

Oligostilbenoids from Dipterocarpaceaeous Plants: A New Resveratrol Tetramer from *Vateria indica* and the Revised Structure of Isohopeaphenol

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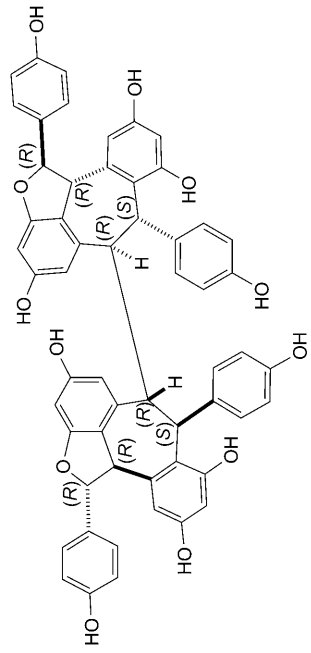
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The investigation of phenolic constituents in *Vateria indica* afforded five resveratrol tetramers, vateriaphenols B and C, isohopeaphenol, hopeaphenol, and shoreaketone. Their structures and configurations were established by spectroscopic methods. The structure assigned to vateriaphenol C was found to be identical with the structure reported in the literature for the resveratrol tetramer isohopeaphenol. The structure of isohopeaphenol was revised and confirmed by spectroscopic evidences.

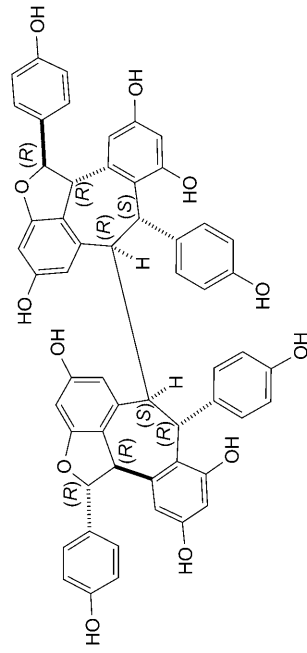
Introduction. – In the course of our research directed toward the isolation and identification of bioactive constituents from Dipterocarpaceaeous plants, we previously reported the characterization of 12 resveratrol oligomers from the stem bark of *Vateria indica* L. [1]. Further investigation of the stem bark led to the isolation of a new resveratrol tetramer, named vateriaphenol C (**1**), together with four resveratrol tetramers, isohopeaphenol (**2**) [2], hopeaphenol (**3**) [3], vateriaphenol B (**4**) [1], and shoreaketone [4]. The structure of **1** was found to be identical with isohopeaphenol in literature. Thus, we compared the spectroscopic data of **1** and **2**. The NMR data were similar, but the specific rotation was completely different. Detailed analysis of ¹H, ¹H-NOESY data enabled the differentiation of their configurations, namely **1** was found to be identical with the resveratrol tetramer known as ‘isohopeaphenol’. The data was in agreement with the structure **2** for isohopeaphenol; consequently, the true structure of isohopeaphenol is **2**, not **1**.

Results and Discussion. – Vateriaphenol C (**1**) ($[\alpha]_{\text{D}}^{25} = +133$) and isohopeaphenol (**2**) ($[\alpha]_{\text{D}}^{25} = +205$) were purified from the acetone extract of the stem bark of *Vateria indica* by column chromatography over silica gel, *Sephadex LH-20*, *ODS*, and prep. TLC. Both compounds were obtained as pale yellow amorphous powders and showed positive reactions to the *Gibbs* reagent. The UV spectra of both **1** and **2** displayed an absorption maximum at 284 nm, which is consistent with the presence of one or more non-conjugated Ph rings. Their composition was deduced to be C₅₆H₄₂O₁₂ from the pseudo-molecular ion peak $[M + H]^+$ observed at m/z 907.2763 (**1**) and 907.2751 (**2**) in the positive ion HR-FAB-MS. The NMR spectral data of **1** and **2** were very similar (*Fig. 1* and *Table 1*). **2** was identified as isohopeaphenol by comparison of spectral data [2], suggesting that **1** is a stereoisomer of **2**.

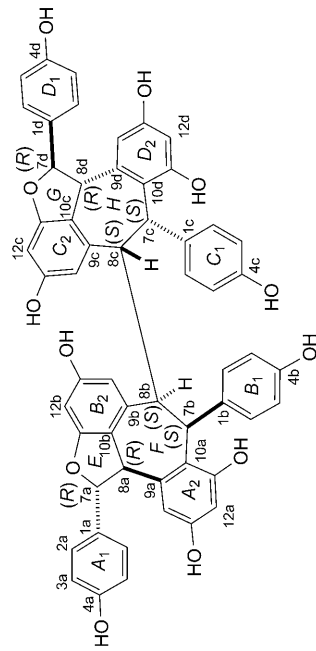


isohopeaphenol (2)

revised structure

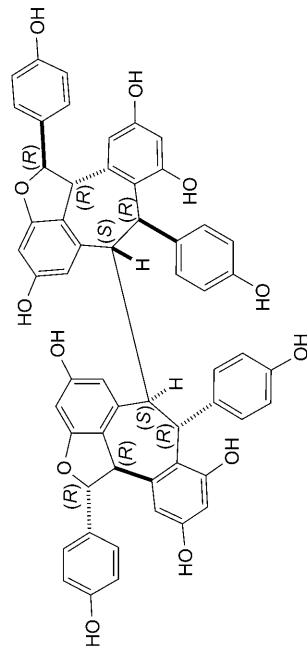


vateriaphenol B (4)



vateriaphenol C (1)

proposed isohopeaphenol structure in [2]



hopeaphenol (3)

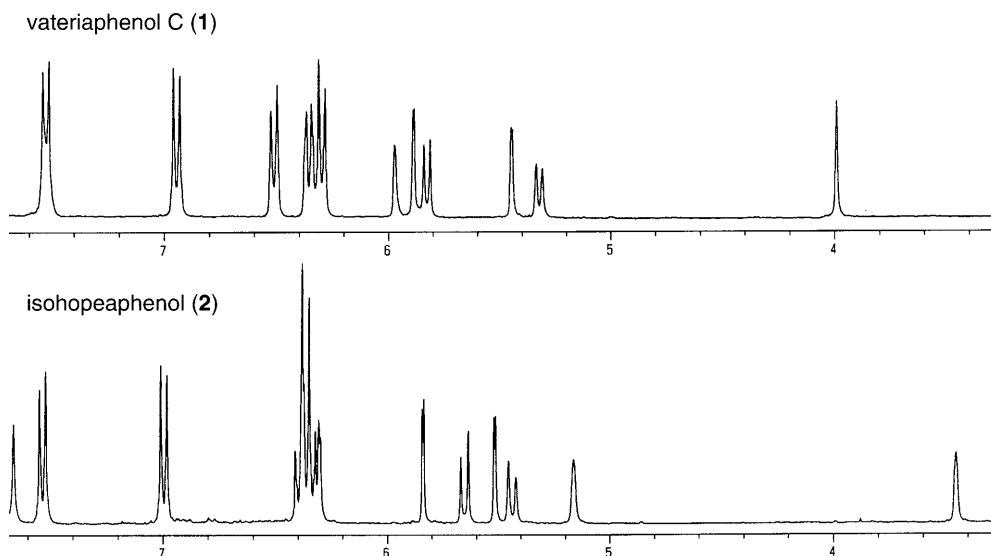


Fig. 1. $^1\text{H-NMR}$ Spectra of **1** and **2** (measured in $\text{D}_6(\text{acetone})$, 400 MHz)

The structure of **1** was determined as follows. The $^{13}\text{C-NMR}$ spectrum of **1** showed 24 signals for 28 C-atoms, out of which 24 were aromatic and four were CH groups. Therefore, **1** was considered to be a molecule comprised of two equivalent units. From analysis of the $^1\text{H-}$ and $^{13}\text{C-NMR}$ spectra (Fig. 1 and Table 1), and of the $^1\text{H,}^1\text{H-}$ and $^{13}\text{C,}^1\text{H-COSY}$, as well as HMBC spectra (Fig. 2 and Table 2), four aromatic rings were identified, which comprised two *para*-oxygenated Ph groups (designated as rings A_1 and B_1) and two 3,5-dioxygenated-1,2-disubstituted benzene rings (A_2 and B_2). The COSY spectrum also showed two sets of mutually coupled aliphatic H-atoms: H–C(7a,8a) and H–C(7b,8b).

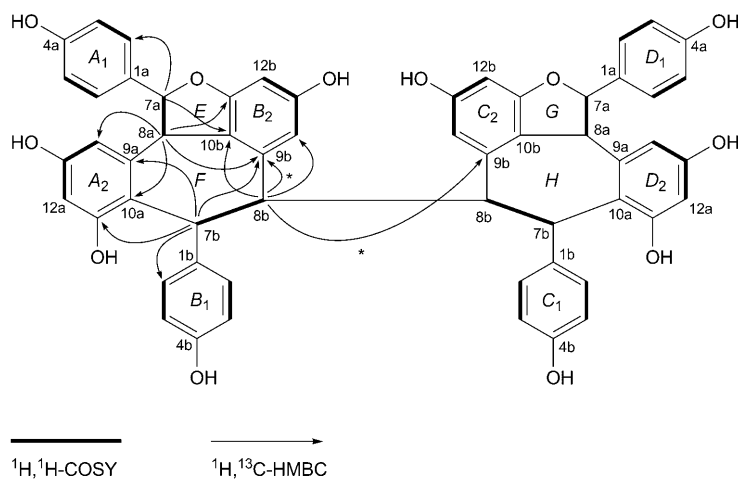
The connection of the partial structures was established as follows. HMBC correlations observed between H–C(7a)/C(2a,6a) and H–C(8a)/C(14a) showed the connection within the first resveratrol unit, *i.e.*, between rings A_1 and A_2 via atoms C(7a) and C(8a). HMBC Correlations similarly supported the connection within the second resveratrol unit. Other bonds such as C(8a)–C(10b) and C(7b)–C(10a) were substantiated with the aid of 3J -type HMBC cross-peaks (Fig. 2). In this way, the skeleton of dibenzocycloheptadiene (ring F) was established. The ether linkage (C(7a)–O–C(11b)), which forms the dihydrobenzofuran unit (ring E), was established by comparison of the chemical shifts with those of vateriaphenol B (**4**) [1]. Consequently, the half planar structure of **1** was determined. These data allowed to assign the full planar structure of vateriaphenol C as indicated in **1**.

The relative configuration of **1** was determined by $^1\text{H,}^1\text{H-NOESY}$ experiments (Fig. 3 and Table 3). The significant NOEs observed between H–C(2a,6a)/H–C(8a), H–C(7a)/H–C(14a), and H–C(2a,6a)/H–C(14a) suggested that the two CH H-atoms on the dihydrobenzofuran rings (ring E) were *trans*-oriented. The relative *cis* disposition for H–C(7a) and ring B_1 , and H–C(8a) and H–C(8b) were inferred from

Table 1. NMR Data for Vatriaphenol **1** and Isohopeaphenol (**2**)^{a)}

1		2			
	δ (H)	δ (C)			
C(1a)		133.8	C(1a)	134.0	
H–C(2a,6a)	7.53 (<i>d</i> , <i>J</i> = 8.4)	130.0	H–C(2a,6a)	7.53 (<i>d</i> , <i>J</i> = 8.8)	130.9
H–C(3a,5a)	6.95 (<i>d</i> , <i>J</i> = 8.4)	116.1	H–C(3a,5a)	6.98 (<i>d</i> , <i>J</i> = 8.8)	116.8
C(4a)		158.21 ^{b)}	OH–C(4a)	8.70 (br. <i>s</i>)	158.8
H–C(7a)	5.83 (<i>d</i> , <i>J</i> = 8.3)	93.4	H–C(7a)	5.65 (<i>d</i> , <i>J</i> = 9.8)	93.8
H–C(8a)	5.32 (br. <i>d</i> , <i>J</i> = 8.3)	52.3	H–C(8a)	5.44 (br. <i>d</i> , <i>J</i> = 9.8)	54.0
C(9a)		141.2 ^{c)}	C(9a)		141.0
C(10a)		122.6	C(10a)		118.4
C(11a)		157.3	OH–C(11a)	7.99 (br. <i>s</i>)	158.7
H–C(12a)	6.35 (br. <i>s</i>)	101.7	H–C(12a)	6.39 (<i>d</i> , <i>J</i> = 2.2)	102.7
C(13a)		156.5	OH–C(13a)	8.16 (br. <i>s</i>)	157.0
H–C(14a)	6.37 (br. <i>s</i>)	106.4	H–C(14a)	6.30 (<i>d</i> , <i>J</i> = 2.2)	107.3
C(1b)		134.4	C(1b)		137.6
H–C(2b,6b)	6.51 (<i>d</i> , <i>J</i> = 8.6)	130.6	H–C(2b,6b)	6.39 (<i>d</i> , <i>J</i> = 8.6)	130.0
H–C(3b,5b)	6.30 (<i>d</i> , <i>J</i> = 8.6)	114.1	H–C(3b,5b)	6.34 (<i>d</i> , <i>J</i> = 8.6)	114.9
C(4b)		155.3	OH–C(4b)	7.80 (br. <i>s</i>)	155.4
H–C(7b)	5.97 (br. <i>s</i>)	41.6	H–C(7b)	5.16 (br. <i>s</i>)	43.8
H–C(8b)	3.99 (<i>s</i>)	44.5	H–C(8b)	3.45 (br. <i>s</i>)	52.9
C(9b)		141.6 ^{c)}	C(9b)		141.9
C(10b)		117.6	C(10b)		117.2
C(11b)		159.4	C(11b)		160.6
H–C(12b)	5.89 (<i>d</i> , <i>J</i> = 1.8)	94.4	H–C(12b)	5.84 (<i>d</i> , <i>J</i> = 2.0)	95.4
C(13b)		158.16 ^{b)}	OH–C(13b)	7.74 (br. <i>s</i>)	158.4
H–C(14b)	5.45 (<i>d</i> , <i>J</i> = 1.8)	107.6	H–C(14b)	5.51 (<i>d</i> , <i>J</i> = 2.0)	109.9
C(1c)		134.4	C(1c)		137.6
H–C(2c,6c)	6.51 (<i>d</i> , <i>J</i> = 8.6)	130.6	H–C(2c,6c)	6.39 (<i>d</i> , <i>J</i> = 8.6)	130.0
H–C(3c,5c)	6.30 (<i>d</i> , <i>J</i> = 8.6)	114.1	H–C(3c,5c)	6.34 (<i>d</i> , <i>J</i> = 8.6)	114.9
C(4c)		155.3	OH–C(4c)	7.80 (br. <i>s</i>)	155.4
H–C(7c)	5.97 (br. <i>s</i>)	41.6	H–C(7c)	5.16 (br. <i>s</i>)	43.8
H–C(8c)	3.99 (<i>s</i>)	44.5	H–C(8c)	3.45 (br. <i>s</i>)	52.9
C(9c)		141.6 ^{c)}	C(9c)		141.9
C(10c)		117.6	C(10c)		117.2
C(11c)		159.4	C(11c)		160.6
H–C(12c)	5.89 (<i>d</i> , <i>J</i> = 1.8)	94.4	H–C(12c)	5.84 (<i>d</i> , <i>J</i> = 2.0)	95.4
C(13c)		158.16 ^{b)}	OH–C(13c)	7.74 (br. <i>s</i>)	158.4
H–C(14c)	5.45 (<i>d</i> , <i>J</i> = 1.8)	107.6	H–C(14c)	5.51 (<i>d</i> , <i>J</i> = 2.0)	109.9
C(1d)		133.8	C(1d)		134.0
H–C(2d,6d)	7.53 (<i>d</i> , <i>J</i> = 8.4)	130.0	H–C(2d,6d)	7.53 (<i>d</i> , <i>J</i> = 8.8)	130.9
H–C(3d,5d)	6.95 (<i>d</i> , <i>J</i> = 8.4)	116.1	H–C(3d,5d)	6.98 (<i>d</i> , <i>J</i> = 8.8)	116.8
C(4d)		158.21 ^{b)}	OH–C(4d)	8.70 (br. <i>s</i>)	158.8
H–C(7d)	5.83 (<i>d</i> , <i>J</i> = 8.3)	93.4	H–C(7d)	5.65 (<i>d</i> , <i>J</i> = 9.8)	93.8
H–C(8d)	5.32 (br. <i>d</i> , <i>J</i> = 8.3)	52.3	H–C(8d)	5.44 (br. <i>d</i> , <i>J</i> = 9.8)	54.0
C(9d)		141.2 ^{c)}	C(9d)		141.0
C(10d)		122.6	C(10d)		118.4
C(11d)		157.3	OH–C(11d)	7.99 (br. <i>s</i>)	158.7
H–C(12d)	6.35 (br. <i>s</i>)	101.7	H–C(12d)	6.39 (<i>d</i> , <i>J</i> = 2.2)	102.7
C(13d)		156.5	OH–C(13d)	8.16 (br. <i>s</i>)	157.0
H–C(14d)	6.37 (br. <i>s</i>)	106.4	H–C(14d)	6.30 (<i>d</i> , <i>J</i> = 2.2)	107.3
OH	7.80, 8.17, 8.59 (br. <i>s</i>)				

^{a)} (D₆)Acetone soln.; at 400 (¹H) and 100 MHz (¹³C); δ in ppm, *J* in Hz. ^{b)} Signals interchangeable. ^{c)} Signals interchangeable.



* overlapping or undistinguishable

Fig. 2. Main connectivities found in the HMBC and $^1\text{H}, ^1\text{H-COSY}$ experiments of **1**

Table 2. HMBC Data of **1**

H-Atom	HMBC
H-C(2a,6a)	C(4a), C(7a)
H-C(3a,5a)	C(1a), C(4a)
H-C(7a)	C(1a), C(2a,6a), C(8a), C(9a)
H-C(8a)	C(1a), C(7a), C(9a), C(10a), C(11a) ^a ^b), C(14a) ^a), C(9b), C(10b), C(11b)
H-C(12a)	C(10a), C(11a), C(13a), C(14a)
H-C(14a)	C(8a), C(10a), C(12a), C(13a)
H-C(2b,6b)	C(4b), C(7b)
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), C(9b), C(8c) ^c
H-C(8b)	C(10a), C(11a) ^a ^b), C(1b), C(7b) ^d), C(9b) ^e), C(10b), C(14b), C(7c) ^d), C(9c) ^e
H-C(12b)	C(10b), C(11b), C(13b), C(14b)
H-C(14b)	C(8b), C(10b), C(12b), C(13b)
H-C(2c,6c)	C(4c), C(7c)
H-C(3c,5c)	C(1c), C(4c)
H-C(7c)	C(8b) ^f), C(9d), C(10d), C(11d), C(1c), C(2c,6c), C(8c) ^f), C(9c)
H-C(8c)	C(7b) ^g), C(9b) ^h), C(10d), C(11d) ^a ^b), C(1c), C(7c) ^g), C(9c) ^h), C(10c), C(14c)
H-C(12c)	C(10c), C(11c), C(13c), C(14c)
H-C(14c)	C(8c), C(10c), C(12c), C(13c)
H-C(2d,6d)	C(4d), C(7d)
H-C(3d,5d)	C(1d), C(4d)
H-C(7d)	C(1d), C(2d,6d), C(8d), C(9d)
H-C(8d)	C(1d), C(7d), C(9d), C(10d), C(11d) ^a ^b), C(14d) ^a), C(9c), C(10c), C(11c)
H-C(12d)	C(10d), C(11d), C(13d), C(14d)
H-C(14d)	C(8d), C(10d), C(12d), C(13d)

^a) Weak correlation. ^b) ⁴J Coupling. ^c) to ^h) Overlapping or undistinguishable signals.

NOEs for H–C(7a)/H–C(2b,6b) and H–C(8a)/H–C(8b), respectively. This situation only permits the *trans* diaxial orientation of ring B_1 and H–C(8b), and H–C(7a) and H–C(8a). Based on the NMR and MS data, the compound contains two identical units and cannot be the *meso* form because of its optical activity. From the above data, vateriaphenol **1** was determined as (1*R**,1'*R**,6*S**,6'*S**,7*S**,7'*S**,11*bR**,11*b'R**)-1,1',6,6',7,7',11*b*,11*b'*-octahydro-1,1',7,7'-tetrakis(4-hydroxyphenyl)-6,6'-bi-2-oxadibenzo[*cd,h*]azulene-4,4',8,8',10,10'-hexol.

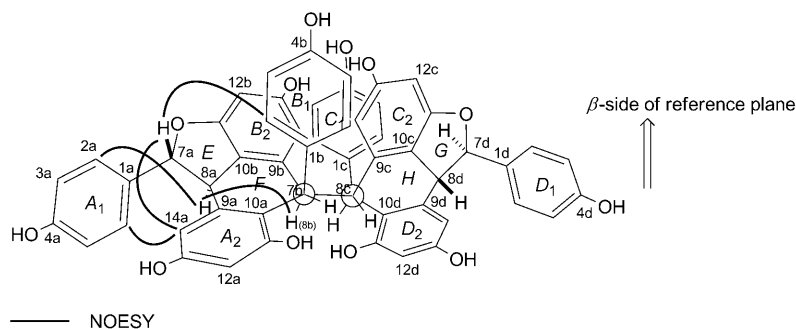


Fig. 3. Stereo structure of **1** and selected NOEs observed in the ^1H , ^1H -NOESY experiment

Table 3. ^1H , ^1H -NOESY Data of **1** and **2**

H-Atom	1	2
H–C(2a,6a)	H–C(7a), H–C(8a), H–C(14a)	H–C(7a), H–C(8a), H–C(14a)
H–C(7a)	H–C(2a,6a), H–C(14a), H–C(2b,6b)	H–C(2a,6a), H–C(14a)
H–C(8a)	H–C(2a,6a), H–C(14a), H–C(8b)	H–C(2a,6a), H–C(14a), H–C(2c,6c), H–C(8c), H–C(14c)
H–C(14a)	H–C(2a,6a), H–C(7a), H–C(8a)	H–C(2a,6a), H–C(7a), H–C(8a)
H–C(2b,6b)	H–C(7a), H–C(7b), H–C(8b)	H–C(7b), H–C(8b), H–C(14b), H–C(8d)
H–C(7b)	H–C(2b,6b), H–C(8b)	H–C(2b,6b), H–C(8b)
H–C(8b)	H–C(8a), H–C(2b,6b), H–C(7b), H–C(14b)	H–C(2b,6b), H–C(7b), H–C(14b), H–C(8d)
H–C(14b)	H–C(8b)	H–C(2b,6b), H–C(8b), H–C(8d)
H–C(2c,6c)	H–C(7c), H–C(8c), H–C(7d)	H–C(7c), H–C(8c), H–C(14c), H–C(8a)
H–C(7c)	H–C(2c,6c), H–C(8c)	H–C(2c,6c), H–C(8c)
H–C(8c)	H–C(2c,6c), H–C(7c), H–C(14c), H–C(8d)	H–C(2c,6c), H–C(7c), H–C(14c), H–C(8a)
H–C(14c)	H–C(8c)	H–C(8a), H–C(2c,6c), H–C(8c)
H–C(2d,6d)	H–C(7d), H–C(8d), H–C(14d)	H–C(7d), H–C(8d), H–C(14d)
H–C(7d)	H–C(2d,6d), H–C(14d), H–C(2c,6c)	H–C(2d,6d), H–C(14d)
H–C(8d)	H–C(2d,6d), H–C(14d), H–C(8c)	H–C(2b,6b), H–C(8b), H–C(14b), H–C(2d,6d), H–C(14d)
H–C(14d)	H–C(2d,6d), H–C(7d), H–C(8d)	H–C(2d,6d), H–C(7d), H–C(8d)

The proposed structure of **1** is identical to the one reported for isohopeaphenol (**2**) [2]. The present information of the configuration of **1** definitely calls the structure of **2** into question. To clarify this question, the relative conformation of **2** was inspected by ^1H , ^1H -NOESY experiments (Fig. 4 and Table 3). *trans*-Orientation of the CH H-atoms

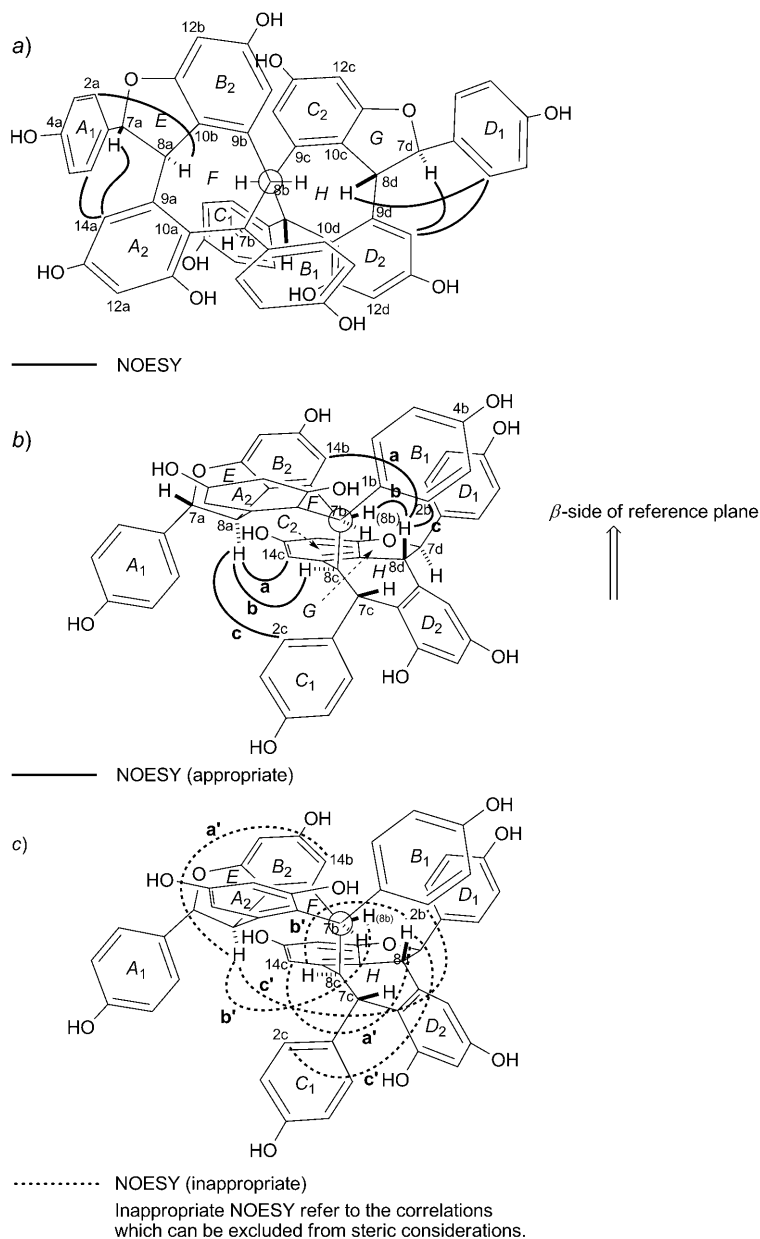


Fig. 4. Stereo structure of **2** and selected NOEs observed in the $^1\text{H},^1\text{H}$ -NOESY experiment. a) Vertical view based on C–C bond (C(8b)/C(8c)). b), c) Horizontal view based on C–C bond (C(8b)/C(8c)).

on the dihydrobenzofuran rings (rings *E* and *G*) was evident by the significant NOEs (Fig. 4,a). When the NOEs (Fig. 4,b; rings *A*–*C*) are taken into consideration, the axial bond (C(8b)–C(8c)) and the equatorial bonds (C(1b)–C(7b) and C(1c)–C(7c))

in the dibenzocycloheptadiene systems (rings *F* and *H*) are evident, namely, H–C(7b), H–C(8b), H–C(7c), and H–C(8c) are situated in α , β , β , and α , respectively.

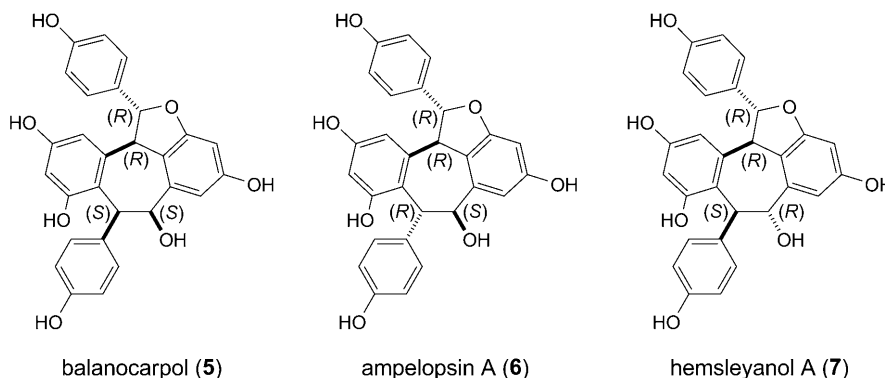
As **2** also has two equivalent units in the molecule, differentiation of the correlations among equal H-atoms is impossible. For example, the correlation between H–C(8a)/H–C(8c) (Fig. 4, *b*; correlation **b**) could not be differentiated from H–C(8a)/H–C(8b) (Fig. 4, *c*; correlation **b'**), because the H-atoms (H–C(8c) and H–C(8b)) are equal. The differentiation of appropriate NOE correlations (Fig. 4, *b*) and inappropriate NOE correlations (Fig. 4, *c*) is essential. Inappropriate NOE correlations refer to the corresponding NOE correlations within one unit which can be excluded from steric considerations. Reasons to exclude such NOEs (Fig. 4, *c*; correlations **a'–c'**) are as follows: NOEs between H–C(8a)/H–C(14b) and H–C(8d)/H–C(14c) (Fig. 4, *c*; correlation **a'**) are impractical due to the skeleton. If the NOE correlations **b'** and **c'** were accepted, the compatible structure would be **3**, where H–C(8a), ring *B*₁, and H–C(8b) have the same orientation. Actually, **2** and **3** were separately isolated from the material and their spectral data are different. Moreover, the absolute structure of (–)-hopeaphenol (**3**) was confirmed by the aid of X-ray crystallography [5]. Consequently, the NOE correlations **b'** and **c'** are unacceptable. Therefore all the inappropriate NOE correlations (Fig. 4, *c*; correlations **a'–c'**) can be rejected. From the above data, the relative configuration of isohopeaphenol was revised to (1*R**,1'*R**,6*R**,6'*R**,7*S**,7'*S**,11*bR**,11'*bR**)-1,1',6,6',7',11*b*,11'*b*-octahydro-1,1'-7,7'-tetrakis(4-hydroxyphenyl)-6,6'-bi-2-oxadibenzo[*cd,h*]azulene-4,4',8,8',10,10'-hexol.

The consideration of NOEs, not only within one unit, but between both units is essential for the structure elucidation of such dimeric molecules. NOEs are observed when the C–C bond linking the two equivalent units is situated in axial orientation in the ring system. This is the case of **2**, where the bond (C(8b)–C(8c)) is situated in *axial* orientation. One equivalent unit (rings *A*₁, *A*₂, *B*₂, *B*₂, *E*, *F*) is lying on the edge of the other (rings *C*₁, *C*₂, *D*₂, *D*₂, *G*, *H*), forming a compact molecule. NOE Correlations (Fig. 4, *b*) confirm the *axial* orientation. On the other hand, if the bond (C(8b)–C(8c)) is situated in *equatorial* orientation, NOEs between the equivalent units would hardly be observed. This is the case in **1**, where the bond (C(8b)–C(8c)) is situated in *equatorial* orientation, and one of the equivalent units (rings *A*₁, *A*₂, *B*₂, *B*₂, *E*, *F*) is lying horizontally to the other (rings *C*₁, *C*₂, *D*₂, *D*₂, *G*, *H*), forming an extended molecule (Fig. 3).

Although the ¹H-NMR spectral data of **1** and **2** are similar (Fig. 1), the molecular shape is quite different due to the opposite orientations of C(8b) and C(8c) (Figs. 3 and 4). The characteristic resemblances are small *J*-values of the aliphatic H-atoms, H–C(7b)/H–C(8b) and H–C(7c)/H–C(8c). When the conformational differences based on rings *F* and *H* were considered, the similar dihedral angles of H–C(7b)/H–C(8b) and H–C(7c)/H–C(8c) agree with both the orientations in **1** (*cis*) and **2** (*trans*). In the ¹³C-NMR spectrum (Table 1), the apparent differences are observed for the signals of C(8b) and C(8c) (**1**: δ (C) 44.5; **2**: δ (C) 52.9), which also reflect the opposite orientations of C(8b) and C(8c).

The structure of **1** and **2** is identical to those of known resveratrol tetramers such as hopeaphenol (**3**) [3], vateriaphenol B (**4**) [1], pauciflorol C [6], neohopeaphenol A [7], and noisohopeaphenol A [7] isolated from Dipterocarpaceaeous plants, which are

composed of two resveratrol dimers. In case of **1–3**, two identical dimers (of balanocarpol (**5**) [8] in **1**, of hemsleyanol A (**6**) [9] in **2**, and of ampelopsin A (**7**) [10] in **3**) are coupled through a C–C bond of C(8b)–C(8c). Half signals of the total atom numbers are observed in the ^1H - and ^{13}C -NMR spectrum of them. In case of **4**, two heterogenic dimeric units (ampelopsin A and hemsleyanol A) are the components.



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Experimental Part

General. Anal. TLC: Merck Kieselgel F_{254} (0.25 mm). Prep. TLC: Merck Kieselgel F_{254} (0.5 mm). Column chromatography (CC): Merck Kieselgel 60 (70–230 mesh), or Sephadex LH-20. Optical rotation: Jasco DIP-370 polarimeter. UV Spectra: Shimadzu UV-3100 spectrophotometer; λ_{max} in nm. IR Spectra: Jasco FT-IR-8000 spectrophotometer; KBr microplate; in cm^{-1} . ^1H - and ^{13}C -NMR spectra: JEOL JNM AL-400 spectrometer; measured at r.t.; (D_6)acetone soln.; δ in ppm relative to Me_4Si (0 ppm) as an internal reference in ^1H -NMR spectra; δ in ppm relative to solvent (C=O group, 206.0 ppm) in ^{13}C -NMR spectra; coupling constants J in Hz. FAB-MS: JEOL JMS-DX-300 mass spectrometer.

Plant Material. The stem bark of *Vateria indica* was collected in Karnataka in India in June, 2004, and a voucher specimen (number DP-031) was deposited with the Gifu Pharmaceutical University, Gifu, Japan.

Extraction and Isolation. The dried and ground stem bark of *V. indica* (600 g) was successively extracted with acetone (1.51×3), MeOH (1.51×3), and 70% MeOH (21×2) at r.t. Concentrated extracts gave respective residues of 65 g (acetone), 40 g (MeOH), and 12 g (70% MeOH). A part (60 g) of the acetone extract was subjected to column chromatography (CC; SiO_2 ; $\text{CHCl}_3/\text{MeOH}$) with increasing polarity to give 18 fractions (Fr. 1–18). Fr. 14 (3 g, $\text{CHCl}_3/\text{MeOH}$ 5:1) was further subjected to reversed-phase CC ($\text{H}_2\text{O}/\text{MeOH}$ gradient system, 20%–60% MeOH) to give 13 fractions (Fr. 14A–Fr. 14M). Compounds **1** (20 mg), **2** (30 mg), and **3** (550 mg) were obtained from Fr. 14J, Fr. 14G, and Fr. 14C, respectively, after purification by Sephadex LH-20 CC (MeOH) and prep. TLC ($\text{AcOEt}/\text{CHCl}_3/\text{MeOH}/\text{H}_2\text{O}$ 15:8:4:1). Compound **4** (6 mg) was obtained from Fr. 12 (8 g, $\text{CHCl}_3/\text{MeOH}$ 5:1) after purification by two times purification by Sephadex LH-20 CC (MeOH). Shoreaketone (25 mg) was obtained from Fr. 8 (700 mg, $\text{CHCl}_3/\text{MeOH}$ 8:1) after purification by Sephadex LH-20 CC (MeOH) and prep. TLC ($\text{AcOEt}/\text{CHCl}_3/\text{MeOH}/\text{H}_2\text{O}$ 80:40:11:2).

Vateriaphenol C (= (1R*,1'R*,6S*,6'S*,7S*,7'S*,11bR*,11b'R*)-1,1',6,6',7,7',11b,11b'-Octahydro-1,1',7,7'-tetrakis(4-hydroxyphenyl)-6,6'-bi-2-oxadibenzof[cd,h]azulene-4,4',8,8',10,10'-hexol; **1**). Pale yellow solid. $[\alpha]_{\text{D}}^{25} = +133$ ($c=0.1$, MeOH). UV: 284 (4.26). IR: 3305, 1605, 1512, 1360, 1173, 1132, 834.

$^1\text{H-NMR}$, $^{13}\text{C-NMR}$, $^1\text{H},^{13}\text{C-HMBC}$, $^1\text{H},^1\text{H-NOESY}$: Tables 1–3. FAB-MS: 907 ($[M+H]^+$). HR-FAB-MS 907.2763 ($[M+H]^+$, $\text{C}_{56}\text{H}_{43}\text{O}_{12}$; calc. 907.2755).

(+)-Isohopeaphenol (= (1R*,1'R*,6R*,6'R*,7S*,7'S*,11bR*,11b'R*)-1,1',6,6',7,7',11b,11b'-Octahydro-1,1',7,7'-tetrakis(4-hydroxyphenyl)-6,6'-bi-2-oxadibenz[cd,h]azulene-4,4',8,8',10,10'-hexol; **2**). Pale yellow solid. $[\alpha]_{\text{D}}^{25} = +205$ ($c = 0.1$, MeOH). UV: 284 (4.22). $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, $^1\text{H},^{13}\text{C-HMBC}$, $^1\text{H},^1\text{H-NOESY}$: Tables 1–3. FAB-MS: 907 ($[M+H]^+$). HR-FAB-MS: 907.2751 ($[M+H]^+$, $\text{C}_{56}\text{H}_{43}\text{O}_{12}$; calc. 907.2755).

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