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FIVE NEW OLIGOSTILBENES WITH ONE OR TWO DIHYDROFURANS FROM THE STEM BARK OF *VATICA RASSAK*

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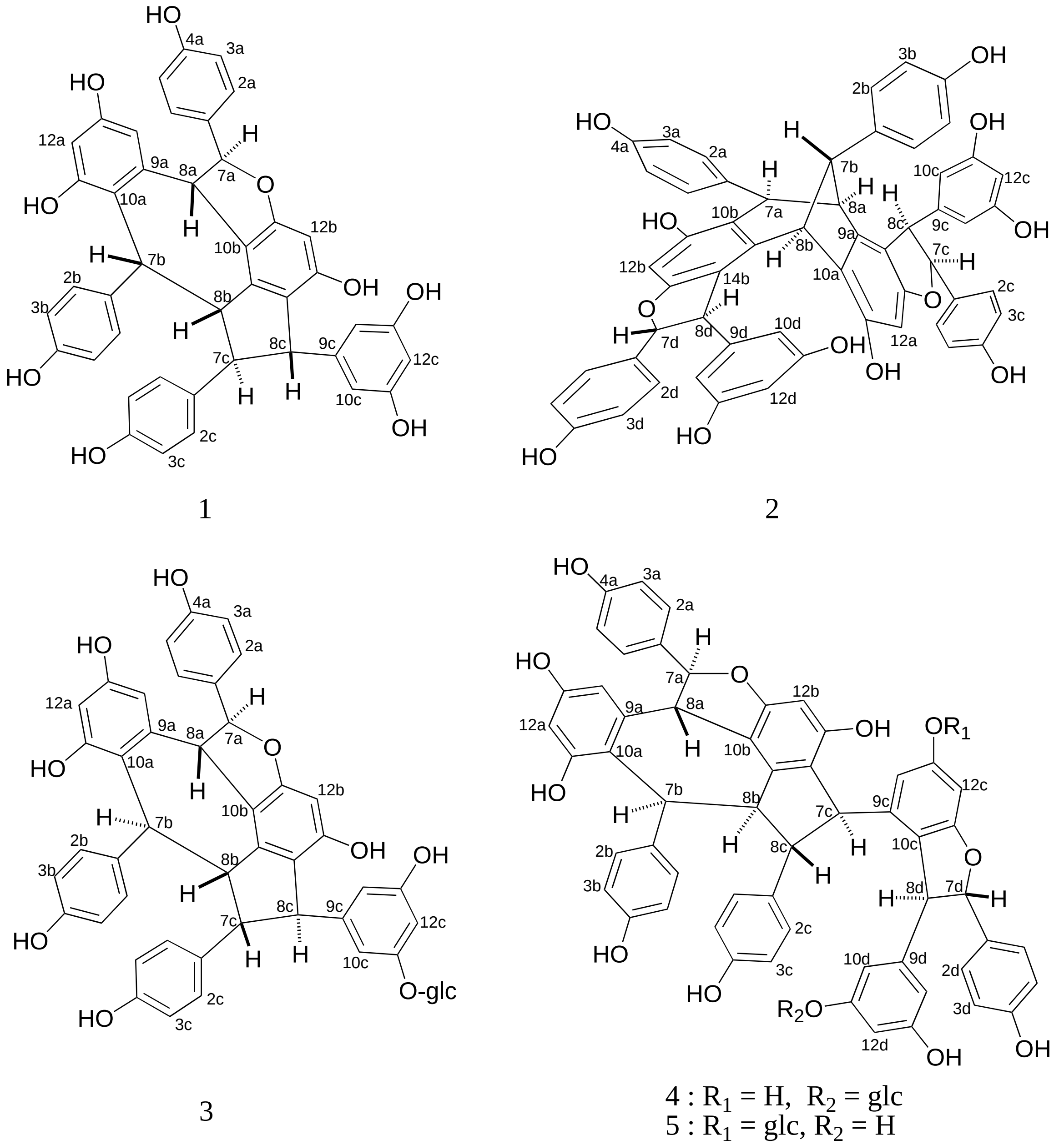
Abstract - From the stem bark of *Vatica rassak*, five new stilbenoids (vaticanols E, F and vaticasides A-C) were isolated. The structures including the relative configuration were established on the basis of spectroscopic analysis.

Plants belonging to the family Dipeterocarpaceae are known to abundant source of stilbenoids.[1, 2] Various biological effects such as chemopreventive,[3] anti-inflammatory activity,[4] and inhibitory activity of histamine release[5] and gastric ATPase[6] have been recently found in the stilbene derivatives. Stilbenoids are then regarded as useful candidates for drug development. In continuation of our phytochemical studies[7-11] of Dipterocarpaceous plants oriented to search for biological active principles, the structures of stilbenoids in some plants of *Hopea*,[7] *Vatica*,[8, 9] and *Shorea*[10, 11] were characterized and their distinctive cytotoxicty was disclosed.[12]

In our preceding papers dealt with oligostilenes in the stem bark of *Vatica rassak*, the structures of a stilbene trimer (vaticanol A),[8] two tetramers (vaticanols B and C)[8] and a hexamer (vaticanol D),[9] were described. They are commonly composed of a 3,5,4'-trihydroxystilbene (resveratrol). Further investigation of the acetone extract resulted in isolation of two new oligostilbenoids, vaticanols E (**1**) and F (**2**), together with three new *O*-glucosyl oligostilbenoids, vaticasides A-C (**3**-**5**). This paper deals with their structure elucidation including the relative configuration.

Vaticanol E (**1**), a pale yellow amorphous powder, showed a positive reaction to the Gibbs test. The absorption band in the UV spectra showed the presence of aromatic rings (284 nm). The $[M-H]^-$ ion peak at *m/z* 679.1971 in the high-resolution (HR) FABMS corresponds to the molecular formula of $C_{42}H_{32}O_9$. The ^1H NMR spectrum (Table) showed the presence of three 4-hydroxyphenyl groups [δ 7.77,



3

4 : R_1 = H, R_2 = glc
5 : R_1 = glc, R_2 = H

Figure 1

6.99 (2H each, d, *J* = 8.3 Hz, H-2a, 6a and 3a, 5a); δ 6.05, 6.32 (2H each, d, *J* = 8.6 Hz, H-2b, 6b and 3b, 5b); δ 7.20, 6.85 (2H each, d, *J* = 8.6 Hz, H-2c, 6c and 3c, 5c)] and a 3,5-dihydroxyphenyl group [δ 6.30 (2H, d, *J* = 2.0 Hz, H-10c and 14c), 6.13 (1H, t, *J* = 2.0 Hz, H-12c)]. The spectrum also exhibited a set of *meta*-coupled aromatic protons on a 1,2,3,5-tetrasubstituted benzene ring [δ 6.15 (1H, d, *J* = 2.0 Hz, H -12a), 6.12 (1H, br d, *J* = 2.0 Hz, H-14a)] and an aromatic proton on a pentasubstituted benzene ring [δ 6.08 (1H, s, H-12b)]. A sequence of four aliphatic methine protons coupled successively in the ^{1}H-^{1}H COSY spectrum (Figure 2) in the order [δ 4.83 (1H, d, *J* = 2.9 Hz, H-7b), 4.30 (1H, dd, *J* = 8.3, 2.9 Hz, H-8b), 4.07 (1H, dd, *J* = 10.3, 8.3 Hz, H-7c), 3.59 (1H, d, *J* = 10.3 Hz, H-8c)] and a set of mutually coulped aliphatic protons [δ 5.66 (1H, d, *J* = 9.3 Hz, H-7a), 5.35 (1H, d, *J* = 9.3 Hz, H-8a)] were shown

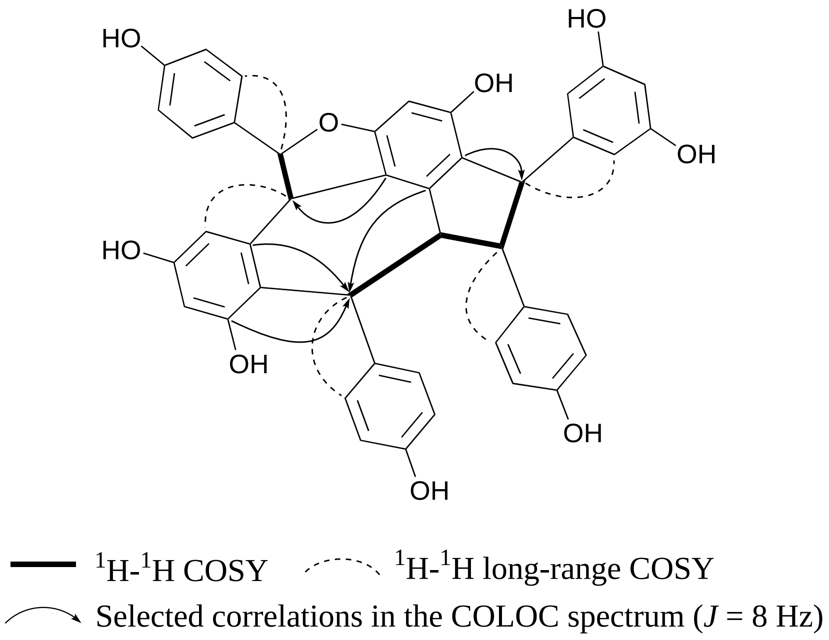


Figure 2 Connection of partial structures of **1**

in addition to eight phenolic hydroxyl groups (δ 6.45 - 8.68) in the spectrum. These results suggested that **1** was a stilbene trimer composed of three resveratrol units [resveratrol A (ring A_1-7a -8a-ring A_2) – resveratrol C (ring C_1-7c-8c-ring C_2)]. Analysis of the ^{13}C-^{1}H COSY and COLOC spectrum enabled the complete assignment of all protonated and quaternary carbons on the six aromatic rings (ring A_1 – ring C_2) and established the position of the hydyoxyl groups. In the ^{1}H-^{1}H long-range COSY spectrum (Figure 2), clear cross peaks were observed between the aromatic protons and the methine protons as follows; H-2a(6a)/H-7a, H-14a/H-8a, H-2b(6b)/H-7b, H-2c(6c)/H-7c and H-10c(14c)/H-8c, which indicated the respective connections of C-1a/C-7a, C-9a/C-8a, C-1b/C-7b, C-1c/C-7c and C-9c/C-8c. In the COLOC spectrum (Figure 2), the carbon signals at δ140.4 (C-9a) and δ 157.9 (C-11a) showed a cross peak with the methine proton at δ 4.83 (H-7b). From these cross peaks, the linkage between C-9a and C-7b was substantiated. The linkages; C-10b/C-8a, C-9b/C-8b and C-14b/C-8c, were deduced by the correlations of C-10b/H-8a, C-9b/H-7b and C-14b/H-8c. Although a long-range correlation between C-11b/H-7a was not observed, the presence of a dihydrofran ring in **1** could be considered by the molecular formula. The planar structure of **1** was then deduced as shown in Figure 2. For confirmation of the relative stereochemistry and explanation of the upper field shift of the hydrogens [H-2b(6b) and OH-13b], NOE experiments were examined (Figure 3). In this study, significant NOEs were observed between H-8a/H-2a(6a), and H-7a/H-14a, suggesting that the orientation of the dihydrofran ring was *trans*. The methine hydrogen signals (H-8b and H-8c) showed NOE interactions with the aromatic protons on ring C_1 [H-2c(6c)]. The former (H-8b) was further displayed an NOE with H-8a, which can be observed only when H-8a, H-8b and H-8c are situated in the same configuration and in an opposite side to H-7c. The configuration of H-7b was confirmed to be β, which reasonably explained that the upper field shift of H-2b(6b) was caused by anisotropic effect of ring B_2. The relative configuration on the benzocyclopentane ring [8b(β), 7c(α) and 8c(β)] explained the upper field shift of OH-13b which situated on the ring C_2. On

Table ^{1}H and ^{13}C NMR Spectral Data of **1** and **2**

No.	**1***		**2****	
	δH	δC	δH	δC
1a		133.5		138.5
2a, 6a	7.77 (d, *J* = 8.3)	130.6	7.08 (d, *J* = 8.3)	129.8
3a, 5a	6.99 (d, *J* = 8.3)	116.4	6.68 (d, *J* = 8.3)	115.6
4a (OH)	8.68 (br s)	158.6		156.1
7a	5.66 (d, *J* = 9.3)	95.6	4.33 (br d)	46.3
8a	5.35 (d, *J* = 9.3)	52.3	3.22 (br s)	51.6
9a		140.4		143.8
10a		123.5		128.1
11a (OH)	7.93 (br s)	157.9		153.2
12a	6.15 (d, *J* = 2.0)	102.0	6.18 (s)	96.3
13a (OH)	8.02 (br s)	156.3		160.1
14a	6.12 (br d, *J* = 2.0)	108.0		120.1
1b		132.8		134.2
2b, 6b	6.05 (d, *J* = 8.6)	132.9	6.17 (d, *J* = 8.8)	129.5
3b, 5b	6.32 (d, *J* = 8.6)	113.7	6.33 (d, *J* = 8.8)	115.4
4b (OH)	7.88 (br s)	155.9[a]		155.7
7b	4.83 (d, *J* = 2.9)	42.4	3.42 (s)	49.6
8b	4.30 (dd, *J* = 8.3, 2.9)	51.2[b]	3.96 (s)	48.3
9b		144.1		144.1
10b		116.0		114.6
11b		160.4		157.8
12b	6.08 (s)	96.3	6.17 (s)	95.8
13b (OH)	6.45 (br s)	155.6		159.8
14b		123.8		117.7
1c		130.3		138.5
2c, 6c	7.20 (d, *J* = 8.6)	131.3	7.15 (d, *J* = 8.8)	128.6
3c, 5c	6.85 (d, *J* = 8.6)	115.4	6.65 (d, *J* = 8.8)	115.2
4c (OH)	8.26 (br s)	156.3[a]		157.0
7c	4.07 (dd, *J* = 10.3, 8.3)	58.1	5.97 (d, *J* = 8.3)	90.0
8c	3.59 (d, *J* = 10.3)	51.2[b]	4.90 (d, *J* = 8.3)	53.1
9c		148.1		143.2
10c	6.30 (d, *J* = 2.0)	107.6	6.10 (br s)	109.1
11c (OH)	8.02 (br s)	159.3		158.9
12c	6.13 (t, *J* = 2.0)	101.7	6.04 (t, *J* = 2.0)	101.7
13c (OH)	8.02 (br s)	159.3		158.9
14c	6.30 (d, *J* = 2.0)	107.6	6.10 (br s)	109.1
1d				134.3
2d, 6d			7.22 (d, *J* = 8.8)	128.6
3d, 5d			6.82 (d, *J* = 8.8)	116.0
4d				158.1
7d			5.41 (d, *J* = 6.4)	94.2
8d			4.93 (d, *J* = 6.4)	56.6
9d				148.3
10d			6.37 (d, *J* = 2.0)	107.4
11d				159.8
12d			6.35 (t, *J* = 2.0)	101.9
13d				159.8
14d			6.37 (d, *J* = 2.0)	101.9
OH			7.62-8.43 (10xOH)	

Measured in CD_3COCD_3. * 400 MHz (^{1}H) and 100 MHz (^{13}C). ** 500 MHz (^{1}H) and 125 MHz (^{13}C).

a : interchangeable., b : overlapping.

the basis of these results, the relative structure of vaticanol E was characterized as **1**. Vaticanol A[8] isolated from an identical extract has the same planar structure as **1**. Then, vaticanol E is one of stereoisomers of vaticanol A.

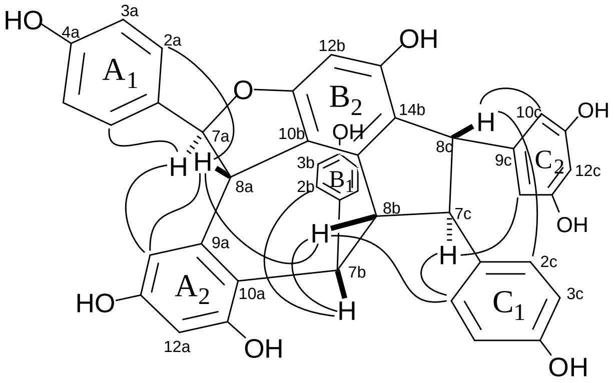


Figure 3 NOEs in the DIFNOE spectrum of **1**

Vaticanol F (**2**), a brown amorphous powder, reacted positive to Gibbs reagent and had the molecular formula of $C_{56}H_{42}O_{12}$ supported by the HR-FABMS ($[M-H]^-$: *m/z* 905.2609). The ^{1}H NMR spectrum showed the presence of four sets of *ortho*-coupled aromatic protons assigned to four 4-hydroxyphenyl groups [δ 7.08, 6.68 (2H each, d, *J* = 8.3 Hz, H-2a, 6a and 3a, 5a); δ 6.17, 6.33 (2H each, d, *J* = 8.8 Hz, H-2b, 6b and 3b, 5b); δ 7.15, 6.65 (2H each, d, *J* = 8.8 Hz, H-2c, 6c and 3c, 5c); δ 7.22, 6.82 (2H each, d, *J* = 8.8 Hz, H-2d, 6d and 3d, 5d)] and two 3,5-dihydroxyphenyl groups [δ 6.10 (2H, br s, H-10c and 14c), 6.04 (1H, t, *J* = 2.0 Hz, H-12c); δ 6.37 (2H, d, *J* = 2.0 Hz, H-10d and 14d), 6.35 (1H, t, *J* = 2.0 Hz, H-12d)]. Two aromatic protons on a pentasubstituted benzene ring [δ 6.18 (1H, s, H-12a); 6.17 (1H, s, H-12b)], four aliphatic methine protons [δ 4.33 (1H, br d, H-7a), 3.22 (1H, br s, H-8a), 3.42 (1H, s, H-7b), 3.96 (1H, s, H-8b)] and two sets of mutually coupled aliphatic protons assignable to two dihydrofuran rings [δ 5.97 (1H, d, *J* = 8.3 Hz, H-7c), 4.90 (1H, d, *J* = 8.3 Hz, H-8c); δ 5.41 (1H, d, *J* = 6.4 Hz, H-7d), 4.93 (1H, d, *J* = 6.4 Hz, H-8d)] were also exhibited in the spectrum in addition to ten phenolic hydroxyl groups (δ 7.62-8.43) as shown in Table. These results showed that **2** was a resveratrol tetramer with two dihydrofuran units. In the HMBC spectrum (Figure 4), significant ^{3}J long range correlations were observed between H-2a(6a) /C-7a and H-2b(6b)/C-7b, indicating that rings A_1 and B_1 were connected at C-7a and C-7b, respectively. Other ^{3}J long range correlations were observed between H-8a/C-1a, H-8b/C-8a, H-8a/C-1b and H-8b/C-1b. The methine protons were connected in the order, H-7a, H-8a, H-7b and H-8b. Long range correlations were observed between the aliphatic methine protons and the quaternary carbons on the two penta-substituted benzene rings (rings A_2 and B_2) as follows; 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 **2** had a dibenzobicyclo[3.2.1]octadiene system. On the basis of HMBC spectral analysis, the two dihydrofuran units were joined at rings A_2 and B_2 as shown in Figure 4. The planar structure of **2** was then determined to be the same as vaticanol C.[8] In the NOESY experiment, a distinct NOE between H-7b/H-2a(6a) showed that the configuration of H-7b is the same as that of ring A_1. NOEs between H-7d/H-10d(14d) and H-8d/H-2d(6d) indicated that two methine protons (H-7d and H-8d) on the dihydrofuran ring were

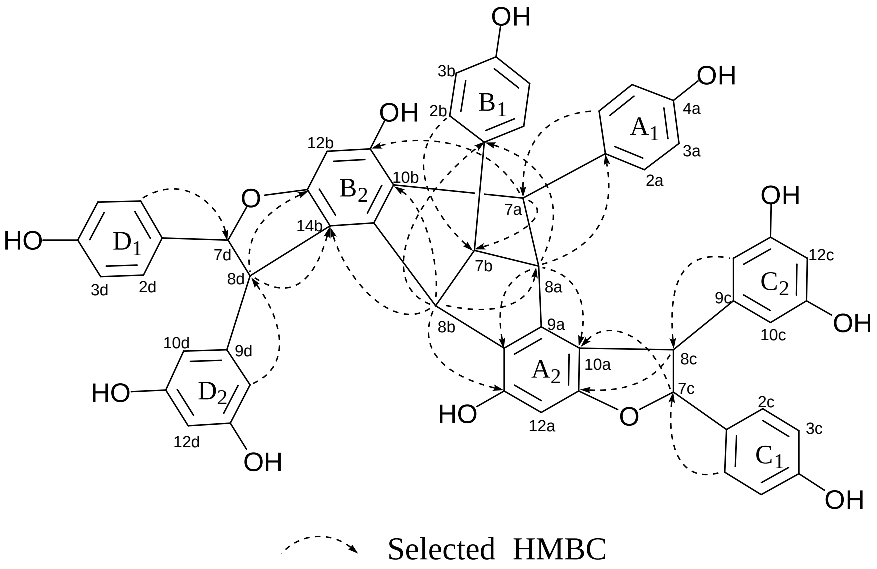


Figure 4 Correlations observed in the HMBC spectrum of **2**

trans. By comparison of vaticanol C and amplelopsin F[13] which have the same planar structure including the dibenzobicyclo[3.2.1]octadiene moiety, the relative stereochemistry of the ring system was concluded tobe the same as those compounds. The relationship between the ring system and the two dihydrofran unitswas determined as follows. A distinct NOEs (H-7a/H-8c and H-8b/H-8d), which were observed as in the case of vaticanol C, suggested that the relative configulations including three methine protons (H-8c, H-7d and H-8d) were identical with those of vaticanol C. The difference between **2** and vaticanol C was the configuration attributed to H-7c which was situated in *cis* towards H-8c. These results were supported by the differences of chemical shift values of 7c (δ_H 5.97, δ_C 90.0) and 8c (δ_H 4.90, δ_C 53.1) by comparison to those of vaticanol C [7c (δ_H 5.61, δ_C 94.3) and 8c (δ_H 4.56, δ_C 57.9)]. The aromatic protons on ring C_2 (δ 6.10) were observed at a lower field compared to that of vaticanol C (δ 6.55). The lower field shift was explained by anisotropic effect of ring C_1. Thus the relative stereostructure of **2** was

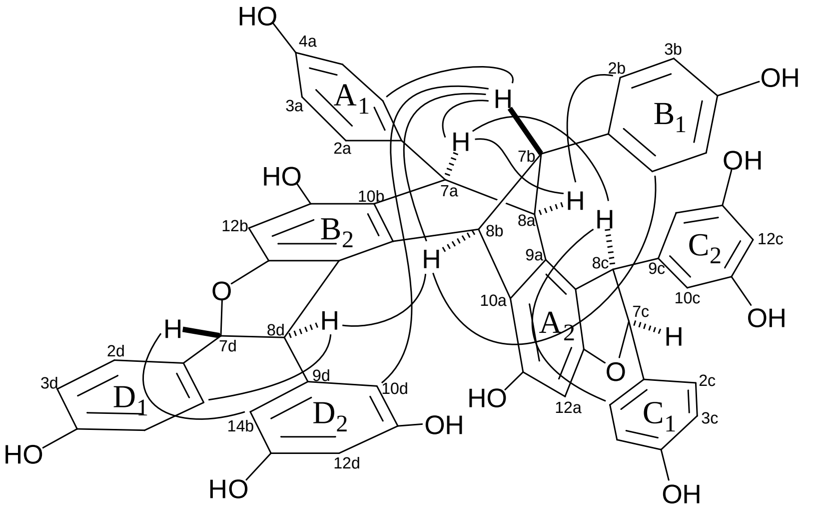


Figure 5 NOEs in the NOESY experiments in **2**

confirmed as shown in Figure 5.

Vaticaside A (**3**) was isolated as a brown amorphous powder. Its molecular formula was established as $C_{48}H_{42}O_{14}$ by the results of the HR-FABMS ($[M-H]^-$: *m/z* 841.2500) and ^{13}C NMR spectral data. The presence of a *β*-glucopyranosyl moiety was supported by the NMR spectra which showed six carbon signals at δC 101.7, 74.6, 77.5, 71.1, 77.9, 62.5 and an anomeric proton at δH 4.90 (1H, d, *J* = 7.7 Hz). The ^1H and ^{13}C NMR spectral data except for the *β*-glucopyranosyl moiety showed closed similarity to those of vaticanol A.[8] Acid hydrolysis of **3** with H_2SO_4 in MeOH gave vaticanol A. Those results indicated that **3** was a *β*-glucopyranoside of vaticonol A. To confirm the location of the glucosidic linkage, the ^1H and ^{13}C NMR signals were assigned by ^1H-^1H COSY, ^1H-^1H long-range COSY, ^{13}C-^1H COSY, COLOC spectra. In the NOE experiment, the aromatic protons (δ 6.46 and δ 6.43) assignable to H-10c and H-12c were enhanced when the anomeric proton (δ 4.90) was irradiated. Therefore, the glucosyl moiety was attached at C-11c of vaticanol A. Consequently, the structure of **3** was characterized as vaticanol A-11c-*O*-*β*-glucopyranoside. The detail of NMR spectral data assigned by the aid of 2D NMR are shown in experimental section.

Vaticaside B (**4**), obtained as a brown amorphous powder, gave positive reaction to Gibbs reagent and had the molecular formula of $C_{62}H_{52}O_{17}$ supported by the HR-FABMS (*m/z* 1067.3104). The ^1H and ^{13}C NMR spectral data closely resembled those of vaticanol B[8] except for the presence of an *O*-glucopyranosyl moiety [δH 5.01 (1H, d, *J* = 7.7 Hz); δC 101.0, 74.9, 77.9, 71.5, 78.0, 63.0]. Acid hydrolysis of **4** gave vaticanol B. The location of the *O*-glucosyl moiety was determined to be at C-11d by NOEs which supplied the effects between the anomeric proton (δ 5.01) and the two aromatic protons at H-10d (δ 6.47) and H-12d (δ 6.47). Therefore, the structure of **4** was concluded to be vaticanol B-11d-*O*-*β*-glucopyranoside.

Vaticaside C (**5**), a blown amorphous powder, gave a molecular ion peak at *m/z* 1067.3124 in the HR-FABMS corresponding to the molecular formula $C_{62}H_{52}O_{17}$. The pattern of the ^1H and ^{13}C NMR spectral data was similar to those of **4**. The difference was the position of the *O*-glucosidic linkage in the molecule. In the NOE experiment of **5**, irradiation of the anomeric proton (δ 4.91) caused enhancement of two aromatic protons assigned to H-12c (δ 6.34) and H-14c (δ 6.55). The structure was then determined to be vaticanol B-13c-*O*-*β*-glucopyranoside.

As far as we know, vaticasides B and C are the first instances of a glucoside of resveratrol tetramer.

EXPERIMENTAL

General Method

The following instruments were used: FABMS spectra, JEOL JMS-DX-300 instrument; ^1H and ^{13}C NMR spectra, JEOL JNM A-500, EX-400 and LA-300 (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 F254 (0.25 mm); preparative TLC, Merck Kieselgel 60 F254 (0.5 mm); column chromatography, Merck Kieselgel 60, Pharmacia Fine Chemicals AB Sephadex LH-20 and Fuji Silysia Chemical Chromatorex; vacuum liquid chromatography (VLC), Merck Kieselgel 60.

Plant material.

Stem bark of *Vatica rassak* was collected in Indonesia in October, 1997.

Extraction and isolation

The dried and ground stem bark (700 g) of *V. rassak* was extracted successively with acetone (3L x 24h x 3), MeOH (3L x 24h x 3) and 70% MeOH (3 L x 24h x 3) at rt. Concentrated extracts gave respective residues; 120 g (acetone), 80 g (MeOH) and 35 g (70% MeOH). A part of the acetone extract (60 g) was subjected to chromatography on silica gel column eluted with a mixture of $CHCl_3$-MeOH increasing in the polarity to give 19 fractions (Fr. 1 - 19). Fr. 6 [$CHCl_3$-MeOH (10:1), 1.2 g] was further chromatographed by VLC eluted with $CHCl_3$-MeOH mixtures. The $CHCl_3$-MeOH (8:1) fraction of the chromatography gave **1** (220 mg). Fr. 8 [$CHCl_3$-MeOH (10:1), 11.2 g] was further divided into 11 fractions (Frs. 8.1-8.11) by VLC eluted with $CHCl_3$-MeOH mixtures. The 11th fraction [$CHCl_3$-MeOH (10:1), 1.5 g] was chromatographed repeatedly with VLC and Sephadex LH 20 (MeOH) to give **2** (8 mg). Fr. 14 [$CHCl_3$-MeOH (5:1), 13.3 g] was further subjected to chromatography on reversed phase silica gel column eluted with a mixture of H_2O-MeOH mixture (5% - 40% MeOH) to give six fractions. The third fraction (25% MeOH, 2.4 g) was further purified with Sephadex LH 20 (MeOH), and PTLC [EtOAc-$CHCl_3$-MeOH-H_2O (15:8:4:1) to give **3** (15 mg), **4** (12 mg) and **5** (5 mg), respectively.

Vaticanol E (1) : A pale yellow amorphous powder. Negative ion HR-FAB-MS: $[M-H]^-$ *m/z* 679.1971 (Calcd 679.1968 for $C_{42}H_{31}O_9$); Negative ion FABMS: $[M-H]^-$ *m/z* 679; UV λ (nm): 217, 284; $[\alpha]_D$ +177 ° (c= 0.1, MeOH); The ^1H and ^{13}C NMR spectral data are listed in Table.

Vaticanol F (2) : A brown amorphous powder. Negative ion HR-FAB-MS: $[M-H]^-$ *m/z* 905.2609 (Calcd 905.2598 for $C_{56}H_{41}O_{12}$); Negative ion FAB-MS: $[M-H]^-$ *m/z* 905; UV λ (nm): 228, 282; $[\alpha]_D$ +5 ° (c= 0.1, MeOH); The ^1H and ^{13}C NMR spectral data are shown in Table.

Vaticaside A (3) : A brown amorphous powder. Negative ion HR-FABMS: $[M-H]^-$ *m/z* 841.2500 (Calcd 841.2496 for $C_{48}H_{41}O_{14}$); Negative ion FAB-MS: $[M-H]^-$ *m/z* 841; UV λ(nm): 224, 282; $[\alpha]_D$ -79 ° (c= 0. 1, MeOH); ^1H NMR [400 MHz, $(CD_3)_2CO$] δ: 7.28 [2H, d, J = 8.8 Hz, H-2a(6a)], 6.82 [2H, d, J = 8.8 Hz, H-3a(5a)], 6.17 [1H, d, J = 3.9 Hz, H-7a], 4.51 [1H, d, J = 3.9 Hz, H-8a], 6.08 [1H, d, J = 2.4 Hz, H-12a], 6.47 [1H, d, J = 2.4 Hz, H-14a], 7.06 [2H, d, J = 8.8 Hz, H-2b(6b)], 6.59 [2H, d, J = 8.8 Hz, H-3b(5b)], 5.16 [1H, s, H-7b], 4.47 [1H, d, J = 6.8 Hz, H-8b], 6.23 [1H, s, H-12b], 6.56 [2H, d, J = 8.8 Hz, H-2c(6c)], 6.37 [2H, d, J = 8.8 Hz, H-3c(5c)], 3.70 [1H, d, J = 6.8 Hz, H-7c], 4.23 [1H, s, H-8c], 6.46 [1H, d, J = 2.0 Hz, H-10c], 6.43[a] [1H, t, J = 2.0 Hz, H-12c], 6.43[a] [1H, d, J = 2.0 Hz, H-14c], 7.33-8.39 [7H, br s, 7xOH], 4.90 [1H, d, J = 7.7 Hz, H-glc-1], 3.42[b] [1H, m, H-glc-2], 3.42[b] [1H, m, H-glc-3], 3.77 [1H, m, H-glc-4], 3.50 [1H, m, H-glc-5], 3.70, 3.81 [1H, m, H-glc-6]; ^{13}C NMR [100 MHz, $(CD_3)_2CO$] δ:

134.4 (C-1a), 128.1 [C-2a(6a)], 116.1 [C-3a(5a)], 158.0 (C-4a), 86.8 (C-7a), 50.4 (C-8a), 144.8 (C-9a), 119.4 (C-10a), 157.8 (C-11a), 101.4 (C-12a), 156.4 (C-13a), 103.4 (C-14a), 138.7 (C-1b), 129.3 [C-2b(6b)], 115.5 [C-3b(5b)], 155.8 ^{c} (C-4b), 36.1 (C-7b), 48.7 (C-8b), 144.9 (C-9b), 118.8 (C-10b), 160.1 (C-11b), 95.4 (C-12b), 155.6 (C-13b), 122.0 (C-14b), 135.7 (C-1c), 129.7 [C-2c(6c)], 115.0 [C-3c(5c)], 156.5 ^{c} (C-4c), 64.2 (C-7c), 57.5 (C-8c), 147.4 (C-9c), 108.1 (C-10c), 159.9 (C-11c), 102.1 (C-12c), 159.1 (C-13c), 108.9 (C-14c), 101.7 (C-glc-1), 74.6 (C-glc-2), 77.5 (C-glc-3), 71.1 (C-glc-4), 77.9(C-glc-5), 62.5 (C-glc-6). (^{a,b}overalapping, ^{c}interchangeable)

Vaticaside B (4) : A brown amorphous powder. Negative ion HR-FABMS: [M-H]$^-$ *m/z* 1067.3104 (Calcd 1067.3126 for $C_{62}H_{51}O_{17}$); Negative ion FAB-MS: [M-H]$^-$ *m/z* 1067; UV λ(nm): 219, 284; [α]$_D$ –46 ° (c= 0.1, MeOH); ^{1}H NMR [400 MHz, $(CD_3)_2CO$] δ: 7.28 [2H, d, *J* = 8.8 Hz, H-2a(6a)], 6.78 [2H, d, *J* = 8.8 Hz, H-3a(5a)], 5.78 [1H, d, *J* = 12.2 Hz, H-7a], 4.42 [1H, d, *J* = 12.2 Hz, H-8a], 6.29 [1H, d, *J* = 2.0 Hz, H-12a], 6.11 [1H, d, *J* = 2.0 Hz, H-14a], 7.16 [2H, d, *J* = 8.8 Hz, H-2b(6b)], 6.68 [2H, d, *J* = 8.8 Hz, H-3b(5b)], 5.19 [1H, d, *J* = 3.9 Hz, H-7b], 3.32 [1H, dd, *J* = 11.3, 3.9 Hz, H-8b], 6.03 [1H, s, H-12b], 6.45 [2H, d, *J* = 8.8 Hz, H-2c(6c)], 6.47 [2H, d, *J* = 8.8 Hz, H-3c(5c)], 4.02 [1H, dd, *J* = 11.3, 10.7 Hz, H-7c], 4.44 [1H, d, *J* = 10.7 Hz, H-8c], 6.23 [1H, d, *J* = 2.4 Hz, H-12c], 6.47 [1H, d, *J* = 2.4 Hz, H-14c], 7.19 [2H, d, *J* = 8.8 Hz, H-2d(6d)], 6.75 [2H, d, *J* = 8.8 Hz, H-3d(5d)], 5.30 [1H, d, *J* = 3.9 Hz, H-7d], 4.58 [1H, d, *J* = 3.9 Hz, H-8d], 6.47 ^{a} [3H, br s, H-10d, 12d and 14d], 7.88-8.45 [9H, br s, 9xOH], 5.01 [1H, d, *J* = 7.7 Hz, H-glc-1], 3.50 [1H, m, H-glc-2], 3.40-3.55 [3H, m, H-glc-3(glc-4)(glc-5)], 3.66, 3.70 [1H, m, H-glc-6]; ^{13}C NMR [100 MHz, $(CD_3)_2CO$] δ: 131.0 (C-1a), 130.3 [C-2a(6a)], 116.2 ^{b} [C-3a(5a)], 158.7 (C-4a), 90.6 (C-7a), 49.0 (C-8a), 141.9 ^{c} (C-9a), 124.9 (C-10a), 155.9 (C-11a), 101.8 (C-12a), 156.9 (C-13a), 105.9 (C-14a), 133.7 (C-1b), 130.8 [C-2b(6b)], 115.7 [C-3b(5b)], 156.0 (C-4b), 37.4 (C-7b), 55.6 (C-8b), 143.6 (C-9b), 115.9 (C-10b), 159.7 (C-11b), 96.6 (C-12b), 155.0 (C-13b), 122.2 (C-14b), 131.5 (C-1c), 128.9 [C-2c(6c)], 116.2 ^{b} [C-3c(5c)], 156.3 (C-4c), 58.6 (C-7c), 51.1 (C-8c), 142.7 ^{c} (C-9c), 123.3 (C-10c), 161.9 (C-11c), 96.0 (C-12c), 159.5 (C-13c), 107.3 (C-14c), 134.8 (C-1d), 128.3 [C-2d(6d)], 116.2 ^{b} [C-3d(5d)], 158.2 (C-4d), 94.7 (C-7d), 57.0 (C-8d), 148.2 (C-9d), 107.4 (C-10d), 159.8 (C-11d), 102.5 (C-12d), 159.1 (C-13d), 108.7 (C-14d), 101.0 (C-glc-1), 74.9 (C-glc-2), 77.9 (C-glc-3), 71.5 (C-glc-4), 78.0 (C-glc-5), 63.0 (C-glc-6). (^{a,b}overalapping, ^{c}interchangeable).

Vaticaside C (5) : A brown amorphous powder. Negative ion HR-FABMS: [M-H]$^-$ *m/z* 1067.3124 (Calcd 1067.3126 for $C_{62}H_{51}O_{17}$); Negative ion FAB-MS: [M-H]$^-$ *m/z* 1067; UV λ(nm): 213, 283; [α]$_D$ +1 ° (c= 0.1, MeOH); ^{1}H NMR [300 MHz, $(CD_3)_2CO$] δ: 7.18 [2H, d, *J* = 8.8 Hz, H-2a(6a)], 6.73 [2H, d, *J* = 8.8 Hz, H-3a(5a)], 8.44 [1H, br s, OH-4a], 5.71 [1H, d, *J* = 11.7 Hz, H-7a], 4.41 [1H, d, *J* = 11.7 Hz, H-8a], 8.17 [1H, br s, OH-11a], 6.23 [1H, d, *J* = 2.0 Hz, H-12a], 8.00 [1H, br s, OH-13a], 6.06 [1H, br s, H-14a], 7.13 [2H, d, *J* = 8.8 Hz, H-2b(6b)], 6.69 [2H, d, *J* = 8.8 Hz, H-3b(5b)], 8.14 [1H, br s, OH-4b], 5.17 [1H, d, *J* = 3.6 Hz, H-7b], 3.08 [1H, dd, *J* = 11.3, 3.6 Hz, H-8b], 6.00 [1H, s, H-12b], 7.68 [1H, br s, OH-13b], 6.45 [2H, d, *J* = 8.8 Hz, H-2c(6c)], 6.38 [2H, d, *J* = 8.8 Hz, H-3c(5c)], 7.85 [1H, br s, OH-4c], 4.05 [1H, t, *J* = 11.3 Hz, H-7c], 4.53 [1H, d, *J* = 11.3 Hz, H-8c], 6.34 [1H, d, *J* = 2.0 Hz, H-12c], 6.55 [1H, d, *J* = 2.0 Hz, H-14c], 7.15 [2H, d, *J* = 8.8 Hz, H-2d(6d)], 6.72 [2H, d, *J* = 8.8 Hz, H-3d(5d)], 8.34 [1H, br s, OH-4d], 5.35 [1H, d, *J* = 5.5 Hz, H-7d], 4.70 [1H, d, *J* = 5.5 Hz, H-8d], 6.05 [1H, br s, H-10d(14d)], 7.98 [1H, br s, OH-11d(13d)], 6.25 [1H, t, *J* = 2.0 Hz, H-12d], 4.91 [1H, d, *J* = 7.5 Hz, H-glc-1], 3.25-3.56 [6H, m, H-glc-2(glc-3)(glc-4)(glc-5)]; ^{13}C NMR [75 MHz, $(CD_3)_2CO$] δ: 130.2 [a] (C-1a), 130.2 [a] [C-2a(6a)], 116.0 [b] [C-3a(5a)], 158.6 (C-4a), 90.4 (C-7a), 49.3 (C-8a), 141.7 [d] (C-9a), 124.5 (C-10a), 155.7 (C-11a), 101.7 (C-12a), 156.7 (C-13a), 105.8 (C-14a), 133.6 (C-1b), 130.7 [C-2b(6b)], 115.8[c] [C-3b(5b)], 155.9 [e] (C-4b), 37.1 (C-7b), 53.2 (C-8b), 143.3 (C-9b), 115.8 [c] (C-10b), 158.8 (C-11b), 96.5 (C-12b), 154.9 (C-13b), 122.1 (C-14b), 131.4 (C-1c), 129.3 [C-2c(6c)], 115.9 [C-3c(5c)], 156.4 (C-4c), 57.3 (C-7c), 48.8 (C-8c), 141.6 [d] (C-9c), 126.1 (C-10c), 161.3 (C-11c), 96.4 (C-12c), 159.7 (C-13c), 107.1 (C-14c), 134.4 (C-1d), 128.3 [C-2d(6d)], 116.0 [b] [C-3d(5d)], 158.1 [e] (C-4d), 94.8 (C-7d), 57.5 (C-8d), 147.6 (C-9d), 107.6 [C-10d(14d)], 159.9 [C-11d(13d)], 102.3 (C-12d), 101.7 (C-glc-1), 74.6 (C-glc-2), 77.3 (C-glc-3), 70.7 (C-glc-4), 77.8 (C-glc-5), 62.0 (C-glc-6). ([a-c] overalapping, [d,e] interchangeable).

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