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Acetophenone *C*-glucosides and stilbene *O*-glucosides in *Upuna borneensis*

Zulfiqar Ali [a,b], Tetsuro Ito [a,*], Toshiyuki Tanaka [a], Ken-ichi Nakaya [a], Jin Murata [c], Dedy Darnaedi [d], Munekazu Iinuma [b]

[a] *Gifu Prefectural Institute of Health and Environmental Sciences, 1-1 Naka-fudogaoka, Kakamigahara 504-0838, Japan*
[b] *Gifu Pharmaceutical University, 5-6-1, Mitahora-higashi, Gifu 502-8585, Japan*
[c] *Botanical Gardens, Koishikawa, Graduate School of Science, University of Tokyo, 3-7-1, Hakusan, Bunkyo-Ku, Tokyo, 112-0001, Japan*
[d] *Herbarium Bogoriense, The Indonesian Institute of Sciences, Research and Development Center for Biology, J1 Ir. Juanda 18, Bogor 16122, Indonesia*

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Abstract

Three acetophenone *C*-glycosides; 2,4,6-trihydroxyacetophenone 3-*C*-β-(2′-*O*-*p*-hydroxybenzoyl)-glucopyranoside, 2,4,6-trihydroxyacetophenone 3-*C*-β-(2′-*O*-*E*-coumaroyl)-glucopyranoside, 2,4,6-trihydroxyacetophenone 3-*C*-β-(2′-*O*-*E*-cinnamoyl)-glucopyranoside, and two resveratrol *O*-glycosides; piceid 2′-*O*-*p*-hydroxybenzoate and, piceid 2′-*O*-*E*-ferulate, together with three known compounds were isolated from the acetone soluble part of stem of *Upuna borneensis* (Dipterocarpaceae). The structures of isolates were determined by spectral analysis including extensive 2D-NMR spectral analyses.

Keywords: *Upuna borneensis*; Dipterocarpaceae; Acetophenone *C*-glucoside; Resveratrol *O*-glucoside

1. Introduction

Dipterocarpaceae is rich source of polyphenols, particularly resveratrol oligomers (Sotheeswaran and Pasupathy, 1993) showing various biological activities such as cytotoxicity (Ohyama et al., 1999), anti-viral (Dai et al., 1998) and anti-inflammatory (Huang et al., 2001). During the course of our studies on bioactive polyphenols focused on resveratrol oligomers, we have described certain skeletal variations and compared the isolates among several Dipterocarpaceous plants of the genus, *Vatica*, *Shorea*, and so on (Ito et al., 2003a,b, 2001). The Dipterocarpaceous plant, *Upuna borneensis*, is distributed in Malaysia and belongs to a monotypic genus of the largest subfamily, Dipterocarpoideae (Ashton, 1982). In our preceding paper, the structures of resveratrol oligomers in stem of this plant were discussed (Ito et al., 2004). To examine the extent of the variability of resveratrol derivatives and/or other polyphenolic components in this plant, an acetone extract was further investigated. This paper deals with the isolation and the structure determination of three new acetophenone *C*-glycosides; 2,4,6-trihydroxyacetophenone 3-*C*-β-(2′-*O*-*p*-hydroxybenzoyl)-glucopyranoside (**1**), 2,4,6-trihydroxyacetophenone 3-*C*-β-(2′-*O*-*E*-coumaroyl)-glucopyranoside (**2**), 2,4,6-trihydroxyacetophenone 3-*C*-β-(2′-*O*-*E*-cinnamoyl)-glucopyranoside (**3**), two new resveratrol glucosides; piceid 2′-*O*-4-hydroxybenzoate (**5**), piceid 2′-*O*-*E*-ferulate (**6**) along with three known glucosides; 2,4,6-trihydroxyacetophenone 3-*C*-β-glucopyranoside (**4**) (Tanaka et al., 1993), piceid 2′-*O*-*E*-coumarate (**7**) (Lee et al., 2003) and piceid (**8**) (Mattive et al., 1995).

* Corresponding author. Tel.: +81-583-80-2120; fax: +81-583-71-5016.
E-mail address: zvn00510@nifty.ne.jp (T. Ito).

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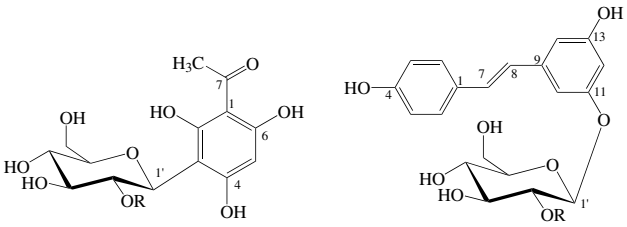

1 R = *p*-hydroxybenzoyl
2 R = *E*-coumaroyl
3 R = *E*-cinnamoyl
4 R = H

5 R = *p*-hydroxybenzoyl
6 R = *E*-feruloyl
7 R = *E*-coumaroyl
8 R = H

2. Results and discussion

Isolates (**1–8**) were purified from the acetone-soluble part of stem of *U. borneensis* by column chromatography using silica gel, *Sephadex LH-20*, ODS, Sep Pak Cartridge and prep. TLC, respectively. All compounds gave a positive reaction to the Gibbs reagent and compounds **1–4** also showed a positive reaction to the $FeCl_3$ reagent. Structural assignments of (**1–8**) were made by analysis of 2D NMR spectral data including ^1H–^1H COSY, ^{13}C–^1H COSY and HMBC (see Fig. 1) for compounds **1**,**2**,**5** and **6**.

Compound **1** was obtained as a white amorphous powder, whose molecular weight was determined to be 450 by a ion peak of $[M–H]^-$ at m/z 449 in the negative FAB–MS, with a molecular formula of $C_{21}H_{22}O_{11}$ as deduced from the HRFAB–MS m/z 449.1078 $[M–H]^-$. The IR spectrum of **1** showed absorption bands at 3272 and 1630 cm^{-1} assignable to hydroxyl and carbonyl functions. In the ^1H and ^{13}C NMR spectra of **1** (Table 1), characteristic signals of a phloroglucinol ring were observed as follows; an one-proton singlet at δ 5.83 (H-5) in the aromatic region associated with a carbon at δ 96.0 (C-5) and three quaternary carbons at δ 164.17, 164.18 and 164.19 (C-2, C-4 and C-6). The spectrum also displayed signals due to a three-proton singlet at δ 2.50 (δ 32.8) and a quaternary carbon at δ 203.7, revealing the presence of an acetyl group. The positive reaction of **1** to $FeCl_3$ reagent indicated that the acetyl group was attached to a phloroglucinol ring and the acetyl carbonyl group formed a hydrogen bonding with hydroxyl groups. The ^{13}C NMR spectrum (Table 1) revealed the presence of a *C*-linked sugar moiety in the region at δ 61.6–82.2 (C-1′–C-6′), which was considered to be glucose from the fact that the chemical shifts were in good agreement with those of 2,4,6-trihydroxyacetophenone 3-*C*-β-glucopyranoside (**4**) (Tanaka et al., 1993) except for a small change of chemical shift due to substitution at C-2′ of glucose moiety. The coupling constant values of H-1′/H-2′ ($J = 9.9$ Hz) and H-2′/H-3′ ($J = 9.2$ Hz) revealed diaxial couplings and the diaxial orientations of H-1′/H-5′ and H-2′/H-4′ were also confirmed by NOEs, the *C*-linked sugar moiety was determined as glucose. The ^1H NMR spectrum also displayed a set of A_2B_2 type *ortho*-coupled aromatic protons assignable to a 4-hydroxyphenyl group [δ 7.76 (2H, *d*, $J =$ 8.8 Hz, H-2″, 6″)/6.81 (2H, *d*, $J = 8.8$ Hz, H-3″, 5″)]. Correlations between H-2″ (6″) and H-2′ with a quaternary carbon at 165.6 in the HMBC spectrum (Fig. 1) revealed that a 4-hydroxybenzoyl moiety was substituted at C-2′ of the glucose moiety, which resulted downfield chemical shift for C-2′ by ca. 3.5 ppm (Tanaka et al., 1993). The *C*-glucosyl linkage in phloroglucinol was confirmed by correlations between H-1′/C-2, H-1′/C-3, H-1′/C-4 (Fig. 1). Thus, structure was characterized as 2,4,6-trihydroxyacetophenone 3-*C*-β-(2′-*O*-4-hydroxybenzoyl)-glucopyranoside.

Compounds **2** and **3**, white amorphous powders, with molecular formulae of $C_{23}H_{24}O_{11}$ and $C_{23}H_{24}O_{10}$, respectively, were established by analysis of the HRFAB–MS ($[M–H]^-$ ion at m/z 475.1246: **2**; 459.1282: **3**). The ^1H spectrum of **2** (Table 1) was very similar to that of **1**, except for signals of an additional *trans*-coupled olefinic methine moiety [δ 7.43 (1H, *d*, $J = 15.9$ Hz, H-7″)/6.12 (1H, *d*, $J = 15.9$ Hz, H-8″)]. In the HMBC spectrum, correlations between H-2′/C-9″, H-7″/C-9″ and H-7″/C-2″(6″) (Fig. 1) revealed the presence of a *p*-coumaroyl substitution at C–2′ on the glucose instead of a 4-hydroxybenzoyl in **1**. Structure **2** was then determined to be 2,4,6-trihydroxyacetophenone 3-*C*-β-(2′-*O*-*E*-coumaroyl)-glucopyranoside. Compound **3** was observed to have a *E*-cinnamoyl group attached to C-2′ of the glucose which was supported from the molecular ion as well as for interpretation of resonances due to a phenyl group in **3** [δ 7.60 (2H, *m*, H-2″,6″)/7.42 (3H, *m*, H–3″,4″,5″)] instead of the signals for 4-hydroxyphenyl group in **2**. Thus, structure of **3** was determined to be 2,4,6-trihydroxyacetophenone 3-*C*-β-(2′-*O*-*E*-cinnamoyl)-glucopyranoside.

Compounds **5–7** were determined to be acylated derivatives of piceid (**8**) (resveratrol-3-*O*-β-glucopyranoside) (Mattive et al., 1995). Compounds **5** and **6**, white amorphous powders, had molecular formulae of $C_{27}H_{26}O_{10}$ and $C_{30}H_{30}O_{11}$, respectively, as established by the HRFAB–MS ($[M–H]^-$ ion at *m/z* 509.1441: **5**; 565.1719: **6**). The ^1H and ^{13}C NMR spectra of **5** (Table 2) showed a set of *p*-substituted phenyl groups [δ 7.39 (2H, *d*, $J = 8.6$ Hz, H-2, 6)/6.89 (2H, *d*, $J = 8.6$ Hz, H-3, 5)] a set of *trans*-coupled olefinic methine protons [δ 7.01 (1H, *d*, $J = 16.3$, H-7)/6.89 (1H, *d*, $J = 16.3$, H-8)], three *m*-coupled protons in an ABC spin system on a 1,3,5-trisubstituted benzene ring [δ 6.71 (1H, *br s*, H-10)/6.35 (1H, *t*, $J = 2.0$, H-12)/6.64 (1H, *br s*, H-14)] and resonances corresponding to a sugar moiety [δ_C 100.4/δ_H 5.25 (*d*, $J = 7.9$ Hz), 74.7/5.20 (*m*), 75.9, 71.6, 78.0,

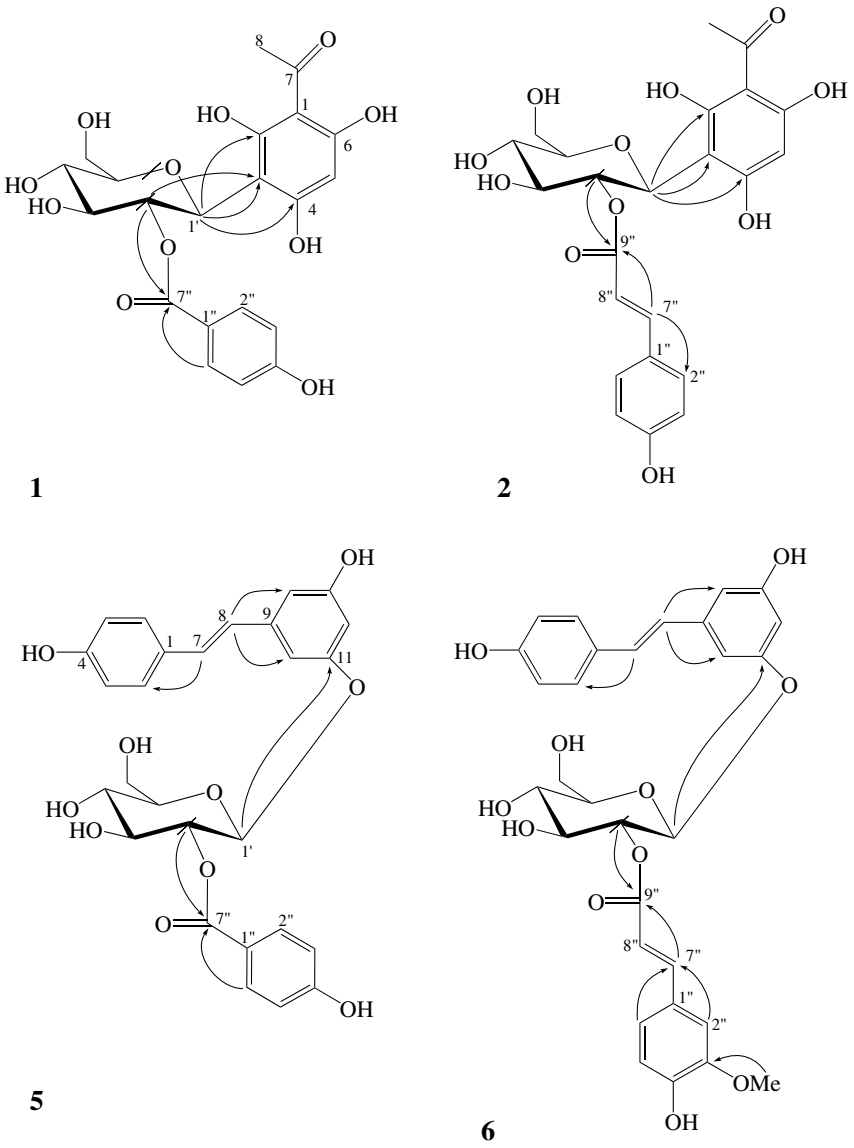

Fig. 1. Selected HMBC correlations for **1**, **2**, **5** and **6**.

62.4]. These NMR signals resembled those of **8** with slight difference due to substitution of the glucose at C–2′. In the ^{1}H and ^{13}C NMR spectra, the other signals of another *p*-substituted phenyl group [δ 7.93 (2H, *d*, $J = 8.8$ Hz, H-2″, 6″)/6.90 (2H, *d*, $J = 8.8$ Hz, H-3″, 5″)] and a carbonyl group (δ 165.7, C-7″) were assignable to a 4-hydroxybenzoyl group. In the HMBC spectrum, distinct correlations were observed between H-7/C-2(6), H-8/C-10 and H-2′/C-11C (Fig. 1), confirming the presence of a piceid unit in the molecule. Correlations of H-2′and H-2″(6″) with the carbonyl carbon at C-7″ revealed that C-2′ of the glucose is substituted with a 4-hydroxybenzoyl group. Therefore, structure **5** was determined to be piceid 2′-*O*-*p*-hydroxybenzoate. The structure of compound **6** was elucidated as the same manner, with ^{1}H and ^{13}C NMR spectra revealing signals due to a piceid moiety and a *E*-feruloyl group (Table 2). The signals of the latter were assigned as follows: a set of *trans*-coupled olefinic methines [δ 7.66 (1H, *d*, $J = 15.9$, H-7″)/6.43 (1H, *d*, $J = 15.9$, H-8″)], a set of protons in an ABX spin system for a 1,2,4-trisubstituted phenyl group [δ 7.33 (1H, *d*, $J = 1.8$ Hz, H-2″)/7.14 (1H, *dd*, $J = 8.2$, 1.8 Hz, H-6″)/6.85 (1H, *d*, $J = 8.2$, H-5″)], a methoxyl group at C-3″ [δ 3.90 (3H, *s*)], and a carbonyl group [δ 165.7, C-9″]. The chemical shifts of this moiety were also in agreement with those in kaempferol 3-*O*-β-L-(2′,4′-di-*E*-feruloyl)-rhamnoside (Kawahara et al., 2002). The correlations between H-7″/C-9″ and H-2′/C-9″ in the HMBC spectrum (Fig. 1) showed that the substituent at C-2′ in the glucose is an *E*-feruloyl instead of *p*-hydroxybenzoyl group in **5**. Thus, structure **6** was piceid 2′-*O*-*E*-ferulate.

Table 1
NMR spectral data[a] for compounds **1–3**

Position	**1**		**2**		**3**	
	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)
1	105.3		105.3		105.8	
2	164.19[b]		164.29[b]		164.25[b]	
3	102.6		102.7		102.6	
4	164.17[b]		164.22[b]		164.23[b]	
5	96.0	5.83 *s*	96.0	5.87 *s*	95.9	5.88 *s*
6	164.18[b]		164.25[b]		164.24[b]	
7	203.7		203.9		203.8	
8	32.8	2.50 *s*	32.8	2.52 *s*	32.7	2.52 *s*
1′	74.0	5.20 *d* (9.9)	74.0	5.12 *d* (10.1)	73.9	5.13 *d* (9.9)
2′	74.0	5.39 *dd* (9.9,9.2)	73.8	5.29 *brt* (7.6)	74.0	5.31 *t* (9.9)
3′	77.2	3.81 *m*	77.1	3.79 *m*	76.9	3.83 *m*
4′	71.0	3.79 *m*	70.9	3.78 *m*	70.8	3.80 *m*
5′	82.2	3.59 *m*	82.2	3.57 *m*	82.1	3.57 *m*
6′	61.6	3.91 *m*	61.6	3.84 *m*	61.5	3.91 *m*
1″	122.5		127.0		135.3	
2″ (6″)	132.6	7.76 *d* (8.8)	130.8	7.44 *d* (8.6)	128.8	7.60 *m*
3″ (5″)	115.6	6.81 *d* (8.8)	116.6	6.86 *d* (8.6)	129.6	7.42[c] *m*
4″	162.5		160.5		130.9	7.42[c] *m*
7″	165.6		145.1	7.43 *d* (15.9)	144.9	7.50 *d* (16.1)
8″			115.5	6.12 *d* (15.9)	118.8	6.33 *d* (16.1)
9″			166.3		165.7	

[a] Measured in CD_3COCD_3 at 300 Mz (^1H) and 75 Mz (^{13}C).
[b] Interchangeable.
[c] Overlapped.

Table 2
NMR spectral data[a] for compounds **5–7**

Position	**5**		**6**		**7**	
	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)
1	129.7[b]		128.8		128.9[b]	
2(6)	128.8	7.39 *d* (8.6)	127.9	7.35 *d* (8.6)	127.9	7.36 *d* (8.4)
3(5)	116.3	6.89 *d* (8.6)	115.5	6.81 *d* (8.6)	115.5	6.81 *d* (8.4)
4	158.1		157.3		157.3	
7	129.7[b]	7.01 *d* (16.3)	128.9	7.04 *d* (16.3)	128.9[b]	7.04 *d* (16.5)
8	126.2	6.89 *d* (16.3)	125.3	6.87 *d* (16.3)	125.3	6.86 *d* (16.5)
9	140.9		140.1		140.1	
10	106.5	6.71 *br s*	105.7	6.75 *br s*	105.7	6.75 *br s*
11	160.0		159.1		159.1	
12	103.8	6.35 *t* (2.0)	103.0	6.41 *t* (2.0)	103.0	6.41 *br s*
13	159.2		158.5		158.5	
14	108.5	6.64 *br s*	107.7	6.67 *br s*	107.7	6.67 *br s*
1′	100.4	5.25 *d* (7.9)	99.5	5.16 *d* (7.9)	99.5	5.16 *d* (8.0)
2′	74.7	5.20 *m*	73.5	5.12 *m*	73.5	5.11 *m*
3′	75.9	3.87 *m*	75.1	3.79 *m*	75.1	3.79 *m*
4′	71.6	3.59 *m*	70.8	3.59 *m*	70.8	3.59 *m*
5′	78.0	3.64 *m*	77.1	3.62 *m*	77.1	3.62 *m*
6′	62.4	3.77, 3.96 *m*	61.6	3.79, 3.97 *m*	61.6	3.76, 3.96 *m*
1″	122.6		126.5		126.1	
2″	132.7	7.93 *d* (8.8)	110.3	7.33 *d* (1.8)	130.0	7.55 *d* (8.6)
3″	115.9	6.90 *d* (8.8)	147.9		115.8	6.88 *d* (8.6)
4″	162.5		149.2		159.7	
5″	115.9	6.90 *d* (8.8)	115.2	6.85 *d* (8.2)	115.8	6.88 *d* (8.6)
6″	132.7	7.93 *d* (8.8)	123.2	7.14 *dd* (8.2,1.8)	130.0	7.55 *d* (8.6)
7″	165.7		145.2	7.66 *d* (15.9)	144.8	7.67 *d* (15.9)
8″			114.9	6.43 *d* (15.9)	114.6	6.38 *d* (15.9)
9″			165.7		165.7	
OMe			55.4	3.90 *s*		

[a] Measured in CD_3COCD_3 at 300 Mz (^1H) and 75 Mz (^{13}C).
[b] Overlapped.

The known compounds (**4, 7** and **8**) were characterized by total analysis of spectral data (MS, NMR) and comparison of their spectral data with literature values.

3. Experimental

3.1. General

NMR spectra were recorded on a Jeol LA-300 spectrometer. Chemical shift values are given in δ (ppm) relative to tetramethylsilane (TMS, 0 ppm) as internal reference ^{1}H NMR spectroscopy; δ (ppm) relative to solvent (carbonyl carbon atom of CD_3COCD_3, 206.0 ppm) for ^{13}C NMR spectroscopy. Peak multiplicities are quoted in Hz. Optical rotations were recorded on a JASCO P-1020 polarimeter and UV spectra were recorded on a Shimadzu UV 2200 spectrometer. IR spectra were measured on a Jasco FT-IR 410 spectrometer. Negative ion FAB–MS was measured on JEOL JMS-DX 300 spectrometer equipped with a JMA 3500 data analysis system. Silica gel 60 (70–230 mesh, Merck), Sephadex LH-20 (Pharmacia), ODS (100-200 mesh, Fuji Silysia Chemical) and ODS Sep-Pak C_{18} Cartridge (Merck) were used for CC. Kieselgel 60 F_{254} (Merck) was used as analytical and preparative TLC.

3.2. Plant material

U. borneensis Sym. was cultivated in Bogor Botanical Garden, Bogor, Indonesia, from where stems were collected in May 2000 and identified by one of co-authors (D.D.). A voucher specimen was deposited in Gifu Prefectural Institute of Health and Environmental Sciences, Kakamigahara, Gifu, Japan.

3.3. Extraction and isolation

The dried and ground stems (820 g) of *U. borneensis* were extracted successively with acetone, MeOH and 70% MeOH at rt. An aliquot (172 g) of the acetone extract (175 g) was fractionated by silica gel CC with a mixture of $CHCl_3$–MeOH by increasing polarity into 12 fractions (Fr. 1–Fr. 12) by visualization of TLC after Gibbs test. Fr. 6 ($CHCl_3$–MeOH, 9:1) was further subjected to Sephadex LH-20 CC (MeOH) to give 7 fractions (Fr. 6a–Fr. 6g). Compounds **3** (4 mg), **6** (11 mg) and **7** (4 mg) were purified by PTLC (EtOAc–$CHCl_3$–MeOH–H_2O, 15:8:4:1, **3**), ($CHCl_3$–MeOH–H_2O 30:10:1, **6** and **7**) from the sub-fractions obtained after CC over Sephadex LH-20 (acetone) of the fraction Fr. 6d. Fr. 7 ($CHCl_3$–MeOH, 9:1) was divided into 8 fractions (Fr. 7a–Fr. 7h) in the same way as that of Fr. 6. Compounds **1** (12 mg) and **2** (35 mg) were purified from the fraction Fr. 7a after CC over ODS (MeOH–H_2O, 1:1). The chromatography over C_{18} Sep Pak Cartridge (MeOH–H_2O, 1:1) of Fr. 7c resulted in isolation of **5** (5 mg). Fr. 8 ($CHCl_3$–MeOH, 8:1) was fractionated into 7 parts (Fr. 8a–Fr. 8g) by Sephadex LH-20 CC (MeOH). Compounds **4** (260 mg) and **8** (3 g) were purified from fractions Fr. 8a and Fr. 8b after CC over silica gel (EtOAc–$CHCl_3$–MeOH–H_2O, 15:8:4:1).

3.4. 2,4,6-Trihydroxyacetophenone 3-C-β-(2′-O-p-hydroxybenzoyl)-glucopyranoside (*1*)

White amorphous powder; $[\alpha]_D$ −70° ($c = 0.24$, MeOH); UV (MeOH) λ_{max} nm: 260, 276; IR ν_{max} cm^{-1}: 3272 (OH), 1700, 1630 (CO), 1609, 1515 (aromatic ring); negative ion FAB–MS *m/z* : 449 [M–H]$^-$; negative ion HRFAB–MS *m/z* : 449.1078 (calc. 449.1084 for $C_{21}H_{21}O_{11}$); For ^{1}H and ^{13}C NMR: Spectral data, Table 1.

3.5. 2,4,6-Trihydroxyacetophenone 3-C-β-(2′-O-E-coumaroyl)-glucopyranoside (*2*)

White amorphous powder; $[\alpha]_D$ −104° ($c = 0.10$, MeOH); UV (MeOH) λ_{max} nm: 330, 289; IR ν_{max} cm^{-1}: 3380 (OH), 1696, 1631 (CO), 1604, 1514 (aromatic ring); negative ion FAB–MS *m/z* : 475 [M–H]$^-$; negative ion HRFAB–MS *m/z* : 475.1246 (calc. 475.1240 for $C_{23}H_{23}O_{11}$); For ^{1}H and ^{13}C NMR: Spectral data, Table 1.

3.6. 2,4,6-Trihydroxyacetophenone 3-C-β-(2′-O-E-cinnamoyl)-glucopyranoside (*3*)

White amorphous powder; $[\alpha]_D$−79° ($c = 0.08$, MeOH); UV (MeOH) λ_{max} nm: 280; IR ν_{max} cm^{-1}: 3373 (OH), 1702, 1632 (CO), 1610, 1543, 1515 (aromatic ring); negative ion FAB–MS *m/z* : 459 [M–H]$^-$; negative ion HRFAB–MS *m/z* : 459.1282 (calc. 475.1291 for $C_{23}H_{23}O_{10}$); For ^{1}H and ^{13}C NMR: Spectral data, Table 1.

3.7. Piceid 2′-O-p-hydroxybenzoate (*5*)

White amorphous powder; $[\alpha]_D$−9° ($c = 0.10$, MeOH); UV (MeOH) λ_{max} nm: 320, 306, 258; IR ν_{max} cm^{-1}: 3368 (OH), 1699 (CO), 1607, 1514 (aromatic ring); negative ion FAB–MS *m/z* : 509 [M–H]$^-$; negative ion HRFAB–MS *m/z* : 509.1441 (calc. 509.1448 for $C_{27}H_{25}O_{10}$); for ^{1}H and ^{13}C NMR: Spectral data, Table 2.

3.8. Piceid 2′-O-E-ferulate (*6*)

White amorphous powder; $[\alpha]_D$−13° ($c = 0.20$, MeOH); UV (MeOH) λ_{max} nm: 321, 302; IR ν_{max} cm^{-1}: 3300 (OH), 1698 (CO), 1627, 1514 (aromatic ring); negative ion FAB–MS *m/z* : 565 [M–H]$^-$; negative ion

HRFAB–MS *m/z* : 565.1719 (calc. 565.1710 for $C_{30}H_{29}O_{11}$); For ^{1}H and ^{13}C NMR: Spectral data, Table 2.

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References

Ashton, S.H., 1982. Flora Malesiana. Series I – Spermatophyta. Flowering Plants, vol. 9, Part 2, Dipterocarpaceae. Martinun Nijhoff Pub, The Netherlands, pp. 337–340.

Dai, J.-R., Hallock, Y.F., Cardellina II, J.H., Boyd, M.R., 1998. HIV-inhibitory and cytotoxic oligostilbenes from the leaves of *Hopea malibato*. J. Nat. Prod. 61, 351–353.

Huang, K.-S., Lin, M., Cheng, G.-F., 2001. Anti-inflammatory tetramers of resveratrol from the roots of *Vitis amurensis* and the conformations of the seven-membered ring in some oligostilbenes. Phytochemistry 58, 357–362.

Ito, T., Tanaka, T., Ali, Z., Akao, Y., Nozawa, Y., Takahashi, Y., Sawa, R., Nakaya, K., Murata, J., Darnaedi, D., Iinuma, M., 2004. A new resveratrol hexamer from *Upuna borneensis*. Heterocycles, 63 (in press).

Ito, T., Tanaka, T., Iinuma, M., Iliya, I., Nakaya, K., Ali, Z., Takahashi, Y., Sawa, R., Shirataki, Y., Murata, J., Darnaedi, D., 2003a. New resveratrol oligomers in the stem bark of *Vatica pauciflora*. Tetrahedron 59, 5347–5363.

Ito, T., Tanaka, T., Iinuma, M., Nakaya, K., Takahashi, Y., Nakamura, H., Naganawa, H., Riswan, S., 2003b. A new dimeric stilbenoid with a five-membered lactone ring from *Shorea hemsleyana*. Helv. Chim. Acta 86, 3394–3401.

Ito, T., Tanaka, T., Nakaya, K., Iinuma, M., Takahashi, Y., Naganawa, H., Ohyama, M., Nakanishi, Y., Bastow, K.F., Lee, K.-H., 2001. A novel bridged stilbenoid trimer and four highly condensed stilbenoid oligomers in *Vatica rassak*. Tetrahedron 57, 7309–7321.

Kawahara, N., Satake, M., Goda, Y., 2002. A new acylated flavonol glycoside from the leaves of *Eriobotrya japonica*. Chem. Pharm. Bull. 50, 1619–1620.

Lee, J.P., Min, B.S., An, R.B., Na, M.K., Lee, S.M., Lee, H.K., Kim, J.G., Bae, K.H., Kang, S.S., 2003. Stilbenes from the roots of *Pleuropterus ciliinervis* and their antioxidant activities. Phytochemistry 64, 759–763.

Mattive, F., Reniero, F., Korhammer, S., 1995. Isolation, characterization, and evolution in red wine vinification of resveratrol monomers. J. Agri. Food Chem. 43, 1820–1823.

Ohyama, M., Tanaka, T., Ito, T., Iinuma, M., Bastow, K.F., Lee, K.-H., 1999. Antitumor agents 200. Cytotoxicity of naturally occurring resveratrol oligomers and their acetate derivatives. Bioorg. Med. Chem. Lett. 9, 3057–3060.

Sotheeswaran, S., Pasupathy, V., 1993. Distribution of resveratrol oligomers in plants. Phytochemistry 32, 1083–1092.

Tanaka, T., Orii, Y., Nonaka, G., Nishioka, I., 1993. Tannins and related compounds. CXXIII. Chromone, acetophenone and phenylpropanoid glycosides and their galloyl and/or hexahydroxydiphenoyl esters from leaves of *Syzygium aromaticum* Merr. et Perry. Chem. Pharm. Bull. 41, 1232–1237.