Resveratrol Oligomers and Their *O*-Glucosides from *Cotylelobium lanceolatum*

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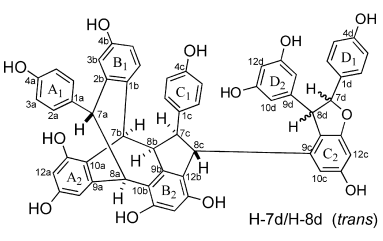
Three new resveratrol oligomers, cotylelophenol C (1) (resveratrol tetramer) and cotylelosides A (2) and B (3) (*O*-glucosides of resveratrol trimer), together with four known glucosides of resveratrol oligomers (vaticasides A, B, C, D) and piceid, were isolated from an acetone soluble part of stem of *Cotylelobium lanceolatum* (Dipterocarpaceae). The structures of new compounds were determined by spectral data analysis. The characteristic properties observed in the NMR spectra of 1 were also discussed.

Key words *Cotylelobium lanceolatum*; Dipterocarpaceae; resvertrol tetramer; resveratrol oligomer glucoside; anisotropy

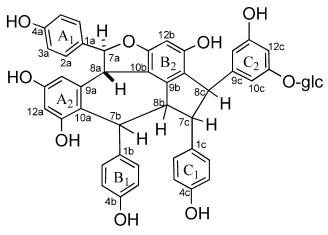
Stilbenoids are a family of polyphenols elaborated by plants of the families Dipterocarpaceae, Vitaceae, Gnetaceae, Cyperaceae, and Leguminosae.[1,2] Resveratrol and its oligomers have been drawn to attentions because of their multifunctional bioactivities, *e.g.*, chemoprevention of cancers,[3] activation of human *SIRT1*,[4] and anti HIV effect.[5] Recent phyotochemical investigation of Dipterocarpaceous plants has revealed a considerable structural diversity of resveratrol oligomers,[1,2,5—7] their glucosides,[7—10] and acetophenone derivatives.[11] In our previous research works, some biological properties of the characterized oligomers[12—16] were discussed in addition to the structural elucidation of resveratrol oligomers in the family. The phytochemical and biologically active interest in resveratrol oligomers in the family led us the current study of stem of *Cotylelobium lanceolatum* (Dipterocarpaceae). In our previous studies of chemical constituents in the material, some new structures of resveratrol oligomers were characterized.[17] Further detailed examination of high polar components in the acetone extract resulted in the isolation of a new resveratrol tetramer, cotylelophenol C (**1**) and two new resveratrol trimer *O*-glucosides, cotylelosides A (**2**) and B (**3**). The structural determination and the characteristics observed in the NMR spectra are described.

Cotylelophenol C (**1**) ($[\alpha]_D^{25}$ +78°), and cotylelosides A (**2**) ($[\alpha]_D^{25}$ +106°) and B (**3**) ($[\alpha]_D^{25}$ −21°) were purified from an acetone-soluble part of stem of *C. lanceolatum* by column chromatography over silica gel, Sephadex LH-20, ODS, and PTLC. All compounds showed positive reactions to the Gibbs reagent.

Cotylelophenol C (**1**), a pale yellow solid, had the molecular formula of $C_{56}H_{42}O_{12}$ supported by the high resolution (HR)-FAB-MS ($[M-H]^-$ at *m*/*z* 905.2606). Analysis of the ^{1}H- and ^{13}C-NMR spectral data (Table 1), ^{1}H–^{1}H and ^{13}C–^{1}H correlation spectroscopy (COSY), and heteronuclear multiple-bond correlation (HMBC) data of **1** revealed the presence of three 4-hydroxyphenyl groups (designated as A_1, C_1, D_1), a 4-hydroxy-1,2-disubstituted benzene ring (B_1), two 3,5-dioxygenated-1,2-disubstituted benzene rings (A_2, C_2), a 3,5-dihydroxy-1,2,6-trisubstituted benzene ring (B_2), and a 3,5-dihydroxyphenyl group (D_2). The presence of two sets of mutually coupled aliphatic protons (H-7a, H-8b; H-7d, H-8d) and a sequence of four aliphatic protons (H-7b, H-8b, H-7c, H-8c) were also shown. The chemical shift of C-7d (δ_C 93.6) was typical for carbon atoms of a dihydrobenzofuran moiety.[6—11] These results indicated that **1** was a resveratrol tetramer with a dihydrobenzofuran unit. The NMR spectral data of **1** were found to be closely similar to those of vaticanol G,[9] except for the presence of an additional resveratrol unit (resveratrol D: ring D_1–C-7d–C-8d–ring D_2) instead of an aromatic proton due to H-10c. These NMR spectral data indicated the structure of cotylelophenol A to be shown as **1**, which is regarded as a condensed product of a resveratrol trimer (A—C) (vaticanol G) and a monomeric resveratrol (D). The results of HMBC supported the proposed structure of **1** (Fig. 1). The important correlations were observed be-



1



2 : H-7b: β; H-8b: β; H-7c: α; H-8c: β
3 : H-7b: α; H-8b: α; H-7c: β; H-8c: α

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tween H-7a/C-2a(6a) and H-8a/C-14a, which showed the connection of resveratrol A unit. Other correlations supported the connectivity of resveratrols B—D. The other C–C bonds such as C-7a/C-2b, C-8a/C-10b, C-7b/C-10a, C-8c/C-14b, and C-8d/C-10c were substantiated by the correlations of H-7a/C-3b, H-8a/C-11b, H-7b/C-11a, H-8c/C-13b, and H-8d/C-10c, respectively. An additional cross peak of H-7d/C-11c showed the presence of an ether linkage (C-7d–O–C-11c), which formed a dihydrobenzofuran ring (C-7d–C-8d–C-10c–C-11c–O).

The relative stereochemistry of **1** was determined as follows. The results of NOESY experiment (Fig. 2) could be applied to those of vaticanol G.[9] Then the disposition of resveratrols A—C was same as that of vaticanol G. Coupling constant of H-7d/H-8d (J=2.4 Hz) and the NOE interactions of H-7d/H-10d(14d) and H-8d/H-2d(6d) showed that H-7d and H-8d were *trans* in diequatrial orientation. However the stereochemistry of H-7d and H-8d to be α and β or *vice versa* has not been concluded.

In the ^{1}H-NMR spectrum measured in room temperature of vaticanol G, aromatic protons due to ring C_1 had been observed as four broad singlets, which became four double doublets measured at −20 °C.[9] This phenomenon and the upper field shifts of H-2c and H-3c could be well explained

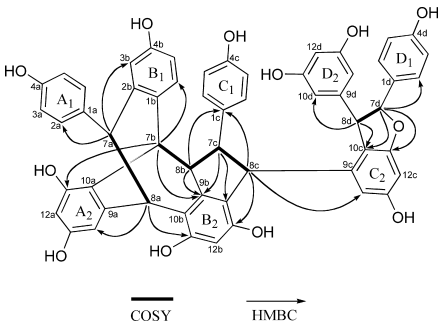

Fig. 1. Selected Correlations in 2D NMR of Cotylelophenol A (**1**)

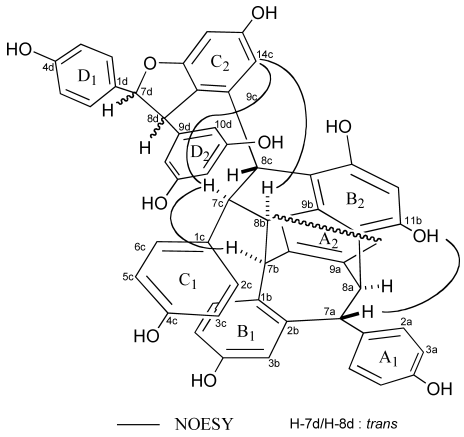

Fig. 2. NOEs Observed for **1**

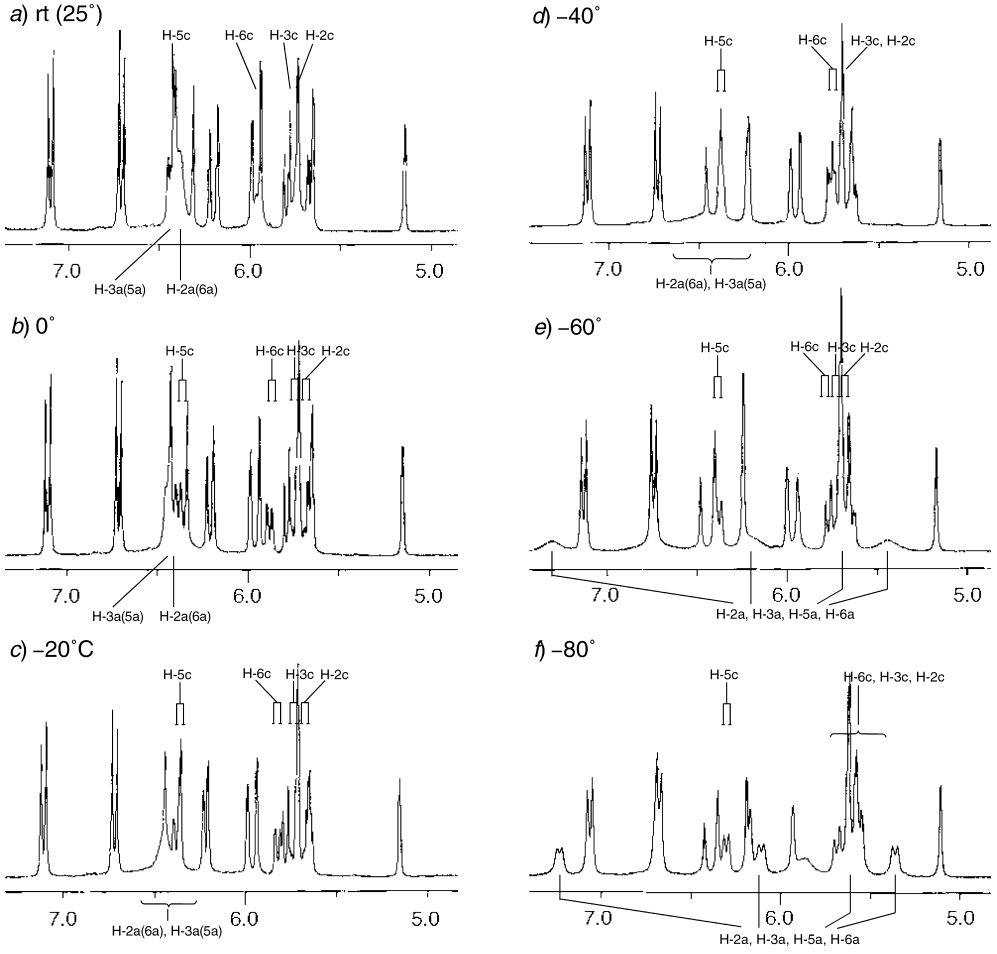

Fig. 3. ^{1}H-NMR Spectra (in Acetone-d_6, 300 MHz) of **1** at Variable Temperatures

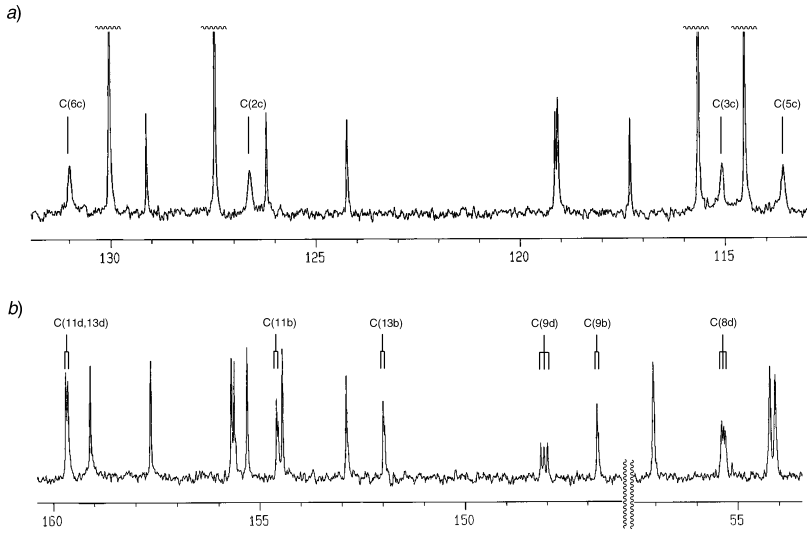

Fig. 4. ^{13}C-NMR Spectrum (in Acetone-d_6, 75 MHz) of **1** at Room Temperature
(a) Four broad signals assigned to ring C_1, (b) duplicated signals.

in terms of the free rotation hindrance of ring C_1 and the anisotropic effect subsequently caused by ring B_1. The same phenomenon was also observed in the ^{1}H-NMR spectrum of **1**, that is, the signals of ring C_1 (H-2c, H-3c, H-5c, H-6c) were broadened and gradually became split according to lower temperature [Fig. 3a (rt)—c (−20 °C)]. Although the carbons of C-2c and C-6c, and C-3c and C-5c were in general equivalent, they were also observed as seperated signals (Fi. 4a). The trimeric unit in vaticanol G and **1** is identical, the chemical shift of H-6c is however quite different (**1**: δ_H 5.83; vaticanol G: δ_H 7.14), which indicated that ring C_1 in **1** was strongly influenced by the further anisotropic effect caused by ring D_2 (Fig. 5). In addition to ring C_1, ring A_1 was also regarded as a restricted rotational substituent, which displayed separated signals [Fig. 3d (−40 °C)—f (−80 °C)]. The mutual couplings of H-2a/H-6a and H-3a/H-5a were confirmed by ^{1}H–^{1}H COSY experiment at −80 °C. These features can be explained as follows. At room temperature, strong steric hindrance disturb the free rotation of aromatic rings such as ring C_1, and the hindrance becomes to weak and the free rotation is permitted according to low temperature. At −80 °C, ring A_1 is restricted its rotation by ring A_2, which causes new anisotropic effect and resulted in higher field shifts of H-5a (δ_H 5.60) and H-6a (δ_H 5.37).

Some signals [C-9b, C-11b, C-13b, C-11d(13d)] in the ^{13}C-NMR spectrum of **1** were observed as duplicated signals and other were singlet or in triplet (C-8d, C-9d) (Fig. 4b). The reason of this phenomenon may be explained by conformational isomerism, but is not clear now.

Cotylelosides A (**2**) and B (**3**) were obtained as yellow solid. Their compositions were deduced to be $C_{34}H_{32}O_{11}$ from the $[M-H]^-$ ion peaks observed at *m/z* 841.2506 (**2**) and 841.2504 (**3**) in the negative ion HR-FAB-MS. The presence of an *O*-*β*-glucopyranosyl moiety was supported by the NMR spectra in both compounds. The ^{1}H- and ^{13}C-NMR spectral data of **2** (Table 1) except for the *β*-glucopyranosyl moiety showed close similarity to those of vaticanol E.[8] The HMBC and NOESY spectra (see Experimental) confirmed the structure of aglycone of **2** to be vaticanol E. The position of *O*-glucosyl moiety was determined to be at C-11c by the

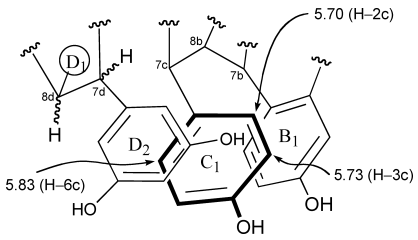

Fig. 5. Upper Field Shift of Aromatic Protons (H-2c, H-3c, H-6c) Caused by Anisotropy in **1**
δ in ppm, in acetone-d_6, 300 MHz at −20 °C.

results of HMBC spectrum which displayed cross peak between the anomeric proton (δ_H 4.75) and the aromatic carbon at C-11c (δ_C 159.6). The structure of cotyleloside A (**2**) was then concluded to be vaticanol E 11c-*O*-*β*-glucopyranoside. The ^{1}H- and ^{13}C-NMR spectral data of aglycone of **3** (Table 1) resembled those of pauciflorol B.[7] By the same results as described in **2**, the structure of cotyleloside B (**3**) was elucidated to pauciflorol B 11c-*O*-*β*-glucopyranoside.

In addition to these new compounds (**1**—**3**), five known glucosides were isolated and their structures were identified as vaticasides A, B, C, D, and piceid by spectral analysis and comparison with respective authentic samples.[8,9]

Experimental

General Experiment Procedures 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 δ 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.

Plant Material *Cotylelobium lanceolatum* Craib. 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 is deposited at the Gifu Prefectural Institute of Health and Environmental Sciences, Kakamigahara, Gifu, Japan.

Extraction and Isolation of Compounds (1—3, Five Known Compounds) The dried and ground stems (800 g) of *C. lanceolatum* were ex-

Table 1. ^{1}H- and ^{13}C-NMR Spectral Data of **1**—**3**

No.	**1**		**2**		**3**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
1a		139.8		133.5		130.6
2a, 6a	6.38 (br s)	130.0	7.56 (d, 8.3)	130.5	7.26 (d, 8.6)	130.0
3a, 5a	6.44 (br s)	114.5	6.99 (d, 8.3)	116.3	6.81 (d, 8.6)	115.9
4a (OH)	7.86 (br s)	155.3	8.66 (br s)	158.4	8.54 (br s)	158.4
7a	4.49 (d, 3.6)	57.0	5.67 (d, 9.4)	95.4	5.83 (d, 11.8)	90.4
8a	4.60 (d, 3.6)	50.2	5.35 (d, 9.4)	52.2	4.47 (br d, 11.8)	48.7
9a		141.6		140.2		141.1
10a		126.2		123.4		124.6
11a (OH)	8.02 (br s)	152.9	7.92 (br s)	157.7	8.31 (br s)	155.7
12a	6.22 (d, 2.2)	101.5	6.15 (d, 2.0)	101.8	6.34 (d, 2.2)	101.5
13a (OH)	7.63 (br s)	155.6	7.99 (br s)	156.2	8.12 (br s)	156.7
14a	5.65 (br s)	111.4	6.12 (d, 2.0)	107.7	6.16 (br d, 2.2)	105.8
1b		129.1		132.7		133.1
2b		141.4	6.06 (d, 8.6)	132.8	7.17 (d, 8.4)	130.3
3b	5.99 (d, 2.6)	119.1	6.32 (d, 8.6)	113.5	6.68 (d, 8.4)	115.4
4b (OH)	7.33 (br s)	154.5	7.87 (br s)	155.7	8.14 (br s)	155.6
5b	5.67 (dd, 8.6, 2.6)	112.6	6.32 (d, 8.6)	113.5	6.68 (d, 8.4)	115.4
6b	5.80 (d, 8.6)	134.7	6.06 (d, 8.6)	132.8	7.17 (d, 8.4)	130.3
7b	4.76 (d, 2.2)	42.5	4.80 (d, 2.9)	42.3	5.26 (d, 3.1)	37.3
8b	4.05 (dd, 7.4, 2.2)	54.2	4.29 (dd, 8.3, 2.9)	51.2	3.65 (m)	52.4
9b		146.8[a]		144.2		144.1
10b		117.3		115.8		115.8
11b (OH)	8.42 (br s)	154.6[a]		160.3		159.4
12b	6.41 (s)	102.0	6.11 (s)	96.1	6.17 (s)	96.5
13b (OH)	7.55 (br s)	152.0[a]	6.86 (br s)	155.4	7.23 (br s)	154.6
14b		124.2		123.3		120.4
1c		135.6		130.0		132.6
2c	5.72 (br s)	126.6	7.21 (d, 8.6)	131.3	7.02 (d, 8.4)	129.9
3c	5.76 (br s)	115.1	6.86 (d, 8.6)	115.2	6.75 (d, 8.4)	115.7
4c (OH)	7.57 (br s)	155.7	8.26 (br s)	156.2	8.25 (br s)	156.6
5c	6.39 (br s)	113.6	6.86 (d, 8.6)	115.2	6.75 (d, 8.4)	115.7
6c	5.96 (br s)	131.0	7.21 (d, 8.6)	131.3	7.02 (d, 8.4)	129.9
7c	3.13 (d, 7.4)	58.8	4.04 (dd, 10.3, 8.3)	58.6	3.79 (dd, 11.6, 9.3)	62.3
8c	4.05 (s)	54.1	3.67 (d, 10.3)	50.9	4.30 (d, 9.3)	57.2
9c		143.3		148.3		146.5
10c		119.1	6.46 (br s)	109.3	6.32 (br s)	108.8
11c		162.0		159.6		159.5
12c	6.17 (d, 1.9)	95.4	6.35 (t, 2.0)	102.3	6.39 (br s)	102.5
13c (OH)	8.17 (br s)	159.1	8.18 (br s)	158.8	8.24 (br s)	158.8
14c	5.74 (d, 1.9)	106.3[b]	6.43 (br s)	109.5	6.34 (br s)	109.2
1d		134.3				
2d, 6d	7.10 (d, 8.5)	127.5				
3d, 5d	6.71 (d, 8.5)	115.6				
4d (OH)	8.32 (br s)	157.6				
7d	5.15 (d, 2.4)	93.6				
8d	4.27 (d, 2.4)	55.3[a]				
9d		148.1[a]				
10d, 14d	5.94 (d, 2.0)	106.3[b]				
11d, 13d (OH)	8.14 (br s)	159.7[a]				
12d	6.31 (br s)	102.0				
Glucose(-1)			4.75 (d, 7.5)	101.7	4.73 (d, 7.7)	102.0
Glucose(-2)			3.38 (m)	74.4	3.38 (m)	74.5
Glucose(-3)			3.40 (m)	77.6	3.40 (m)	77.3
Glucose(-4)			3.45 (m)	71.0	3.47 (m)	71.0
Glucose(-5)			3.50 (m)	77.7	3.50 (m)	77.7
Glucose(-6)			3.68 (br d, 11.2)	62.3	3.70 (dd, 11.2, 4.1)	62.0
			3.82 (br d, 11.2)		3.79 (br d, 11.2)	

Measured in acetone-d_6 at 300 MHz (^{1}H-NMR) and at 75 MHz (^{13}C-NMR). *a*) Each signals was observed as duplicated (Fig. 4). Average chemical shifts were shown. *b*) Overlapping.

tracted successively with acetone, MeOH and 70% MeOH at rt. A part (65 g) of the acetone extract (70 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). Piceid (88 mg) and vaticaside A (96 mg) were obtained from Fr. 6 ($CHCl_3$–MeOH, 7 : 1) and Fr. 9 ($CHCl_3$–MeOH, 6 : 1), respectively, by further purification through CC over Sephadex LH-20 (acetone) and PTLC (EtOAc–$CHCl_3$–MeOH–H_2O, 15 : 8 : 4 : 1). Fraction 10 ($CHCl_3$–MeOH, 5 : 1) was further subject to Sephadex LH-20 CC (MeOH) to give three fractions (Fr. 10a—Fr. 10c). Fraction 10b was further fractioned by CC over ODS (MeOH–H_2O, 3 : 7). To give four fractions (Fr. $10b_A$—Fr. $10b_D$). Compound **1** (25 mg) was purified from the fraction Fr. $10b_A$ after PTLC (EtOAc–$CHCl_3$–MeOH–H_2O,

6 : 3 : 3 : 1). Purification of Fr. $10b_D$ by repeated CC over ODS (MeOH–H_2O, 3 : 7), PTLC (EtOAc–$CHCl_3$–MeOH–H_2O, 6 : 3 : 3 : 1) and reversed-phase medium pressure CC (H_2O–MeOH gradient system) achieved the isolation of **2** (6 mg) and **3** (5 mg). Fraction 11 ($CHCl_3$–MeOH, 5 : 1) was fractionated into five parts (Fr. 11a—Fr. 11e) by ODS CC (MeOH–H_2O, 3 : 7). Subfractions of Fr. 11b and Fr. 11c gave vaticasides B (21 mg) and C (20 mg), respectively, after purification by PTLC (EtOAc–$CHCl_3$–MeOH–H_2O, 6 : 3 : 3 : 1). Vaticaside D (88 mg) was obtained from Fr. 12 ($CHCl_3$–MeOH, 4 : 1) by the same chromatographic procedure used Fr. 11.

Compound **1** (Cotylelophenol C): A pale yellow solid; $[\alpha]_D$ +78° (c=0.1, MeOH); UV (MeOH) λ_{max} (log ε): 282 (4.02), 215 (4.82) nm; negative ion FAB-MS m/z: 905 $[M-H]^-$ negative ion HR-FAB-MS m/z: 905.2606 (Calcd 905.2598 for $C_{56}H_{41}O_{12}$); ^{1}H- and ^{13}C-NMR spectral data, see Table 1; HMBC correlations, see Fig. 1 (selected) and H-3a(5a)/C-1a, C-4a; OH-4a/C-3a(5a), C-4a; H-7a/C-1a, C-8a, C-9a, C-1b, C-2b, C-10b; H-8a/C-1a, C-7a, C-9a, C-10a, C-2b, C-9b, C-10b; OH-11a/C-10a, C-11a, C-12a; H-12a/10a, C-11a, C-13a, C-14a; OH-13a/C-12a, C-13a, C-14a; H-14a/C-8a, C-10a, C-12a, C-13a; H-3b/C-7a, C-1b, C-4b, C-5b; OH-4b/C-3b, C-5b, C-4b; H-5b/C-1b, C-2b, C-4b; H-6b/C-2b, C-4b, C7b; H-7b/C-9a, C-10a, C-1b, C-2b, C-8b, C-7c; H-8b/C-10a, C-1b, C-7b, C-7c; OH-11b/C-10b, C-11b, C-12b; H-12b/C-10b, C-11b, C-13b, C-14b; OH-13b/C-12b, C-13b, C-14b; OH-4c/C-3c, C-4c, C-5c; H-7c/C-8b, C-1c, C-2c, C-6c, C-8c, C-9c; H-8c/C-8b, C-9b, C-14b, C-7c, C-9c, C-10c; H-12c/C-10c, C-11c, C-13c, C-14c; OH-13c/C-12c, 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; OH-4d/C-3d(5d), C-4d; H-7d/C-1d, C-9d; H-8d/C-1d, C-7d, C-9d; H-10d(14d)/C-8d, C-11d(13d), C-12d; OH-11d(13d)/C-10d(14d), C-11d(13d), C-12d; H-12d/C-10d(14d), C-11d(13d); NOESY correlations: see Fig. 2 (selected) and H-2a(6a)/H-7a, H-8a; H-3a(5a)/OH-4a; OH-4a/H-3a(5a); H-7a/H-2a(6a), H-8a, H-3b; H-8a/H-7a, H-14a, OH-11b, H-2a(6a); OH-11a/H-12a, H-7b; H-12a/OH-11a, OH-13a; OH-13a/H-12a, H-14a; H-14a/H-8a, OH-13a; H-3b/H-7a, OH-4b; OH-4b/H-3b, H-5b; H-5b/OH-4b; H-6b/H-7b; H-7b/OH-11a, H-6b, H-8b; H-8b/H-7b, H-7c; OH-11b/H-8a, H-12b; H-12b/OH-11b, OH-13b; OH-13b/H-12b, H-8c, H-14c; H-7c/H-8b, H-8c, H-10d(14d); H-8c/H-7c, H-14c, H-8d, H-10d(14d), OH-13b; H-12c/OH-13c; OH-13c/H-12c, H-14c; H-14c/OH-13c, H-8c, OH-13b; H-2d(6d)/H-7d; H-3d(5d)/OH-4d; OH-4d/H-3d(5d); H-7d/H-2d(6d), H-8d; H-8d/H-8c, H-7d, H-10d(14d); H-10d(14d)/H-7c, H-8c, H-8d, OH-11d(13d); OH-11d(13d)/H-10d(14d), H-12d; H-12d/OH-11d(13d).

Compound **2** (Cotyleloside A): A yellow solid; $[\alpha]_D$ +106° (c=0.1, MeOH); UV (MeOH) λ_{max} (log ε): 282 (4.11), 214 (4.79) nm; negative ion FAB-MS m/z: 841 $[M-H]^-$ negative ion HR-FAB-MS m/z: 841.2506 (Calcd 841.2496 for $C_{48}H_{41}O_{14}$); ^{1}H- and ^{13}C-NMR spectral data, see Table 1; HMBC correlations: H-2a(6a)/C-4a, C-7a; H-3a(5a)/C-1a, C-4a; OH-4a/C-3a(5a), C-4a; H-7a/C-1a, C-2a(6a), C-8a, C-9a; H-8a/C-1a, C-7a, C-9a, C-10a, C-10b; OH-11a/C-10a, C-11a, C-12a; H-12a/C-10a, C-13a, C-14a; OH-13a/C-12a, C-13a, C-14a; H-14a/C-8a, C-10a, C-12a; H-2b(6b)/C-4b, C-7b; H-3b, 5b/C-1b, C-4b; OH-4b/C-3b(5b), C-4b; H-7b/C-9a, C-10a, C-11a, C-1b, C-2b(6b), C-8b, C-9b; H-8b/C-1b, C-1c; H-12b/C-10b, C-11b, C-13b, C-14b; OH-13b/C-12b, C-13b, C-14b; H-2c(6c)/C-4c, C-7c; H-3c(5c)/C-1c, C-4c; OH-4c/C-3c(5c), C-4c; H-7c/C-7b, C-8b, C-1c, C-2c(6c), C-8c, C-9c; H-8c/C-14b, C-7c, C-9c, 10c, C-14c; H-10c/C-8c, C-11c, C-12c; H-12c/C-10c, C-11c, C-14c, C-13c; OH-13c/C-12c, C-13c, C-14c; H-14c/C-8c, C-13c, C-12c; H-glc(1)/C-11c; NOESY correlations: H-2a(6a)/H-7a, H-8a; H-3a(5a)/OH-4a; OH-4a/H-3a(5a); H-7a/H-2a(6a), H-8a, H-14a; H-8a/H-2a(6a), H-7a, H-8b; OH-11a/H-12a, H-7b; H-12a/OH-11a, OH-13a; OH-13a/H-12a, H-14a; H-14a/H-7a, OH-13a; H-2b(6b)/H-7b; H-3b(5b)/OH-4b; OH-4b/H-3b(5b); H-7b/OH-11a, H-2b(6b), H-8b, H-2c(6c); H-8b/H-8a, H-7b, H-2c(6c), H-7c; H-12b/OH-13b; OH-13b/H-12b; H-2c(6c)/H7b, H-8b, H-7c, H-8c, H-10c, H-14c; H-3c(5c)/OH-4c; OH-4c/H-3c(5c); H-7c/H-8b, H-8c, H-2c(6c), H-10c, H-14c; H-8c/H-7c, H-2c(6c), H-10c, H-14c; H-10c/H-2c(6c), H-7c, H-8c, H-glc(1); H-12c/OH-13c, H-glc(1); OH-13c/H-12c, H-14c; H-14c/H-2c(6c), H-7c, H-8c, OH-13c; H-glc(1)/H-10c, H-12c.

Compound **3** (Cotyleloside B): A yellow solid; $[\alpha]_D$ −21° (c=0.1, MeOH); UV (MeOH) λ_{max} (log ε): 282 (4.13), 215 (4.83) nm; negative ion FAB-MS m/z: 841 $[M-H]^-$ negative ion HR-FAB-MS m/z: 841.2504 (Calcd 841.2496 for $C_{48}H_{41}O_{14}$); ^{1}H- and ^{13}C-NMR spectral data, see Table 1; HMBC correlations: H-2a(6a)/C-4a, C-7a; H-3a(5a)/C-1a, C-4a; OH-4a/C-3a(5a), C-4a; H-7a/C-1a, C-2a(6a), C-8a, C-9a; H-8a/C-1a, C-7a, C-9a, C-10b, C-11b; OH-11a/C-10a, C-11a, C-12a; H-12a/C-10a, C-13a, C-14a; OH-13a/C-12a, C-13a, C-14a; H-14a/C-8a, C-10a, C-12a; H-2b(6b)/C-4b, C-7b; H-3b, 5b/C-1b, C-4b; OH-4b/C-3b(5b), C-4b; H-7b/C-9a, C-10a, C-11a, C-1b, C-2b(6b), C-8b, C-9b; H-8b/C-10a, C-1b, C-9b; H-12b/C-10b, C-11b, C-13b, C-14b; OH-13b/C-12b, C-13b, C-14b; H-2c(6c)/C-4c, C-7c; H-3c(5c)/C-1c, C-4c; OH-4c/C-3c(5c), C-4c; H-7c/C-7b, C-8b, C-1c, C-2c(6c), C-8c, C-9c; H-8c/C-10c, C-14c; H-10c/C-8c, C-11c, C-12c; H-12c/C-10c, C-11c, C-14c, C-13c; OH-13c/C-12c, C-13c, C-14c; H-14c/C-8c, C-13c, C-12c; H-glc(1)/C-11c; NOESY correlations: H-2a(6a)/H-7a, H-8a; H-3a(5a)/OH-4a; OH-4a/H-3a(5a); H-7a/H-2a(6a), H-8a, H-14a; H-8a/H-2a(6a), H-7a, H-2b(6b); OH-11a/H-12a, H-7b; H-12a/OH-11a, OH-13a; OH-13a/H-12a, H-14a; H-14a/H-2a(6a), H-7a, OH-13a; H-2b(6b)/H-8a, H-7b, H-8b, H-10c, H-14c; H-3b(5b)/OH-4b; OH-4b/H-3b(5b); H-7b/OH-11a, H-2b(6b), H-8b, H-2c(6c); H-8b/H-7b, H-2b(6b), H-7c, H-8c, H-2c(6c); H-12b/OH-13b; OH-13b/H-12b; H-2c(6c)/H7b, H-8b, H-8c; H-3c(5c)/OH-4c; OH-4c/H-3c(5c); H-7c/H-8b; H-8c/H-8b, H-2c(6c), H-10c, H-14c; H-10c/H-2b(6b), H-8c, H-glc(1); H-12c/OH-13c, H-glc(1); OH-13c/H-12c, H-14c; H-14c/H-2b(6b), H-8c, OH-13c; H-glc(1)/H-10c, H-12c.

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