# Resveratrol Derivatives from *Upuna borneensis*

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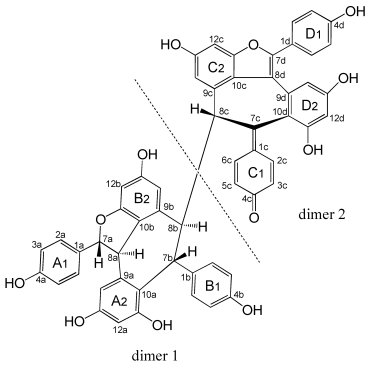
**Four new resveratrol derivatives, upunaphenols B (1), C (4), D (5) (resveratrol tetramer) and E (6, resveratrol dimer with a $C_6$–$C_1$ unit), together with nine known resveratrol oligomers and resveratrol were isolated from an acetone soluble part of stem of *Upuna borneensis* (Dipterocarpaceae). The structures of new compounds were determined by spectral analysis including 1D and 2D NMR experiments.**

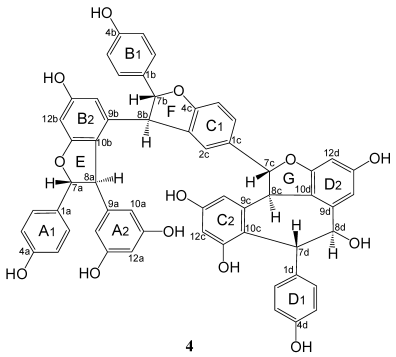
**Key words** *Upuna borneensis*; Dipterocarpaceae; resveratrol oligomer; upunaphenol; structure elucidation

*Upuna borneensis* (Dipterocarpaceae) is a monotypic genus distributed in Malaysia.[1)] In previous papers, we reported the isolation and structure determination of new compounds of a resveratrol hexamer (upunaphenol A), resveratrol *O*-glucosides and acetophenone *C*-glucosides together with four known resveratrol oligomers from an acetone extract of stem of this plant.[2,3)] We report in this paper the isolation and structure elucidation of 14 resveratrol derivatives including four new compounds, upunaphenols B (**1**), C (**4**)—E (**6**).

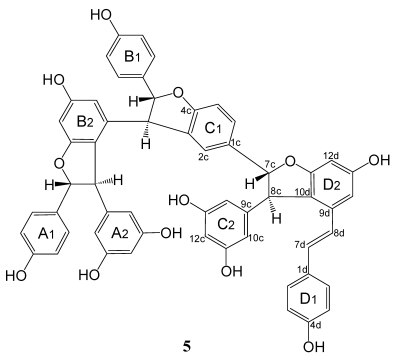
Upunaphenols B (**1**) ($[\alpha]_D^{25}$ −530°), C (**4**) ($[\alpha]_D^{25}$ −175°), D (**5**) ($[\alpha]_D^{25}$ −229°) and E (**6**) ($[\alpha]_D^{25}$ −147°) were purified from an acetone-soluble part of stem of *U. borneensis* by column chromatography over silica gel, Sephadex LH-20, ODS, and preparative TLC. All compounds showed positive reactions to the Gibbs reagent.

Upunaphenol B (**1**) was obtained as a yellow amorphous powder. In the high resolution (HR) FAB-MS, an $[M-H]^-$ ion peak was observed at *m*/*z* 901.2297 suggesting the molecular formula of $C_{56}H_{38}O_{12}$ corresponding to the molecule of an oxidative tetramer of resveratrol. The $^1$H- and $^{13}$C-NMR spectral data (Tables 1, 2) together with $^1$H–$^1$H shift correlation spectroscopy (COSY), $^{13}$C–$^1$H COSY and $^1$H detected heteronuclear multiple bond connectivity (HMBC) spectrum showed the presence of *ortho*-coupled aromatic protons assignable to three 4-hydroxylphenyl groups (rings $A_1$, $B_1$, $D_1$),




**1**
**2** : H-7d; H-8d: dihydro (H-7d: α; H-8d: β)
**3** : H-7d; H-8d: dihydro (H-7d: α; H-8d: β), ring C1: *p*-hydroxyphenyl, H-7c: α



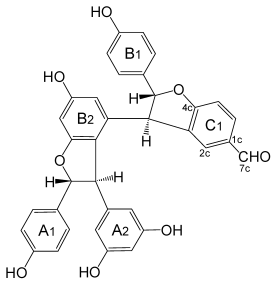




Chart 1

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Table 1. $^1$H-NMR Spectral Data of **1**, **4**—**6**

| No. | **1** | **4** | **5** | **6** |
|---|---|---|---|---|
| 2a, 6a | 7.18 (d, 8.7) | 7.04 (d, 8.6) | 7.01 (d, 8.6) | 7.03 (d, 8.5) |
| 3a, 5a | 6.81 (d, 8.7) | 6.82 (d, 8.6) | 6.82 (d, 8.6) | 6.82 (d, 8.5) |
| 7a | 5.81 (d, 12.1) | 5.29 (d, 5.3) | 5.21 (d, 5.0) | 5.27 (d, 5.0) |
| 8a | 4.28 (d, 12.1) | 3.80 (d, 5.3) | 3.69 (d, 5.0) | 3.74 (d, 5.0) |
| 10a | | 6.06 (d, 2.2) | 5.96 (d, 2.2) | 5.99 (d, 2.4) |
| 12a | 6.58 (d, 2.0) | 6.27 (t, 2.2) | 6.24 (t, 2.2) | 6.19 (t, 2.4) |
| 14a | 6.42 (br d, 2.0) | 6.06 (d, 2.2) | 5.96 (d, 2.2) | 5.99 (d, 2.4) |
| 2b, 6b | 6.76 (d, 8.8) | 7.06 (d, 8.6) | 7.08 (d, 8.6) | 7.11 (d, 8.4) |
| 3b, 5b | 6.54 (d, 8.8) | 6.76 (d, 8.6) | 6.76 (d, 8.6) | 6.78 (d, 8.4) |
| 7b | 5.11 (d, 4.7) | 5.34 (d, 9.5) | 5.27 (d, 9.3) | 5.45 (d, 9.4) |
| 8b | 3.75 (dd, 10.0, 4.7) | 4.37 (d, 9.5) | 4.42 (d, 9.3) | 4.49 (d, 9.4) |
| 12b | 5.86 (d, 2.1) | 6.32 (d, 2.0) | 6.29 (br s) | 6.35 (d, 2.0) |
| 14b | 5.22 (d, 2.1) | 6.20 (d, 2.1) | 6.20 (br d, 2.0) | 6.20 (d, 2.0) |
| 2c | 7.38 (dd, 10.1, 2.6) | 6.87 (d, 2.5) | 6.86 (br s) | 7.27 (br d, 2.0) |
| 3c | 6.16 (dd, 10.1, 2.6) | | | |
| 5c | 6.13 (dd, 10.3, 2.6) | 6.63[a)] | 6.78 (d, 8.3) | 6.98 (d, 8.3) |
| 6c | 7.27 (dd, 10.3, 2.6) | 6.63[a)] | 7.13 (br d, 8.3) | 7.79 (dd, 8.3, 2.0) |
| 7c | | 5.68 (d, 11.2) | 5.37 (d, 5.1) | 9.77 (br s) |
| 8c | 4.65 (d, 10.0) | 4.18 (d, 11.2) | 4.45 (d, 5.1) | |
| 10c | | | 6.20—6.30 (br s) | |
| 12c | 6.65 (d, 2.0) | 6.43 (d, 2.0) | 6.19 (br s) | |
| 14c | 5.80 (d, 2.0) | 6.15 (br d, 2.0) | 6.20—6.30 (br s) | |
| 2d, 6d | 7.61 (d, 8.7) | 6.88 (br d, 8.6) | 7.19 (d, 8.6) | |
| 3d, 5d | 6.96 (d, 8.7) | 6.64 (d, 8.6) | 6.75 (d, 8.6) | |
| 7d | | 5.43 (br d, 6.8) | 6.91 (d, 16.3) | |
| 8d | | 5.41 (br d, 6.8) | 6.69 (d, 16.3) | |
| 12d | 6.41 (d, 2.3) | 6.10 (d, 2.0) | 6.32 (s) | |
| 14d | 7.00 (d, 2.3) | 6.59 (d, 2.0) | 6.20—6.30 (br s) | |
| OH | 8.43 (br s, OH-13a) | 3.41 (br s, OH-8d) | | 8.44 (br s, OH-4a) |
| | 8.00 (br s, OH-4b) | 8.17, 8.29, 8.32, | | 8.23 (br s, OH-11a,13a) |
| | 7.61 (br s, OH-13b) | 8.42, 8.45, 8.55 | | 8.55 (br s, OH-4b) |
| | 8.16 (br s, OH-13c) | (1H each, br s) | | 8.44 (br s, OH-13b) |
| | 8.66 (br s, OH-13d) | 8.51 (3H, br s) | | |
| | 8.05, 8.49, 8.82, | | | |
| | 8.95 (1H each, br s) | | | |

Measured in acetone-$d_6$ (300 MHz). All protons were assigned by $^1$H–$^1$H, $^1$H–$^1$H long-range, $^{13}$C–$^1$H COSY, COLOC and HMBC spectrum. *a*) Obscured by overlapping with H-3d(5d).

four sets of *meta*-coupled aromatic protons on a 1,2,3,5-tetra-substituted benzene ring (rings $A_2$—$D_2$). The NMR spectral data also disclosed the presence of a set of aliphatic signals characteristic for a 2,3-diaryldihydrobenzofuran moiety (H-7a, H-8a)[4)] in addition to a sequence of three aliphatic methine protons successively coupled in this order (H-7b/H-8b/H-8c). The $^1$H-NMR spectrum further showed the signals of nine phenolic OH groups ($\delta$ 7.61—8.95), which disappeared upon addition of $D_2O$. Considering the molecular formula, the remaining unit in the molecule corresponds to $C_9H_4O$. In the $^1$H-NMR spectrum, the other signals of four olefinic protons [$\delta_H$ 7.38 (H-2c), 6.16 (H-3c), 6.13 (H-5c), 7.27 (H-6c)] are corresponding to the $C_9H_4O$, two of which (H-2c, H-6c) were correlated with a carbonyl carbon ($\delta_C$ 187.3: C-4c) in the HMBC spectrum. An existence of partial structure of *para*-quinoid unit ($C_7H_4O$: C-1—C-7) was confirmed by correlations observed between H-2c/C-7c, H-3c/C-1c, H-5c/C-1c and H-6c/C-7c. The remaining carbon signals [$\delta_C$ 152.8 (C-7d), 114.9 (C-8d)] were assigned to the quaternary olefinic carbons, and the chemical shifts observed in **1** were similar to those of a benzofuran moiety in malibatol A ($\delta_C$ 151.2, 117.3) isolated from *Hopea malibato*.[5)] The connection of these partial structures was determined as follows. In the HMBC spectrum (Fig. 1), correlations *via* $^3J$ were observed between H-7a/C-2a(6a), H-8a/C-10a, H-7b/C-2b(6b), H-8b/C-10b, H-8c/C-10c, H-2d(6d)/C-7d and H-14d/C-8d, indicating that the rings $A_1$, $A_2$, $B_1$, $B_2$, $C_2$, $D_1$ and $D_2$ were attached at C-7a, C-8a, C-7b, C-8b, C-8c, C-7d and C-8d, respectively. Then the expanded partial unit formed by resveratrols A, B and D [(resveratrol A: ring $A_1$–C-7a–C-8a–ring $A_2$)] was established. Four C–C bonds of C-8a/C-10b, C-7b/C10a, C-7c/C-8c and C-7c/C-10d were further deduced by correlations of H-8a/C-11b, H-7b/C-11a, H-8b/C-7c and H-8c/C-10d. Although no long-range correlation between H-7a/C-11b was observed, the presence of a dihydrobenzofuran ring (C-7a–C-8a–C-10b–C-11b–O) and a benzofuran ring (C-7d–C-8d–C-10c–C-11c–O) was clear after considering the carbon chemical shifts and the molecular formula. The planar structure of upunaphenol B was then concluded to be **1**. The other correlations in the HMBC spectrum summarized in Fig. 1 and experimental section were in accordance with the proposed planar structure. The structure of **1** is an oxidative tetramer of four resveratrol units (resveratrols A—D) and one of the 4-hydroxylphenyl groups is changed to a *para*-quinoid form (ring $C_1$) in resveratrol C. The stereo structure of **1** was determined by analysis of the nuclear Overhauser spectroscopy (NOESY) spectrum (Fig. 2). The *trans* relationship of H-7a/H-8a on the dihydrobenzofuran ring was confirmed by the distinctive NOEs between H-7a/H-14a, H-8a/H-2a(6a) and H-2a(6a)/H-14a. The large

Table 2. $^{13}$C-NMR Spectral Data of **1**, **4**—**6**

| No. | 1 | 4 | 5 | 6 |
|---|---|---|---|---|
| 1a | 130.4 | 133.3 | 133.4 | 133.4 |
| 2a, 6a | 130.3 | 128.2 | 128.1 | 128.1 |
| 3a, 5a | 116.1 | 116.2 | 116.0 | 116.1 |
| 4a | 158.7 | 158.4[g)] | 158.1[d)] | 158.2 |
| 7a | 88.7 | 93.8 | 93.9 | 93.9 |
| 8a | 50.1 | 56.1 | 55.9 | 56.1 |
| 9a | 142.5 | 147.4 | 147.0 | 147.2 |
| 10a | 118.5 | 107.0 | 106.6 | 106.7 |
| 11a | 157.8[a)] | 159.4 | 159.5 | 159.9 |
| 12a | 102.4 | 102.2 | 102.0 | 102.2 |
| 13a | 157.8[a)] | 159.4 | 159.5 | 159.9 |
| 14a | 107.5 | 107.0 | 106.6 | 106.7 |
| 1b | 132.9 | 131.6 | 131.7 | 130.9 |
| 2b, 6b | 128.9 | 128.4 | 128.6 | 128.7 |
| 3b, 5b | 115.5 | 116.2 | 116.2 | 116.3 |
| 4b | 155.8 | 158.3[g)] | 158.3 | 158.7 |
| 7b | 41.3 | 94.4 | 94.3 | 95.1 |
| 8b | 49.9 | 54.5 | 54.8 | 53.8 |
| 9b | 138.6 | 140.3 | 140.3 | 139.5 |
| 10b | 117.9 | 121.7 | 121.4 | 121.6 |
| 11b | 159.8 | 162.0 | 162.3 | 162.3 |
| 12b | 96.0 | 96.7 | 96.6[e)] | 96.9 |
| 13b | 157.8[a)] | 159.9 | 159.5[f)] | 160.2 |
| 14b | 111.4 | 107.7 | 107.6 | 107.8 |
| 1c | 132.6 | 132.6[c)] | 135.7 | 132.5 |
| 2c | 135.6 | 127.2 | 123.9 | 127.5 |
| 3c | 128.6 | 131.3 | 131.1 | 133.4 |
| 4c | 187.3 | 161.2 | 160.9 | 165.8 |
| 5c | 129.0 | 109.9 | 109.9 | 110.6 |
| 6c | 140.5 | 127.6 | 126.7 | 132.8 |
| 7c | 156.9 | 88.1 | 93.8 | 190.8 |
| 8c | 54.6 | 49.3 | 56.8 | |
| 9c | 136.8 | 143.1 | 147.1 | |
| 10c | 119.6 | 118.7[h)] | 106.4 | |
| 11c | 155.5 | 159.03[i)] | 159.5[f)] | |
| 12c | 96.5 | 101.6 | 102.1 | |
| 13c | 156.1[b)] | 156.9 | 159.5[f)] | |
| 14c | 112.5 | 104.8 | 102.1 | |
| 1d | 123.0 | 132.6[c)] | 129.9 | |
| 2d, 6d | 131.0 | 128.7 | 128.7 | |
| 3d, 5d | 116.4 | 115.5 | 116.1 | |
| 4d | 159.2 | 156.1 | 158.1[d)] | |
| 7d | 152.8 | 43.8 | 130.1 | |
| 8d | 114.9 | 71.0 | 123.4 | |
| 9d | 133.8 | 140.5 | 136.3 | |
| 10d | 116.0 | 118.8[h)] | 119.6 | |
| 11d | 156.1[b)] | 160.2 | 162.1 | |
| 12d | 103.0 | 97.1 | 96.6[e)] | |
| 13d | 159.4 | 158.98[i)] | 159.5[f)] | |
| 14d | 109.6 | 110.5 | 103.9 | |

Measured in acetone-$d_6$ (75 MHz). *a*—*f*) Overlapping. *g*—*i*) Interchangeable. All carbons were assigned by $^{13}$C–$^{1}$H COSY, COLOC and HMBC spectrum.

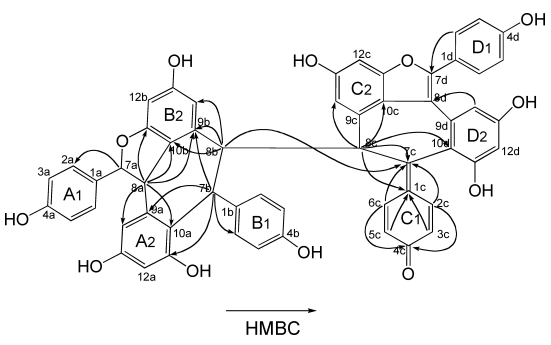


Fig. 1. Selected Correlations Observed in the HMBC Spectrum of **1**

Other correlations: see Experimental.

coupling constant values of H-7a and H-8a ($J$=12.1 Hz) also supported the stereo relationships.[6] In addition, the *syn* orientation of ring $B_1$, H-8a and H-8b was supported by NOEs between H-2b(6b)/H-8a and H-2b(6b)/H-8b. An NOE enhancement between H-7b/H-8c was further observed in **1**, indicating that these two protons were co-facial and the *trans* relationship of H-8b/H-8c. The large coupling constant (10.0 Hz)[7] and the lack of NOE enhancement between H-8b/H-8c supported the stereo relationships. Considering the cycloheptadiene ring (C-7c–C-8c–C-9c–C-10c–C-8d–C-9d–C-10d) in **1**, two conformers based on the bond of H-8c/C-8c (left figure: equatorial, right figure: axial) were proposed. The equatorial form (left figure) can reasonably explain the NOEs (H-6c/H-8c, H-8c/H-14c). The conformer was reinforced by the fact that the protons of H-14b ($\delta_H$ 5.22) and H-14c ($\delta_H$ 5.80) were shielded due to the anisotropic effects caused by rings $C_2$ to $B_2$ and *vice versa*. Therefore, the structure of upunaphenol B can be presented as **1** including relative stereochemistry [*rel*-(7a*R*, 8a*R*, 7b*R*, 8b*S*, 7c*R*, 8c*R*, 7d*R*, 8d*S*)], which is the same as those of stenophyllol A (**2**)[8] and hopeaphenol (**3**).[9] Hopeaphenol is known to present both in (+)- or (−)-form in Vitaceae and Dipterocarpaceae, respectively.[6] As **1** had an $[\alpha]_D$ of −530°, the structure of **1** was concluded to be an oxidative derivative of stenophyllol A (**2**) and (−)-hopeaphenol (**3**).

Upunaphenol C (**4**) was obtained as a pale yellow amorphous powder. HR-FAB-MS ($[M-H]^-$ *m/z* 921.2559) showed a molecular formula of $C_{56}H_{42}O_{13}$. The $^1$H- and $^{13}$C-NMR spectral data of **4** together with $^1$H–$^1$H COSY, $^{13}$C–$^1$H COSY and HMBC spectrum (Tables 1, 2) indicated the presence of eight oxygenated aromatic rings which form three 4-hydroxyphenyl groups (rings $A_1$, $B_1$, $D_1$), a 1,2,4-trisubstituted benzene ring (ring $C_1$), a 3,5-dihydroxyphenyl group (ring $A_2$) and three 1,2,3,5-tetrasubstituted benzene rings (rings $B_2$—$D_2$). The $^1$H-NMR spectrum exhibited signals of 10 hydroxyl groups [$\delta_H$ 3.41 (d, $J$=6.8 Hz, alcoholic-OH at C-8d); 8.17, 8.29, 8.32, 8.42, 8.45, 8.55, 8.51 (×3) (each br s, phenolic-OH)] which became sharp when measured in DMSO-$d_6$ ($\delta_H$ 4.84, 8.85—9.50, see Experimental) and disappeared upon addition of $D_2O$. The spectrum also showed the signals attributed to three sets of mutually coupled aliphatic protons on 2,3-diaryldihydrobenzofuran moieties (H-7a/H-8a, H-7b/H-8b, H-7c/H-8c) and a set of aliphatic protons (H-7d/H-8d). The proton (H-8d) was correlated with the hydroxyl proton at $\delta_H$ 3.41, which indicated that the alcoholic hydroxyl group was located at C-8d. The significant $^3J$ long range correlations were observed between H-7a/C-2a(6a), H-7b/C-2b(6b), H-7c/C-2c, H-7d/C-2d(6d), H-8a/C-10a(14a), H-8b/C-10b, H-8c/C-10c and H-8d/C-10d in the HMBC spectrum (Fig. 3), which indicated that eight rings ($A_1$–$D_1$, $A_2$–$D_2$) and eight methine units form four resveratrols A—D. Long range correlations were further observed between the aliphatic methine protons and the quaternary carbons on rings $A_2$–$D_2$ as follows; H-8a/C-11b, H-8b/C-2c, H-8c/C-9d and H-7d/C-11c, which supported the C–C bonds between C-8a/C-10b, C-8b/C-3c, C-8c/C-10d and C-7d/C-10c, respectively. Further cross peaks observed between H-7a/C-11b showed the presence of an ether linkage (C-7a–O–C-11b) which forms a dihydrobenzofuran ring (ring E) (C-7a–C-8a–C-10b–C-11b–O). The presence of other two dihydrobenzofuran rings (ring F) (C-7b–C-8b–C-3c–C-4c–O)

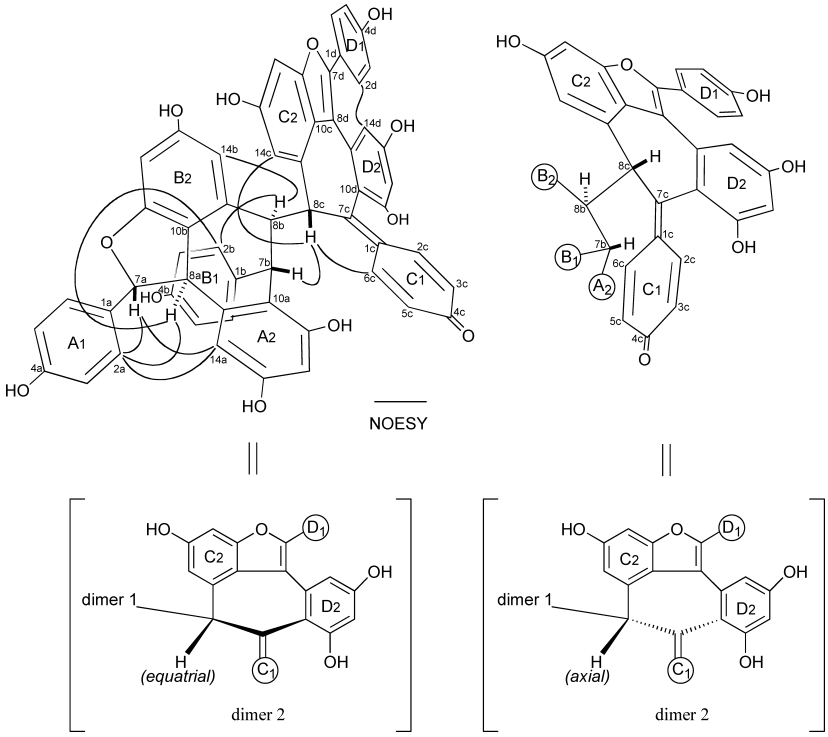


Fig. 2. Two Possibilities of Conformers Due to H-8c of **1** Left: *Equatrial* Conformation of H-7c; Right: *Axial* Conformation of H-7c and NOEs Observed in the NOESY Spectrum

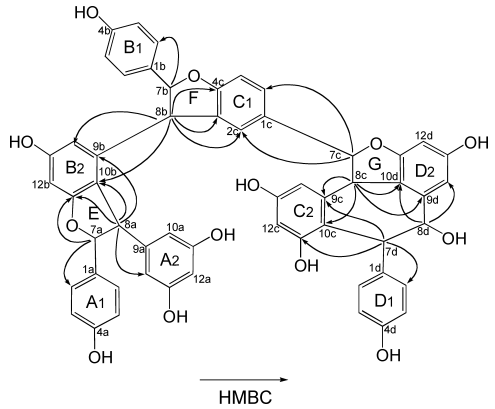


Fig. 3. Selected Correlations Observed in the HMBC Spectrum of **4**
Other correlations: see Experimental.

and (ring G) C-7c–C-8c–C-10d–C-11d–O) was deduced after considering the molecular formula. The planar structure of upunaphenol C was concluded to be **4**. For the confirmation of the relative stereochemistry, NOESY experiments were conducted (Fig. 4). The clear cross peaks observed between H-7a/H-10a(14a), H-8a/H-2a(6a) and H-2a(6a)/H-14a confirmed the *trans* relationship of H-7a and H-8a on ring E. *trans* relationship of rings F (H-7b/H-8b) and ring G (H-7c/H-8c) were also confirmed by the same correlations as in ring E. The stereo relationship among rings E—G was determined as follows. The methine proton (H-8b) displayed NOEs with H-8a and H-10a(14a), which will be observed in both orientation of ring E (Fig. 4A: $\alpha$-orientation of H-8a, Fig. 4B: $\beta$-orientation of H-8a). The point was differentiated by an NOE between H-10a(14a)/H-2c. The orientation of H-7a and H-8a was determined to be $\beta$ and $\alpha$, respectively (Fig. 4A). Further NOEs observed H-10a(14a)/H-7c and H-10a(14a)/H-14c substantiated H-7c to be $\beta$-orientation, because ring $A_2$ is situated above the plane of ring $C_2$ in such stereo relationship between rings E and F (Fig. 5). Therefore, the structure of upunaphenol C including relative stereochemistry can be presented as **4**. The dimeric unit of resveratrols C and D in the structure of **4** is found to be identical to those of ampelopsin A.[10)]

Upunaphenols D (**5**) and E (**6**), were obtained as yellow amorphous powders. Each composition was deduced to be $C_{56}H_{42}O_{12}$ and $C_{35}H_{26}O_8$ by the $[M-H]^-$ ion peaks observed at *m/z* 905.2609 (**5**) and 573.1552 (**6**) in the HR-FAB-MS. The patterns of NMR spectral data of **5** and **6** (Tables 1, 2) were closely similar to those of **4**, in particular, in the partial structure of resveratrols A and B including ring $C_1$. By detail analysis of 2D-NMR spectra (Fig. 6: **5**; Fig. 7: **6**), they were found to have the identical partial structure in the molecule. The structural differences between **4** and **5** were attributable to resveratrols C and D units, presenting $\varepsilon$-viniferin[11)] in **5** instead of ampelopsin A. The HMBC spectrum and NOESY spectrum well explained the structure of **5** including its stereochemistry. By the same reasons described in the stereo structure of **4**, the relative stereo structure of upunaphenol D was elucidated to be **5**. The structure of upunaphenol E, which was analyzed by $^{13}C$–$^{1}H$ shift correlation spectroscopy involving long-range coupling (COLOC) and NOESY spectrum, was also determined to be **6**. C-1c on ring $C_1$ is substituted with an aldehyde group.

Most of the resveratrol oligomers in Dipterocarpaceous plants usually form a dihydrobenzofuran ring after oxidative condensation to a resorcin moiety of resveratrol. The appearance of dihydrobenzofuran ring condensed to a 4-hydroxyphenyl group such as **4** and **5** is a rare case in stilbene com-

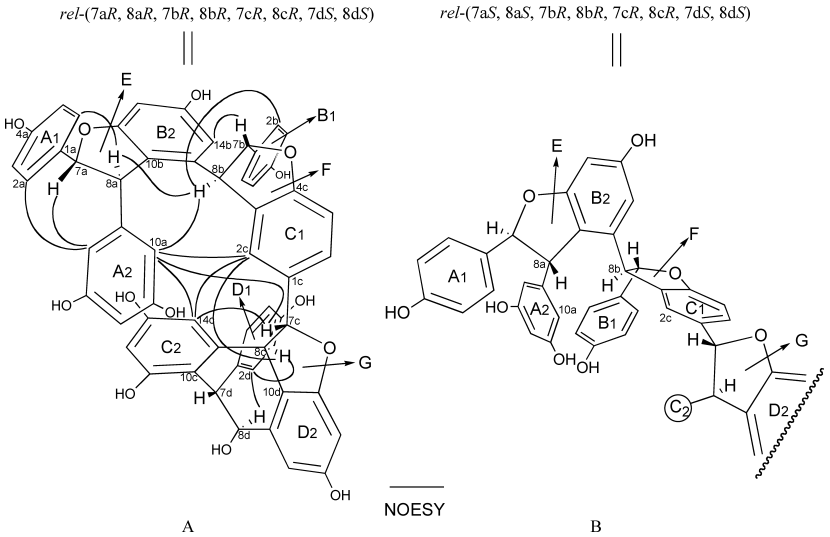


Fig. 4. Two Possiblities of the Stereo Chemical Relation between Rings E and F (Left: *rel-R* Configuration of C-7a and C-8a; Right: *rel-S* Configuration of C-7a and C-8a) and Key NOE Correlations[a] for Differenciation of Them

*a*) Other correlations: see Experimental.

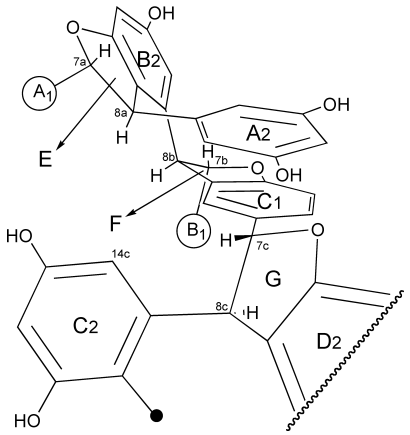

Fig. 5. Spatial Relationship among Rings E—G in **4**

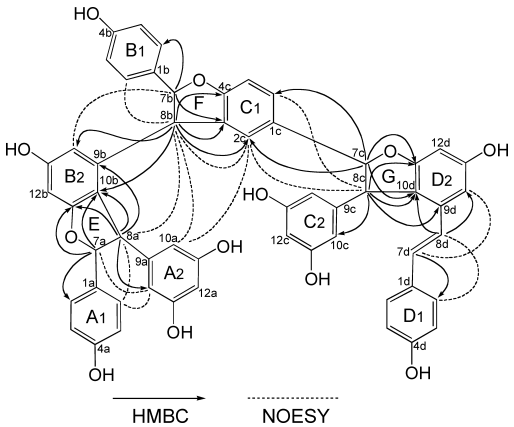


Fig. 6. Selected Correlations Observed in the HMBC and NOESY Spectra of **5**

Other correlations: see Experimental.

ponents of this family.

In addition to these four compounds (**1**, **4**—**6**), nine known resveratrol oligomers were also isolated together with resveratrol. Their structures were identified as stenophyllol A (**2**),[8] (−)-hopeaphenol (**3**),[9] stenophyllol C,[8] isovaticanol B,[12] pauciflorol B,[12] ampelopsin E,[13] (−)-ε-viniferin,[11] *cis*-ε-viniferin[14] and (−)-ampelopsin A,[10] by spectral analysis and comparison with respective authentic samples. Among known compounds, stenophyllols A and C, and *cis*-ε-viniferin are the first to be reported of resveratrol oligomers from the plant of the Dipterocarpaceae.

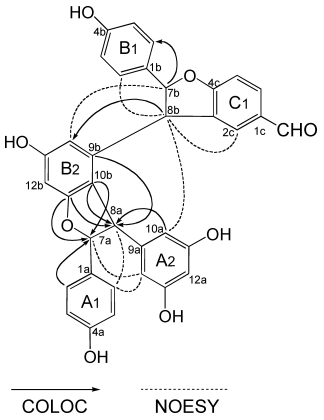


Fig. 7. Selected Correlations Observed in the COLOC and NOESY Spectra of **6**

Other correlations: see Experimental.

**Experimental**

The following instruments were used: optical rotations, JASCO P-1020 polarimeter; UV spectra, Shimadzu UV-2200 spectrophotometer (in methanol solution); $^1$H- and $^{13}$C-NMR spectra, JEOL JNM LA-300 (chemical shift values in $^1$H-NMR spectra are presented as $\delta$ values with TMS as internal standard); EI-MS and FAB-MS, JEOL JMS-DX-300 instrument. 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.

*Upuna borneensis* Sym. was cultivated in Bogor Botanical Garden, Bogor, Indonesia, and its stems were collected in May 2000 and identified by one of co-authors (D.D.). A voucher specimen number DP-012 has been deposited in Gifu Prefectural Institute of Health and Environmental Sciences, Kakamigahara, Gifu, Japan.

**Extraction and Isolation of Compounds (1—6, Nine Known Compounds and Resveratrol)** The dried and ground stems (820 g) of *U.*

*borneensis* were extracted successively with acetone, MeOH and 70% MeOH at rt. A part (172 g) of the acetone extract (175 g) was fractionated by column chromatography (CC) over silica gel with a mixture of $CHCl_3$–MeOH by increasing polarity into 12 fractions (Fr. 1—Fr. 12) by visualization of TLC after Gibbs test. Resveratrol (160 mg) was obtained from Fr. 2 ($CHCl_3$–MeOH, 15 : 1) by further purification through CC over Sephadex LH-20 (acetone). Compound **6** (8 mg) was purified from Fr. 3 ($CHCl_3$–MeOH, 10 : 1) by PTLC (EtOAc–$CHCl_3$–MeOH–$H_2O$, 80 : 40 : 11 : 2). Fr. 4 ($CHCl_3$–MeOH, 10 : 1) was further subject to Sephadex LH-20 CC (MeOH) to give five fractions (Fr. 5a—Fr. 5e). (−)-ε-Viniferin (540 mg) and *cis*-ε-viniferin (12 mg) were purified from the fraction Fr. 5b after CC over ODS (MeOH–$H_2O$, 1 : 1). Fr. 6 ($CHCl_3$–MeOH, 9 : 1) was divided into seven parts (Fr. 6a—Fr. 6g) in the same way as that of Fr. 4. Compounds ampelopsin E (8 mg), (−)-ampelopsin A (5 mg) and **5** (7 mg) were purified by PTLC (EtOAc–$CHCl_3$–MeOH–$H_2O$, 15 : 8 : 4 : 1, ampelopsin E and (−)-ampelopsin A; EtOAc–$CHCl_3$–MeOH–$H_2O$, 10 : 8 : 4 : 1, **5**) from the sub-fractions Fr. 6d (ampelopsin E), Fr. 6e [(−)-ampelopsin A] and Fr. 6f (**5**). Fr. 8 ($CHCl_3$–MeOH, 8 : 1) was fractionated into seven parts (Fr. 8a—Fr. 8g) by Sephadex LH-20 CC (MeOH). Sub fraction of Fr. 8c gave pauciflorol B (420 mg) and stenophyllol C (5 mg) after purification by PTLC (EtOAc–$CHCl_3$–MeOH–$H_2O$, 15 : 8 : 4 : 1). Compounds **1** (24 mg), **2** (11 mg) and **4** (11 mg) were purified from fractions Fr. 8f, 8e and Fr. 8g, respectively. Compounds **3** (8 g) and isovaticanol B (240 mg) were obtained from Fr. 9 ($CHCl_3$–MeOH, 7 : 1) after their CC over Sephadex LH-20 CC (MeOH) and ODS (MeOH–$H_2O$, 65 : 45).

**Compound 1 (Upunaphenol B)** A yellow amorphous powder; $[\alpha]_D^{25}$ −530° ($c$=0.1, MeOH); UV (MeOH) $\lambda_{max}$ (log $\varepsilon$): 324 (3.5), 296 (3.5), 255 (s, 3.6), 230 (s, 3.7), 207 (3.9) nm; negative ion FAB-MS *m/z*: 901 $[M-H]^-$ negative ion HR-FAB-MS *m/z*: 901.2297 (Calcd for $C_{56}H_{37}O_{12}$: 901.2284); $^1$H- and $^{13}$C-NMR spectral data, See Tables 1 and 2; HMBC correlations: See Fig. 1 (selected) and H-2a(6a)/C-4a, C-7a; H-3a(5a)/C-1a,C-4a; H-7a/C-9a; H-8a/C-1a; H-12a/C-10a,C-11a,C-13a; OH-13a/C-12a,C-13a,C-14a; H-14a/C-10a,C-12a,C-13a; H-2b(6b)/C-4b,C-7b; H-3b(5b)/C-1b,C-4b; OH-4b/C-3b(5b),C-4b; H-7b/C-10a,C-1b; H-8b/C-1b; H-12b/C-10b,C-11b,C-13b,C-14b; OH-13b/C-12b,C-13b,C-14b; H-14b/C-10b,C-13b; H-8c/C-9c; H-12c/C-10c,C-11c,C-13c,C-14c; OH-13c/C-12c,C-13c,C-14c; H-14c/C-10c; H-2d(6d)/C-4d; H-3d(5d)/C-1d,C-4d; H-12d/C-11d,C-13d OH-13d/C-12d,C-13d,C-14d; H-14d/C-13b; NOESY correlations, see Fig. 2.

**Compound 4 (Upunaphenol C)** A pale yellow amorphous powder; $[\alpha]_D^{25}$ −175° ($c$=0.1, MeOH); UV (MeOH) $\lambda_{max}$ (log $\varepsilon$): 286 (3.6), 225 (s, 3.9), 207 (4.0) nm; negative ion FAB-MS *m/z*: 921 $[M-H]^-$ negative ion HR-FAB-MS *m/z*: 921.2559 (Calcd for $C_{56}H_{41}O_{13}$: 921.2547); $^1$H- and $^{13}$C-NMR spectral data, see Tables 1 and 2; $^1$H-NMR spectrum (300 MHz, DMSO-$d_6$): $\delta$ 6.91 [2H, d, $J$=8.6 Hz, H-2a(6a)], 6.72 [2H, d, $J$=8.6 Hz, H-3a(5a)], 5.16 (1H, d, $J$=5.0 Hz, H-7a), 3.63 (1H, d, $J$=5.0 Hz, H-8a), 5.82 [2H, d, $J$=2.0 Hz, H-10a(14a)], 6.03 (1H, t, $J$=2.0 Hz, H-12a), 7.00 [2H, d, $J$=8.6 Hz, H-2b(6b)], 6.68 [2H, d, $J$=8.6 Hz, H-3b(5b)], 5.22 (1H, d, $J$=9.5 Hz, H-7b), 4.30 (1H, d, $J$=9.5 Hz, H-8b), 6.20 (1H, d, $J$=2.0 Hz, H-12b), 6.07 (1H, d, $J$=2.0 Hz, H-14b), 6.98 (1H, br s, H-2c), 6.67 (1H, d, $J$=8.6 Hz, H-5c), 6.48 (1H, br d, $J$=8.6 Hz, H-6c), 5.66 (1H, d, $J$=10.8 Hz, H-7c), 3.98 (1H, d, $J$=10.8 Hz, H-8c), 6.27 (1H, br s, H-12c), 5.85 (1H, br s, H-14c), 6.76 [2H, d, $J$=8.6 Hz, H-2d(6d)], 6.55 [2H, d, $J$=8.6 Hz, H-3d(5d)], 5.16 (1H, d, $J$=5.4 Hz, H-7d), 5.22 (1H, br t, $J$=5.6 Hz, H-8d), 6.07 (1H, d, $J$=2.0 Hz, H-12d), 6.41 (1H, d, $J$=2.0 Hz, H-14d), 4.84 (1H, d, $J$=5.7 Hz, OH-8d), 8.85, 9.06, 9.20, 9.25, 9.25, 9.27, 9.40, 9.48, 9.50 (1H each, s, phenolic OH×9); HMBC correlations: See Fig. 3 (selected) and H-2a(6a)/C-4a,C-7a; H-3a(5a)/C-1a,C-4a; H-7a/C-9a; H-8a/C-1a; H-10a(14a)/C-8a,C-11a(13a),C-12a; H-12a/C-10a(14a),C-11a(13a); H-2b(6b)/C-4b,C-7b; H-3b(5b)/C-1b,C-4b; H-7b/C-9b; H-8b/C-1b,9b; H-12b/C-10b,C-11b,C-13b,C-14b; H-14b/C-8b,C-10b,C-12b,C-13b; H-2c/C-4c,C-7c; H-5c/C-4c; H-6c/C-4c,C-7c; H-7c/C-9c; H-8c/C-1c; H-12c/C-10c,C-11c,C-13c,C-14c; H-14c/C-8c,C-10c,C-12c,C-13c; H-2d(6d)/C-4d,C-7d; H-3d(5d)/C-1d,C-4d; H-7d/C-10c,C-1d,C-8d,C-9d; H-8d/C-10c,C-1d,C-7d; H-12d/C-10d,C-11d,C-13d,C-14d; H-14d/C-8d,C-10d,C-12d,C-13d; NOESY correlations: See Fig. 4 (selected) and H-2a(6a)/H-7a; H-8a/H-10a(14a); H-2b(6b)/H-7b; H-8b/H-14b,H-2c, H-8c; H-2c/H-7c; H-6c/H-7c,H-8c,H-14c; H-8c/H-14c; H-2d(6d)/H-7d,H-8d; H-7d/OH-8d; H-8d/H-14d; H-14d/OH-8d.

**Compound 5 (Upunaphenol D)** A yellow amorphous powder; $[\alpha]_D^{25}$ −229° ($c$=0.1, MeOH); UV (MeOH) $\lambda_{max}$ (log $\varepsilon$): 324 (3.5), 296 (3.5), 255 (s, 3.5), 230 (s, 3.7), 207 (3.9) nm; negative ion FAB-MS *m/z*: 905 $[M-H]^-$ negative ion HR-FAB-MS *m/z*: 905.2609 (Calcd for $C_{56}H_{41}O_{12}$: 905.2597); $^1$H- and $^{13}$C-NMR spectral data, see Tables 1 and 2; HMBC correlations: See Fig. 6 (selected) and H-2a(6a)/C-4a,C-7a; H-3a(5a)/C-1a,C-4a; H-7a/C-1a,C-8a,C-9a; H-8a/C-1a,C-7a; H-10a(14a)/C-8a; H-12a/C-10a(14a),C-11a(13a); H-2b(6b)/C-4b,C-7b; H-3b(5b)/C-1b,C-4b; H-7b/C-1b, C-8b,C-9b; H-8b/C-1b,C-7b; H-12b/C-10b,C-11b,C-13b,C-14b; H-14b/C-8b,C-10b,C-12b,C-13b; H-2c/C-8b,C-4c,C-6c,C-7c; H-5c/C-1c,C-3c,C-4c; H-6c/C-2c,C-4c,C-7c; H-7c/C-1c,C-8c,C-9c; H-8c/C-1c,C-7c,C-9c; H-12c/C-10c(14c),C-11c(13c); H-2d(6d)/C-4d,C-7d; H-3d(5d)/C-1d,C-4d; H-7d/C-1d,C-8d,C-9d; H-8d/C-1d,C-7d,C-9d; H-12d/C-10d,C-11d,C-13d,C-14d; NOESY correlations: See Fig. 6 (selected) and H-2a(6a)/H-7a; H-8a/H-10a(14a); H-2b(6b)/H-7b; H-8b/H-14b; H-2c/H-7c; H-6c/H-7c; H-8c/H-7d,H-8d; H-2d(6d)/H-7d; H-8d/H-14d.

**Compound 6 (Upunaphenol E)** A yellow amorphous powder; $[\alpha]_D^{25}$ −147° ($c$=0.1, MeOH); UV (MeOH) $\lambda_{max}$ (log $\varepsilon$): 295 (s, 3.6), 285 (3.6), 226 (4.0), 208 (4.1) nm; negative ion FAB-MS *m/z*: 573 $[M-H]^-$ negative ion HR-FAB-MS *m/z*: 573.1552 (Calcd for $C_{35}H_{25}O_8$: 573.1549); $^1$H- and $^{13}$C-NMR spectral data, see Tables 1 and 2; COLOC correlations ($J$=8 Hz): See Fig. 7 (selected) and C-1a/H-3a(5a),H-7a,H-8a; C-2a(6a)/H-3a(5a); C-3a(5a)/H-2a(6a); C-4a/H-2a(6a); C-7a/H-2a(6a),H-8a; C-8a/H-7a,H-10a(14a); C-9a/H-7a,H-8a; C-10a(14a)/H-12a; C-11a(13a)/H-10a(14a),H-12a,OH-11a(13a); C-12a/H-10a(14a),H-11a(13a); C-1b/H-3b(5b); C-4b/H-2b(6b); C-10b/H-12b,H-14b; C-11b/H12b; C-12b/OH-13b; C-13b/H-12b,H-14b,OH-13b; C-14b/OH-13b; C-1c/H-5c; C-2c/H-6c; C-3c/H-5c; C-4c/H-2c,H-6c, NOESY correlations: See Fig. 7 (selected) and H-2a(6a)/H-7a; H-8a/H-10a(14a); H-2b(6b)/H-7b; H-8b/H-14b.

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