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Oligostilbenoids in stem bark of *Vatica rassak*

T. Tanaka[a,*], T. Ito[a], K. Nakaya[a], M. Iinuma[a], S. Riswan[b]

[a]*Gifu Prefectural Institute of Health and Environmental Sciences, 1-1 Nakafudogaoka, Kakamigahara 504-0838, Japan*
[b]*Herbarium Bogoriense, The Indonesian Institute of Science, Research and Development Center for Biology, J1 Ir. Juanda 18, Bogor 16122, Indonesia*

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Abstract

Three resveratrol oligomers, vaticanols A, B and C, as well as three known stilbenoids, resveratrol, piceid and ε-viniferin were isolated from the stem bark of *Vatica rassak* (Dipterocarpaceae). Their structures were determined by the analysis of NMR spectral data including the application of 2D methods.

Keywords: *Vatica rassak*; Dipterocarpaceae; Oligostilbene; Vaticanol A; Vaticanol B; Vaticanol C

1. Introduction

Many stilbene derivatives have been isolated from various plants (Sotheeswaran and Pasupathy, 1993), and their biological activities such as chemoprevention of cancers (Jang et al., 1977) and hepatoprotective activity (Oshima et al., 1995) have been reported. Stilbenoids are, therefore, regarded as potential lead compounds for drug development. Dipterocarpaceous plants are a well known and abundant source of stilbenoids (Sotheeswaran and Pasupathy, 1993). In a continuing search for stilbenoids, we report here the structures of three new stilbene derivatives, as well as three known compounds, from the stem bark of *Vatica rassak* (Korth.) Bl.

2. Results and discussion

An acetone extract of the stem bark of *Vatica rassak* (Korth.) Bl. was subjected to silica gel column chromatography (silica gel CC) eluted with a $CHCl_3$–MeOH solvent system. The resulting fractions were further purified by silica gel CC, vacuum liquid chromatography, Sephadex LH 20 CC and preparative TLC to give six compounds.

Compound **1**, vaticanol A, obtained as a pale yellow amorphous powder, showed a positive reaction to Gibbs reagent. The compound gave an $[M–H]^-$ ion peak at m/z 679 in negative ion FABMS corresponding to the molecular formula $C_{42}H_{32}O_9$, which suggested that **1** was a stilbene trimer. The ^1H NMR spectrum (Table 1) showed the presence of three sets of *ortho*-coupled aromatic protons. They were assignable to three 4-hydroxyphenyl groups [δ 7.28 (2H, *d*, $J = 8.8$ Hz, H-2a, 6a), 6.83 (2H, *d*, $J = 8.8$ Hz, H-3a, 5a); δ 7.07 (2H, *d*, $J = 8.8$ Hz, H-2b, 6b) and 6.60 (2H, *d*, $J = 8.8$ Hz, H-3b, 5b); δ 6.55 (2H, *d*, $J = 8.8$ Hz, H-2c, 6c) and 6.37 (2H, *d*, $J = 8.8$ Hz, H-3c, 5c)] further analysis of the ^1H NMR spectrum revealed a 3,5-dihydroxyphenyl group [δ 0.627 (2H, *d*, $J = 2.0$ Hz, H-10c, 14c), 6.21 (1H, *t*, $J = 2.0$ Hz, H-12c)], a set of *meta*-coupled aromatic protons based on a 1, 2, 3, 5-tetra-substituted benzene ring [δ 6.09 (1H, *d*, $J = 2.4$ Hz, H-12a) and 6.48 (1H, *d*, $J = 2.4$, Hz, H-14a), an aromatic proton of a penta-substituted benzene ring [δ 6.22 (1H, *s*, H-12b)], a sequence of four aliphatic methine protons coupled successively in the ^1H–^1H long-range COSY in the order [δ 5.17 (1H, *br s*, H-7b), 4.52 (1H, *d*, $J = 7.3$ Hz, H-8b), 3.65 (1H, *d*, $J = 7.3$ Hz, H-7c)

* Corresponding author. Fax: +81-9-582-246-1104.
E-mail address: yhy06063@nifty.ne.jp (T. Tanaka).

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and 4.20 (1H, *br s*, H-8c)], and a set of mutually coupled aliphatic protons [δ 6.18 (1H, *br d*, $J = 3.9$ Hz, H-7a) and 4.51 (1H, *d*, $J = 3.9$ Hz, H-8a) in addition to eight phenolic hydroxyl groups [δ 7.31, 7.89, 7.95, 7.97, 8.00, 8.09 ($\times$ 2) and 8.42]. Among them, H-8a (δ 6.18) and H-8b (δ 4.52) were deshielded by aromatic rings (rings A1 and B2, respectively). Analysis of the $^{13}C-^{1}H$ COSY spectrum enabled the complete assignment of all protonated carbons as shown in Table 2. In the ^{1}H–^{1}H long-range COSY spectrum, correlations between the oxymethine proton (H-7a) and H-2a (6a) on the A1 ring, and between H-8a and H-14a on the A2 ring were observed. In the COLOC spectrum (Fig. 1), significant correlations were also observed between C-2a(6a)/H-7a, C-8a/H-14a, C-9a/H-7a, C-10b/H-8a, C-10b/H-12b, C-11b/H-7a and C-11b/H-8a, respectively. These results indicated that the resveratrol A [ring A1-(C-7a)-(C-8a)-ring A2] formed a dihydrobenzofuran ring with ring B2. Additionally, the ^{1}H–^{1}H long-range COSY correlations observed between H-7b/H-2b(6b), H-7c/H-2c(6c) and H-8c/H-10c(14c) indicated that C-7b, C-7c and C-8c were connected to rings B1, C1 and C2, respectively, which was further confirmed by the COLOC correlations. In the COLOC spectrum, long range correlations were observed between C-11a/H-7b, C-10b/H-8b, C-9b/H-

Table 1
^{1}H NMR spectral data (400 MHz) for **1**–**3**, **1a** and **2a**[a]

No.	**1**	**1a**	**2**	**2a**	**3**
2*a*, 6*a*	7.28 (*d*, 8.8)	7.37 (*d*, 8.8)	7.23 (*d*, 8.8)	7.37 (*d*, 8.8)	7.01 (*d*, 8.3)
3*a*, 5*a*	6.83 (*d*, 8.8)	6.90 (*d*, 8.8)	6.79 (*d*, 8.8)	6.89 (*d*, 8.8)	6.65 (*d*, 8.3)
7*a*	6.18 (*br d*, 3.9)	6.36 (*br d*, 3.9)	5.77 (*d*, 11.7)	5.92 (*d*, 11.7)	4.16 (s)
8*a*	4.51 (*d*, 3.9)	4.50 (*d*, 3.9)	4.44 (*d*, 11.7)	4.46 (*d*, 11.7)	3.10 (s)
12*a*	6.09 (*d*, 2.4)	6.11 (*d*, 2.4)	6.29 (*d*, 2.0)	6.48 (*d*, 2.4)	6.12 (s)
14*a*	6.48 (*d*, 2.4)	6.65 (*d*, 2.4)	6.12 (*d*, 2.0)	6.26 (*d*, 2.4)	
2*b*, 6*b*	7.07 (*d*, 8.8)	7.10 (*d*, 8.8)	7.17 (*d*, 8.8)	7.21 (*d*, 8.8)	6.35 (*d*, 8.8)
3*b*, 5*b*	6.60 (*d*, 8.8)	6.68 (*d*, 8.8)	6.70 (*d*, 8.8)	6.78 (*d*, 8.8)	6.45 (*d*, 8.8)
7*b*	5.17 (*br s*)	5.21 (*s*)	5.21 (*d*, 3.9)	5.15 (*d*, 3.4)	3.38 (*s*)
8*b*	4.52 (*d*, 7.3)	4.59 (*d*, 7.3)	3.13 (*dd*, 11.3, 3.9)	3.38 (*dd*, 10.3, 2.0)	3.99 (*s*)
12*b*	6.22 (*s*)	6.40 (*s*)	6.05 (*s*)	6.22 (*s*)	6.16 (*s*)
2*c*, 6*c*	6.55 (*d*, 8.8)	6.55 (*d*, 8.8)	6.42 (*d*, 8.8)	6.58 (*d*, 8.8)	7.24 (*d*, 8.8)
3*c*, 5*c*	6.37 (*d*, 8.8)	6.47 (*d*, 8.8)	6.52 (*d*, 8.8)	6.52 (*d*, 8.8)	6.84 (*d*, 8.8)
7*c*	3.65 (*d*, 7.3)	3.74 (*d*, 7.3)	4.10 (*dd*, 11.3, 10.7)	4.07 (*dd*, 10.3, 9.8)	5.61 (*d*, 7.8)
8*c*	4.20 (*br s*)	4.26 (*s*)	4.55 (*d*, 10.7)	4.37 (*d*, 9.8)	4.56 (*d*, 7.8)
10*c*	6.27 (*d*, 2.0)	6.44 (*d*, 2.0)			6.55 (*d*, 2.0)
12*c*	6.21 (*t*, 2.0)	6.37 (*t*, 2.0)	6.21 (*d*, 2.0)	6.41 (*d*, 2.4)	6.33 (*t*, 2.0)
14*c*	6.27 (*d*, 2.0)	6.44 (*d*, 2.0)	6.49 (*d*, 2.0)	6.51 (*d*, 2.4)	6.55 (*d*, 2.0)
2*d*, 6*d*			7.19 (*d*, 8.8)	7.32 (*d*, 8.8)	7.23 (*d*, 8.8)
3*d*, 5*d*			6.78 (*d*, 8.8)	6.95 (*d*, 8.8)	6.83 (*d*, 8.8)
7*d*			5.38 (*d*, 4.7)	5.39 (*d*, 4.7)	5.43 (*d*, 6.5)
8*d*			4.68 (*d*, 4.7)	4.58 (*d*, 4.7)	4.93 (*d*, 6.5)
10*d*, 14*d*			6.10 (*d*, 2.4)	n.o.	6.40 (*d*, 2.0)
12*d*			6.30 (*t*, 2.4)	n.o.[c]	6.36(*t*, 2.0)
4*a*-OH	8.42		8.48[b]		7.98
11*a*-OH	7.31		8.17		
13*a*-OH	7.95		8.06		8.23
4*b*-OH	8.00		8.16		7.81
13*b*-OH	7.97		7.45		7.51
4*c*-OH	7.89		7.90		8.49
11*c*-OH	8.09				8.35
13*c*-OH	8.09		8.19		8.35
4*d*-OH			8.37[a]		8.46
11*d*, 13*d*-OH			8.01		8.26
OMe		3.26 (3H)		3.20(3H)	
		3.62 (3H)		3.63 (3H)	
		3.68 (3H)		3.66 (3H)	
		3.70 (3H)		3.73 (3H)	
		3.74 (6H)		3.74 (3H)	
		3.76 (3H)		3.77 (15H)	
		3.77 (3H)			

[a] Measured in acetone-d_6. All protons were assigned by ^{1}H–^{1}H long range COSY, ^{13}C–^{1}H COSY, COLOC and NOE experiments.
[b] Interchangeable.
[c] Not observed.

Table 2
^{13}C NMR spectral data (100 MHz) for **1**–**3**, **1a** and **2a**[a]

No.	1	1a	2	2a	3
1*a*	134.4	135.4	130.8	131.8	138.4
2*a*, 6*a*	128.0	128.0	130.2	130.1	130.1
3*a*, 5*a*	116.0	114.7	116.04[b]	114.8	115.7
4*a*	157.9	160.4	158.5	161.0[b]	156.1
7*a*	86.5	86.3	90.4	90.5	45.7
8*a*	50.3	50.5	48.8	49.3	51.2
9*a*	144.7	144.6	141.8	141.1	143.3
10*a*	119.3	121.4	124.5	127.5	128.4
11*a*	157.7	159.6[c]	155.7	158.6	153.5
12*a*	101.30	95.6	101.6	98.1	96.1
13*a*	156.3	159.6[c]	156.7	159.6	161.1
14*a*	103.3	101.9	105.8	105.3	118.7
1*b*	138.7	138.9	133.5	133.9	134.4
2*b*, 6*b*	129.2	129.2	130.7	130.5	129.6
3*b* 5*b*	115.4	114.1	115.5	114.1	115.6
4*b*	155.7$a	158.42[b]	155.9[b]	158.6[b]	155.9
7*b*	36.0	35.6	37.1	37.3	49.8
8*b*	48.6	48.5	53.1	52.5	47.7
9*b*	144.9	144.5	143.2	142.8	144.2
10*b*	118.6	119.2	115.78	115.8	114.8
11*b*	159.9	160.3	158.8	159.4	157.9
12*b*	95.3	92.0	96.5	93.7	96.0
13*b*	155.4	158.46[b]	154.9	158.0	160.0[c]
14*b*	122.2	124.1	122.1	124.6	118.0
1*c*	135.8	136.8	131.4	132.7	133.6
2*c*, 6*c*	129.6	130.0	129.2	128.9	128.2
3*c*, 5*c*	114.9	113.5	115.84	114.1	116.3
4*c*	156.4[b]	159.2	156.3	158.8	158.3[c]
7*c*	64.3	63.9	57.6	58.7	94.3[c]
8*c*	57.5	57.7	49.3	51.6	57.9
9*c*	147.5	147.2	141.6	143.3	146.1
10*c*	106.7	106.4	123.3	123.5	108.2
11*c*	159.2	161.9	161.7	161.6	160.1
12*c*	101.25	98.1	95.6	94.1	102.5
13*c*	159.2	161.9	159.4	162.0	160.1
14*c*	106.7	106.4	107.0	105.8	108.2
1*d*			134.7	135.8	134.3
2*d*, 6*d*			128.2	127.3	128.7
3*d*, 5*d*			115.98[b]	114.7	116.2
4*d*			157.9[b]	160.3[b]	158.3[b]
7*d*			94.6	93.6	94.3[c]
8*d*			57.5	58.0	56.9
9*d*			147.9	147.7	148.5
10*d*, 14*d*			107.5	n.o.[d]	107.6
11*d*, 13*d*			159.8	n.o.	160.0[c]
12*d*			102.2	n.o.	102.0
OMe	55.3 (Cx2)			55.1	
	55.4 (Cx3)			55.2	
	55.5			55.4 (Cx2)	
	55.6			55.6 (Cx4)	
	55.8			55.8	
				57.0	

[a] Measured in acetone-d_6. All carbons were assigned by ^{13}C–^{1}H COSY and COLOC experiments.
[b] Interchangeable.
[c] Overlappinng.
[d] Not observed.

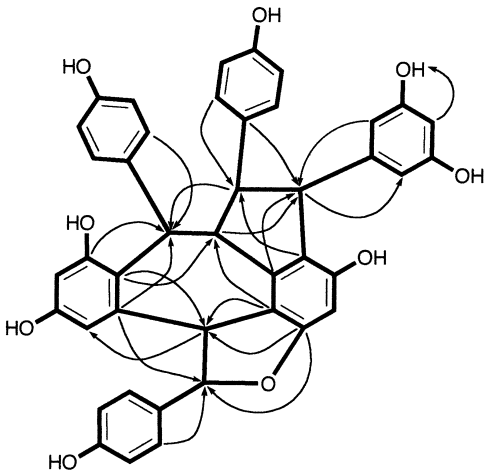


Fig. 1. Significant ^{13}C-^{1}H long range correlations in the COLOC spectrum of **1** (J = 8Hz).

8c, C-14b/H-8c and C-14b/H-7c. Thus, the structure of **1** is as shown in Fig. 1. The relative stereochemistry was determined from the difference NOE spectra of **1** and of a permethyl ether (**1a**) (Fig. 2). NOEs between H-7a/H-14a and H-8a/H-2a(6a) in **1** indicated that two methine protons on the dihydrofuran ring were all *trans*. NOEs were also observed between H-7b/H-2c(6c), H-8c/H-2c(6c), H-8b/H-10c(14c) in **1** and H-8a/H-2b(6b), H-8b/H-2b(6b) in **1a**, respectively. Consequently, the relative stereochemistry of **1** was as shown in Fig. 2.

Compound **2**, vaticanol B, obtained as a pale yellow amorphous powder, showed a positive reaction to Gibbs reagent. Compound **2** gave an $[M–H]^-$ ion peak at m/z 905 in the negative ion FABMS corresponding to the molecular formula $C_{56}H_{42}O_{12}$, which suggested that **2** is a resveratrol tetramer. Its ^{1}H NMR spectrum showed the presence of four sets of *ortho*-coupled aromatic protons assignable to four 4-hydroxyphenyl

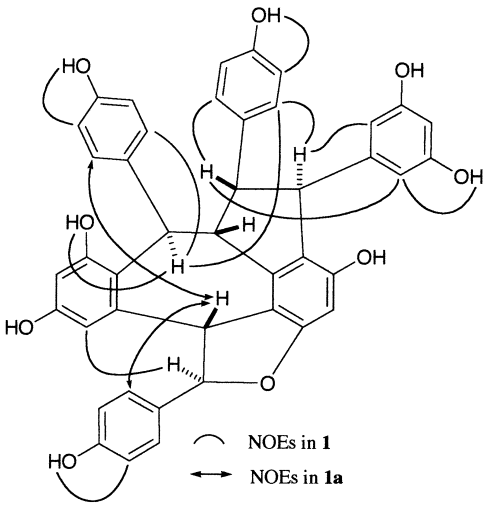


Fig. 2. NOEs in the difference NOE spectra of **1** and **1a**.

groups [δ 7.23 (2H, *d*, $J = 8.8$ Hz, H-2a, 6a) and 6.79 (2H, *d*, $J = 8.8$ Hz, H-3a, 5a); δ 7.17 (2H, *d*, $J = 8.8$ Hz, H-2b, 6b) and 6.70 (2H, *d*, $J = 8.8$Hz, H-3b, 5b); δ 6.42 (2H, *d*, $J = 8.8$ Hz, H-2c, 6c) and 6.52 (2H, *d*, $J = 8.8$ Hz, H-3c, 5c); δ 7.19 (2H, *d*, $J = 8.8$ Hz, H-2d, 6d), 6.78 (2H, *d*, $J = 8.8$ Hz, H-3d, 5d)]. In addition, there was a 3,5-dihydroxyphenyl group [δ 6.10 (2H, *d*, $J = 2.4$ Hz, H-10d, 14d) and 6.30 (1H, *t*, $J = 2.4$ Hz, H-12d)], two sets of *meta*-coupled aromatic protons on a 1, 2, 3, 5-tetra-substituted benzene ring [δ 6.29 (1H, *d*, $J = 2.0$ Hz, H-12a), 6.12 (1H, *d*,$J = 2.0$ Hz, H-14a); δ 6.21 (1H, *d*, $J = 2.0$ Hz, H-12c), 6.49 (1H, *d*, $J = 2.0$ Hz, H-14c)], an aromatic proton on a penta-substituted benzene ring [δ 6.05 (1H, *s*, H-12b)], a sequence of four aliphatic methine protons coupled successively in the $^1H - ^1H$ COSY spectrum in the order [δ 5.21 (1H, *d*, $J = 3.9$ Hz, H-7b), 3.13 (1H, *dd*, $J = 11.3$, 3.9 Hz, H-8b), 4.10 (1H, *dd*, $J = 11.3$, 10.7 Hz, H-7c), 4.55 (1H, *d*, $J = 10.7$ Hz, H-8c)], and two sets of mutually coupled aliphatic protons assignable to the dihydrofuran rings [δ 5.77 (1H, *d*, $J = 11.7$ Hz, H-7a) and 4.44 (1H, *d*, $J = 11.7$ Hz, H-8a); δ 5.38 (1H, *d*, $J = 4.7$ Hz, H-7d) and 4.68 (1H, *d*, $J = 4.7$ Hz, H-8d)] in addition to ten phenolic hydroxyl groups as shown in Table 1. Among them, the *J* value of dihydrofuran ring ($J =$ 11.7 Hz) in **2** was completely different from that of **1**. The *J* values of methine protons in a *trans*-dihyrofuran ring sometimes change [e.g. miyabenol C (1.5 and 5.5 Hz) (Ono et al., 1995), α-viniferin (3, 6 and 10 Hz) (Pryce and Langcake, 1997), ampelopsin A (11.7 Hz) (Oshima et al., 1990)] this being due to the change in conformation of the dihydrofuran rings. The long-range correlations in the COLOC spectrum (Fig. 3) indicated that the stilbene units (A–C) were connected as shown in Fig. 3. The structure is thus the same as that of **1**. Nevertheless, **2** exhibited differences in both chemical shift and *J* values for H-7b, H-8b, H-7c and H-8c as compared to **1**. Especially, H-8b (δ 3.13) was observed at higher field than that of **1**. This phenomenon was explained as follows; H-8b of **1** was deshielded by both rings B1 and B2, whereas **2** was only deshielded by the B2 ring. In the NOE experiment with permethyl ether (**2a**) (Fig. 4), NOEs were observed at H-8b/8c and H-8b/H-7b, indicating the configuration of C-8b in **2** is opposite to that of **1**. Further analysis of the COLOC spectrum, the stilbene unit D was deduced to be coupled to the C2 ring via the dihydrofuran ring (Fig. 3). Thus the structure of **2** was as shown in Fig. 4.

Compound **3**, vaticanol C, obtained as a pale yellow amorphous powder, gave a positive reaction with Gibbs reagent. The compound gave an $[M–H]^-$ ion peak at m/z 905 in the negative ion FABMS, corresponding to the molecular formula $C_{56}H_{42}O_{12}$, suggesting that **3** is a resveratrol tetramer. The ^1H NMR spectrum displayed four sets of *ortho*-coupled aromatic protons assignable to four 4-hydroxyphenyl groups [δ 7.01 (2H, *d*, $J = 8.3$ Hz, H-2a, 6a) and 6.65 (2H, *d*, $J = 8.3$ Hz, H-3a, 5a); δ 6.35 (2H, *d*, $J = 8.8$ Hz, H-2b, 6b) and 6.45 (2H, *d*, $J = 8.8$ Hz, H-3b, 5b); δ 7.24 (2H, *d*, $J = 8.8$ Hz, H-2c, 6c) and 6.84 (2H, *d*, $J = 8.8$ Hz, H-3c, 5c); δ 7.23 (2H, *d*, $J = 8.8$ Hz, H-2d, 6d) and 6.83 (2H, *d*, $J = 8.8$ Hz, H-3d, 5d)], Additionaly, there are two 3, 5-dihydroxyphenyl groups [δ 6.55 (2H, *d*, $J = 2.0$ Hz, H-10c, 14c), 6.33 (1H, *t*, $J = 2.0$ Hz, H-12c), δ 6.40 (2H, *d*, $J = 2.0$ Hz, H-10d, 14d), 6.36 (1H, *t*, $J = 2.0$ Hz, H-12d)], two aromatic protons on a penta-substituted benzene ring [δ 6.12 (1H, *s*, H-12a) and 6.16 (1H, *s*, H-12b)], four aliphatic

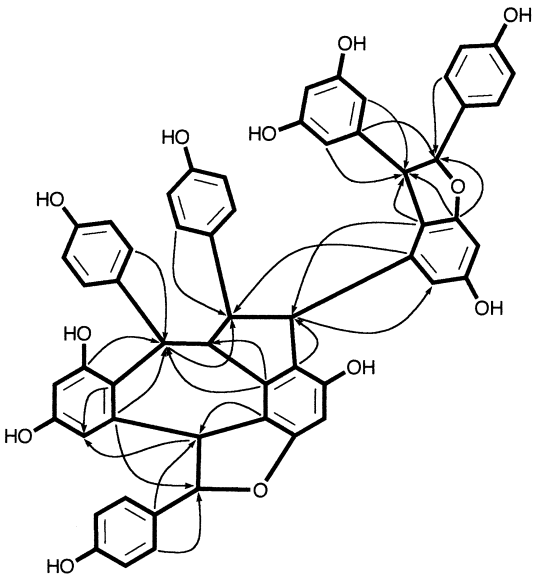


Fig. 3. Significant ^{13}C-^1H long range correlations in the COLOC spectrum (J = 8Hz) of **2**.

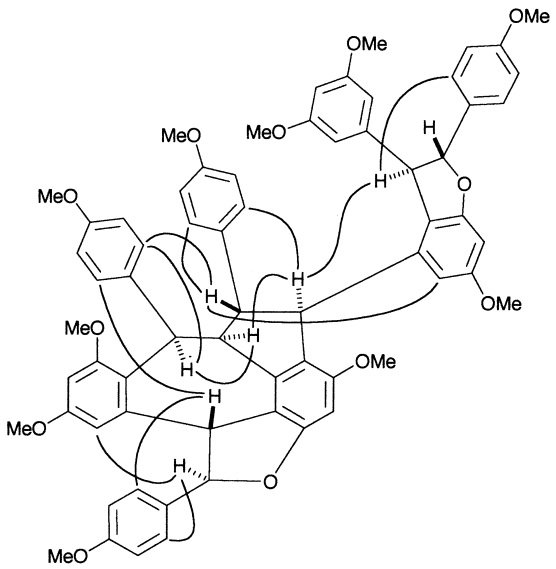


Fig. 4. NOEs in the difference NOE spectra of **2a**.

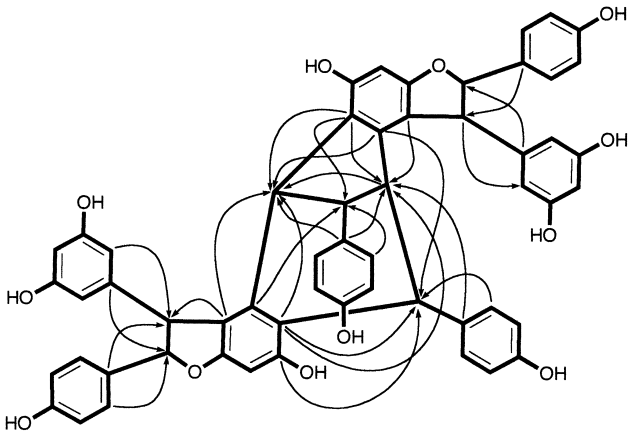


Fig. 5. Significant ^{13}C-^{1}H long range correlations in the COLOC spectrum (J = 8Hz) of **3**.

methine protons [δ 4.16 (1H, *s*, H-7a), 3.10 (1H, *s*, H-8a), 3.38 (1H, *s*, H-7b) 3.99 (1H, *s*, H-8b)], and two sets of mutually coupled aliphatic protons assignable to two dihydrofuran rings [δ 5.61 (1H, *d*, $J = 7.8$ Hz, H-7c), 4.56 (1H, *d*, $J = 7.8$ Hz, H-8c); δ 5.43 (1H, *d*, $J = 6.5$ Hz, H-7d), 4.93 (1H, *d*, $J = 6.5$ Hz, H-8d)], in addition to the ten phenolic hydroxyl groups as shown in Table 1. These results indicated that **3** was a resveratrol tetramer with two dihydrofuran units. In the COLOC spectrum (Fig. 5), significant ^{3}J long range correlations were observed between C-2a(6a)/H-7a and C-2b(6b)/H-7b, indicating that rings A1 and B1 were connected at C-7a and C-7b, respectively. Further ^{3}J long-range correlations were observed between C-1a/H-8a, C-8a/H-8b, C-1b/H-8a and C-1b/H-8b. The four methine protons were connected in the order H-7a, H-8a, H-7b and H-8b. Significant long range correlations were observed between the quaternary carbons on the two penta-substituted benzene rings (A2 and B2) and the aliphatic methine protons as follows; C-9a/H-8b, C-10a/H-8a, C-10a/H-7b, C-10a/H-8b, C-14a/H-8a, C-9b/H-7a, C-9b/H-8b, C-10b/H-7a, C-10b/H-8a, C-11b/H-7a and C-14b/H-8b. This indicated that **3** had a dibenzobicyclo [3.2.1] octadiene system. The two dihydrofuran units were connected at the A2 and B2 rings as shown in Fig. 5 based on the analysis of the COLOC spectrum. In the difference NOE experiment, a distinct NOE between H-7b/H-2a(6a) revealed that the configuration of H-7b is the same as that of ring A1. NOEs between H-7c/H-10c(14c), H-8c/H-2c(6c),

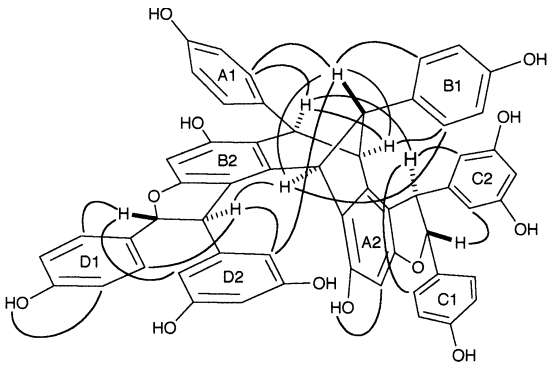
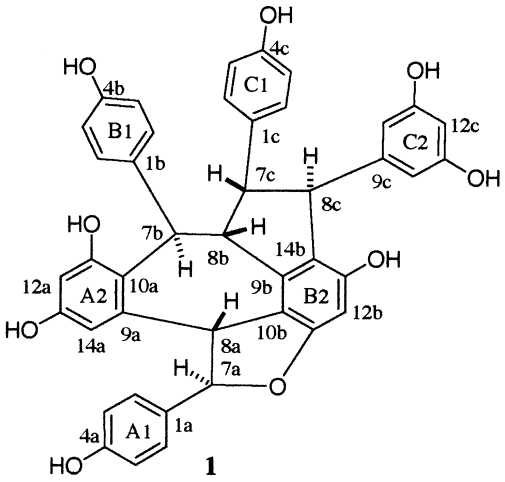
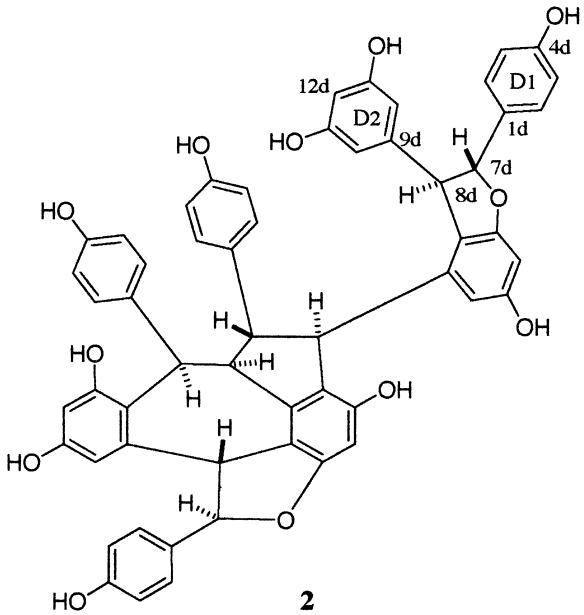


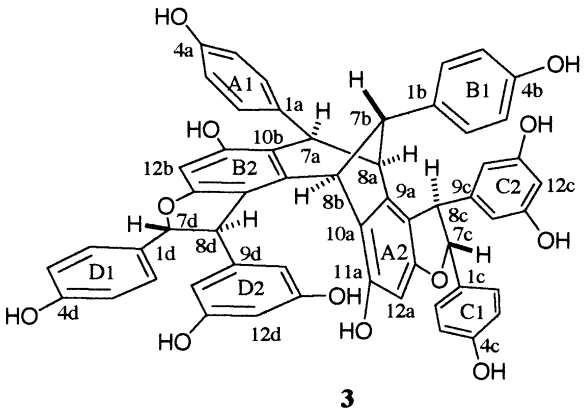
Fig. 6. NOEs in the difference NOE spectrum of **3**.



1



2



3

H-7d/H-10d(14d) and H-8d/H-2d(6d) of **3** indicated that both dihydrofuran rings were *trans*. By comparison with ampelopsin F (Oshima et al., 1993) and isoampelopsin F (Tanaka et al., 1998) which have dibenzobicyclo [3.2.1] octadiene systems, the relative stereochemistry of the ring system was found to be the same as ampelopsin F. Thus, the relative stereo-structure of **3** was as shown in Fig. 6.

Compounds **1**, **2** and **3** could not be obtained in suitable crystalline form for X-ray analysis; therefore, the absolute stereochemistry of these compounds has not yet been determined.

In addition to **1**–**3**, three known compounds were isolated and their structures were identified as resveratrol, piceid (resveratrol 3-O-[unavailable]-glucoside) and (−)-ε-viniferin, respectively, by spectral analysis and comparison with respective authentic samples.

3. Experimental

3.1. Extraction and isolation

Powdered and dried bark (700 g) of *Vatica rassak* (Korth.) B1., collected in Indonesia in October 1997 was extracted successively with acetone (3 1 × 3) and MeOH (3 1 × 3) at room temperature. An aliquot (60 g) of the acetone extract (120 g) was subjected to silica gel column chromtography and eluted with a $CHCl_3$–MeOH gradient to afford 19 fractions. Fr. 3, eluted with $CHCl_3$–MeOH (10 : 1) was next applied to a Sephadex LH 20 column, which was eluted with acetone and the compounds of interest finally purified by preparative silica gel TLC, developed with benzene–EtOAc–MeOH (5 : 3 : 1), to afford resveratrol (8 mg). Fr. 4 [$CHCl_3$–MeOH (10 : 1)] was applied to a Sephadex LH 20 column, eluted with acetone, and then purified further by preparative TLC with benzene–EtOAc–MeOH (10 : 3 : 1) as eluted to afford (−)-ε-viniferin (40 mg). Fr. 6 [$CHCl_3$–MeOH (10 : 1)] was subjected to vacuum liquid chromatography (VLC) eluted with $CHCl_3$–MeOH mixtures; the $CHCl_3$–MeOH (8 : 1) fraction afforded **1** (1.65 g). $CHCl_3$–MeOH (10 : 1) to give 11 fractions (frs. 8.1–8.11), extract was applied to VLC eluted with $CHCl_3$–MeOH mixtures. The 11th fraction [$CHCl_3$–MeOH (10 : 1)] was subject to repeated chromatography by VLC and Sephadex LH 20 (MeOH) repeatedly to afford **2** (2.38 g) and **3** (328 mg). Fr. 9 [$CHCl_3$–MeOH (10 : 1)] was further purified using both Sephadex LH 20 (MeOH) and PTLC [EtOAc–$CHCl_3$–MeOH–H_2O (15 : 8 : 4 : 1) to give piceid (8 mg).

3.2. Compound *1* (vaticanol A)

Pale yellow amorphous solid. Negative ion FABMS: m/z 679 $[M–H]^-$, negative ion HR-FABMS: m/z 679.1959 for $C_{42}H_{31}O_9$ (observed) $[M–H]^-$; calcd. 679.1968; UV (nm, MeOH): 217, 284; $[\alpha]_D^{24}$-165° (MeOH, $c = 0.1$); ^1H and ^{13}C NMR spectral data are shown in Tables 1 and 2.

3.3. Preparation of vaticanol a permethyl ether (*1a*)

Compound **1** (100 mg) was reacted with K_2CO_3 (3 g) and Mel (1 g) in dry acetone (50 ml) under reflux condition. The reaction mixture was purified with PTLC [*n*-hexane–acetone (3 : 1)] to afford **1a** as an amorphous colorless solid (70 mg). Negative ion HR-FABMS: m/z 791.3226 for $C_{50}H_{47}O_9$ (observed) $[M–H]^-$, calcd. 791.3220; ^1H and ^{13}C NMR spectral data are shown in Tables 1 and 2, respectively.

3.4. Compound *2* (vaticanol B)

Pale yellow amorphous solid. Negative ion FABMS: m/z 905 $[M–H]^-$; negative ion HR-FABMS: m/z 905.2571 for $C_{56}H_{41}O_{12}$ (observed) $[M–H]^-$, calcd. 905.2598; UV (nm, MeOH): 212, 220sh, 284; $[\alpha]_D^{25}$-14° (MeOH, $c = 0.1$); ^1H and ^{13}C NMR spectral data are listed in Tables 1 and 2, respectively.

3.5. Preparation of vaticanol B permethyl ether (*2a*)

Compound **2** (50 mg) was treated in the same manner as **1**. The crude material was purified with PTLC [*n*-hexane–acetone (2 : 1)] to give **2a** (54 mg) as an amorphous colorless solid. Negative ion HR-FABMS: m/z 1045.4150 for $C_{66}H_{61}O_{12}$ (observed) $[M–H]^-$, calcd. 1045.4162; ^1H and ^{13}C NMR spectral data are shown in Tables 1 and 2, respectively.

3.6. Compound *3* (vaticanol C)

Pale yellow amorphous solid. Negative ion FABMS: m/z 905 $[M–H]^-$, UV (nm, MeOH): 225, 285; negative ion HR-FABMS: m/z 905.2592 for $C_{56}H_{41}O_{12}$ (observed) $[M–H]^-$, calcd. 905.2598; $[\alpha]_D^{25}$-38° (MeOH, $c = 0.1$); ^1H and ^{13}C NMR spectral data are shown in Tables 1 and 2, respectively.

References

Jang, M., Cai, L., Udeani, G.O., Slowing, K.V., Thomas, C.F., Beecher, C.W.W., Fong, H.H.S., Farnsworth, N.R., Kinghorn, A.D., Mehta, R.G., Moon, R.C., Pezzuto, J.M., 1977. Science 275, 218.

Oshima, Y., Ueno, Y., Hikino, H., Yang, L.-L., Yen, K.-Y., 1990. Tetrahedron 46, 5121.

Oshima, Y., Hisamichi, K., Takeshita, M., 1993. Tetrahedron 49, 5801.

Oshima, Y., Namao, K., Kamijou, A., Matsuoka, S., Nakano, M., Terao, K., Ohizumi, Y., 1995. Experientia 51, 63.
Ono, M., Ito, Y., Kinjo, J., Yahara, S., Nohara, S., Niiho, Y., 1995. Chemical and Pharmaceutical Bulletin 43, 868.
Pryce, R.J., Langcake, P., 1997. Phytochemistry 16, 1452.
Sotheeswaran, S., Pasupathy, V., 1993. Phytochemistry 32, 1083.
Tanaka, T., Ohyama, M., Morimoto, K., Asai, F., Iinuma, M., 1998. Phytochemistry 48, 1241.