C_{56}H_{41}O_{12}$); The ^1H and ^{13}C NMR spectral data and HMBC correlations: see Table 3; NOESY correlations*: H-2a(6a)/H-7a, H-8a, H-14a, H-7a/H-14a, H-8a/H-2b(6b), H-2b(6b)/H-7b, H-7c, H-12b/OH-13b, H-2c(6c)/H-7c, H-8c, H-7c/H-14c, H-8c/H-8d, H-2d(6d)/H-7d. *Selected correlations are designated in Figure 10.

3.3.5. Methylation of 6. Isovaticanol B (**6**) (2 mg) was allowed to react with K_2CO_3 (200 mg) and MeI (50 mg) in dry acetone under reflux for 5 h. The reaction mixture was treated in the usual manner and the crude product (2 mg) obtained was purified by prep. TLC (hexane–EtOAc 1:1) to afford **6a** (1 mg). Compound **6a** (decamethyl ether of **6**). A colorless amorphous powder; negative ion FAB-MS *m/z*: 1045 $[M-H]^-$; The ^1H NMR spectral data: see Table 3.

3.3.6. Acetylation of 1. Isovaticanol B (**6**) (2 mg) was dissolved in a mixture of pyridine (0.5 ml) and Ac_2O (0.2 ml). The reaction mixture was kept at rt for 24 h. The solution was treated with the usual manner and the resulting crude product (3 mg) was purified by prep. TLC with hexane–EtOAc 1:1 to afford **6b** (2 mg). Compound **6b** (deca-acetate of **6**): A colorless amorphous powder; negative ion FAB-MS *m/z*: 1325 $[M-H]^-$; The ^1H NMR spectral data: see Table 3; NOESY correlations*: H-2a(6a)/H-7a, H-8a, H-14a, H-7a/H-14a, H-8a/H-14a, H-2b(6b), H-2b(6b)/H-7b, H-7c, H-7b/H-7c, H-8b/H-2c(6c), H-8c, H-2c(6c)/H-7c, H-8c, H-7c/H-14c, H-8c/H-14c, H-8d, H-10d, H-2d(6d)/H-7d, H-8d, H-10d, H-14d, H-8d/H-10d, H-14d. *Selected correlations are designated in Figure 10.

3.3.7. Isovaticanol C (8). A pale yellow amorphous powder; $[\alpha]_D^{25}$=-28° (*c*=0.1, MeOH); UV (MeOH) λ_{max} (log ε): 224 (4.9), 278 (s, 4.0), 285 (4.0), 296 (s, 3.9) nm; negative ion FAB-MS *m/z*: 905 $[M-H]^-$; negative ion HRFAB-MS *m/z*: 905.2606 (calcd 905.2598 for $C_{56}H_{41}O_{12}$); The ^1H and ^{13}C NMR spectral data and HMBC correlations: see Table 4; NOESY correlations*: H-3a/H-2c(6c), H-5a/H-10c(14c), H-6a/H-7a, H-8a, H-10c(14c), H-7a/H-7b, H-8a/H-2b(6b), H-2b(6b)/H-7b, H-8b, H-7b/H-10d(14d), H-8b/H-8d, H-2c(6c)/H-7c, H-8c, H-7c/H-10c(14c), H-8c/H-10c(14c), H-2d(6d)/H-7d, H-8d, H-7d/H-10d(14d), H-8d/H-10d(14d). *Selected correlations are designated in Figure 14.

3.3.8. Paucifloroside A (11). A yellow amorphous powder; $[\alpha]_D^{25}=-78°$ (*c*=0.1, MeOH);UV (MeOH) λ_{max} (log ε): 224 (4.3), 287 (s, 4.1), 310 (4.3), 323 (4.3) nm; negative ion FAB-MS *m/z*: 615 $[M-H]^-$; negative ion HRFAB-MS *m/z*: 615.1873 $[M-H]^-$ (calcd 615.1866 for $C_{34}H_{31}O_{11}$); ^1H NMR [300 MHz, $(CD_3)_2CO$] δ: 7.20 (2H, d, *J*=8.5 Hz, H-2a, 6a), 6.83 (2H, d, *J*=8.5 Hz, H-3a 5a), 5.45 (1H, d, *J*=5.4 Hz, H-7a), 4.51 (1H, d, *J*=5.4 Hz, H-8a), 6.23 (3H, s, H-10a, 12a, 14a), 7.18 (2H, d, *J*=8.7 Hz, H-2b, 6b), 6.73 (2H, d, *J*=8.7 Hz, H-3a 5a), 7.01 (1H, d, *J*=15.8 Hz, H-7b), 6.71 (1H, d, *J*=15.8 Hz, H-8b), 6.53 (1H, d, *J*=2.0 Hz, H-12b), 7.01 (1H, d, *J*=2.0 Hz, H-14b), 8.43 (1H, br s, OH-C-4a), 8.22 (2H, br s, OH-C-11a, 13a), 8.46 (1H, br s, OH-C-4b), 4.99 (1H, d, *J*=7.3 Hz, H-glc-1), 3.47 (1H, m, H-glc-2), 3.45 (1H, m, H-glc-3), 3.57 (1H, m, H-glc-4), 3.53 (1H, m, H-glc-5), 3.80, 3.95 (1H each, m, H-glc-6); ^{13}C NMR [75 MHz, $(CD_3)_2CO$] δ: 133.7 (C-1a), 128.0 (C-2a, 6a), 116.2 (C-3a, 5a), 158.3 (C-4a)*, 94.0 (C-7a), 57.0 (C-8a), 147.1 (C-9a), 107.0 (C-10a, 14a), 159.9 (C-11a, 13a), 102.2 (C-12a)**, 129.9 (C-1b), 128.8 (C-2b, 6b), 116.3 (C-3b, 5b), 158.3 (C-4b)*, 130.7 (C-7b), 123.2 (C-8b), 136.4 (C-9b), 122.3 (C-10b), 162.1 (C-11b), 98.0 (C-12b), 160.4 (C-13b)*, 105.5 (C-14b), 102.5 (C-glc-1)**, 74.8 (C-glc-2), 71.5 (C-glc-3), 78.0 (C-glc-4), 78.1 (C-glc-5), 62.8 (C-glc-6). (*, ** interchangeable)

3.3.9. Paucifloroside B (13). A yellow amorphous powder; $[\alpha]_D^{25}=-60°$ (*c*=0.1, MeOH); UV (MeOH) λ_{max} (log ε): 224 (4.8), 283 (4.1) nm; negative ion FAB-MS *m/z*: 841 $[M-H]^-$; negative ion HRFAB-MS *m/z*: 841.2486 $[M-H]^-$ (calcd 841.2496 for $C_{48}H_{41}O_{14}$); The ^1H and ^{13}C NMR spectral data: see Table 5.

3.3.10. Paucifloroside C (14). A pale yellow amorphous powder; $[\alpha]_D^{25}=-38°$ (*c*=0.1, MeOH); UV (MeOH) λ_{max} (log ε): 224 (4.8), 283 (4.2) nm; negative ion FAB-MS *m/z*: 841 $[M-H]^-$; negative ion HRFAB-MS *m/z*: 841.2487 $[M-H]^-$ (calcd 841.2496 for $C_{48}H_{41}O_{14}$); The ^1H and ^{13}C NMR spectral data: see Table 5.

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65. With respect to the configurations of glucose in **11**, **13** and **14**, D forms may be preferable from the viewpoint of natural occurrence of these sugars.
66. In the original report, symbol b in the table was miswritten into c adversely (except for 1b and 1c). Therefore, the correct assignment is described in this paper.