NEW LINEAR PYRANOXANTHONES FROM *CALOPHYLLUM APETALUM*

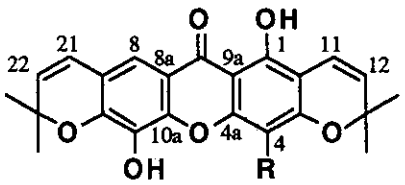
Munekazu Iinuma,[a]* Tetsuro Ito,[a] Hideki Tosa,[a] Toshiyuki Tanaka,[a] Ryoko Miyake,[a] and Veliah Chelladurai[b]

[a]Department of Pharmacognosy, Gifu Pharmaceutical University, 6-1 Mitahora-higashi 5 chome, Gifu 502, Japan, [b]Survey of Medicinal Plant Unit, Central Council for Research in Ayurveda and Siddha, Tirunelveli-627002, Tamil Nada, India

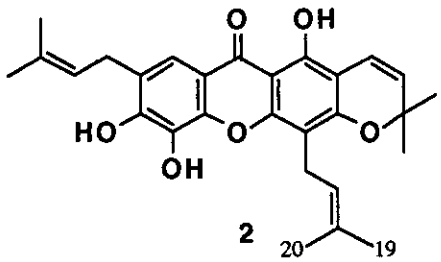
Abstract — The investigation of chemical constituents in stem bark and root of *Calophyllum apetalum* (Guttiferae) led to isolate sixteen xanthones and two coumarin derivatives. Among them, two linear pyranoxanthones [caloxanthones I (**1**) and J (**2**)] from the stem bark, and two xanthones [caloxanthone K (**10**) and 1,3,6,8-trihydroxy-2-methoxyxanthone (**12**)] from the root were new ones. The respective structures were determined by the spectral analysis.

Calophyllum (Guttiferae), which is morphologically classified to the same subfamily (Calophylloideae) as *Mammea* and *Mesua*,[1] is known to a rich source of xanthones,[2] coumarins[3] and biflavonoids.[4] A species of *Calophyllum apetalum* Wild. is a middle size tree distributed in the subtropical area, and the seed oil has been used for various medicinal purposes in India.[5] Although some chemical aspects of *C. apetalum* were mentioned,[6,7] the detail examination of phenolic constituents has not been tried yet. The structural elucidation of xanthones with C_5 chain(s) in *C. inophyllum*[8] and *C. austroidicum*[9] was dealt in our previous research works. In relation to phytochemical and chemotaxonomic interest in the genus, the chemical constituents in *C. apetalum* were examined.

Usual work-up of extraction of stem bark and root of *C. apetalum* and successive purification of the extract by chromatography resulted in the isolation of xanthones (**1**-**7** and **10**-**18**) including four new ones (**1**-**4**)



1 : R = isoprenyl
3 : R = H



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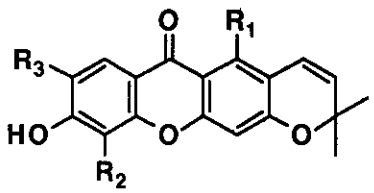
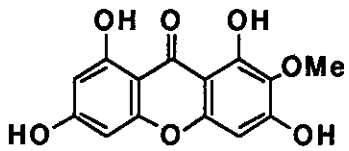


10 : R_1 = OMe, R_2 = OH, R_3 = H
10a : R_1 = R_2 = OH, R_3 = H
11 : R_1 = R_3 = OH, R_2 = H



12

and coumarin derivatives (8 and 9).

Caloxanthone I (1), a yellow amorphous powder, reacted positively to $FeCl_3$ and Gibbs tests. The $[M]^+$ observed at *m/z* 460.1807 in the high-resolution (HR) EIMS corresponds to the molecular formula of $C_{28}H_{28}O_6$. The UV and IR spectra indicated that **1** was a xanthone derivative.[10] The ^1H NMR spectrum showed the presence of two hydroxyl groups including a chelated one [δ 8.34 (1H, br s) and 13.45 (1H, s)] in addition to an isolated aromatic proton [δ 7.42 (1H, s)]. The ^1H NMR spectrum also exhibited the signals due to two dimethylpyrene rings fused to a benzene ring [δ 1.49 (6H, s), 5.72 (1H, d, J = 9.8 Hz), 6.69 (1H, d, J = 9.8 Hz) and δ 1.51 (6H, s), 5.89 (1H, d, J = 9.8 Hz), 6.57 (1H, d, J = 9.8 Hz)]. The assignment was confirmed by the HH COSY spectrum. The presence of an isoprenyl group in the xanthone was shown by the ^1H NMR spectral data [δ 1.65 (3H, s), 1.87 (3H, s), 3.53 (2H, br d) and 5.33 (1H, m)], which was supported by the observation of a base peak at *m/z* 405 [M^+ - 55] in the EIMS. All carbons bearing hydrogen atom(s) were assigned by the CH COSY spectrum (Table 1). On the other hand, in the HMBC (J = 10 Hz) spectrum (Figure 1), the chelated hydroxyl group caused cross peaks to three aromatic carbons (δ 103.6, 105.1 and 156.7), the former was further correlated to the two olefinic protons at δ 6.69 and 5.72 through ^2J and ^3J, respectively, indicating that one of the dimethylpyrene rings was fused to the xanthone in a linear form. The aromatic carbon with an *O*-function at δ 158.6 was correlated to the proton at δ 6.69 assigned to H-11 and to the methylene protons at δ 3.53 on the isoprenyl group, respectively. The methylene protons was then corresponding to a carbon at δ 22.0, the chemical shift of which implied that

both *ortho*-positions of the isoprenyl group were substituted with an *O*-function.[11] These results showed that a partial structure of **1** can be drawn as **A** in Figure 1.

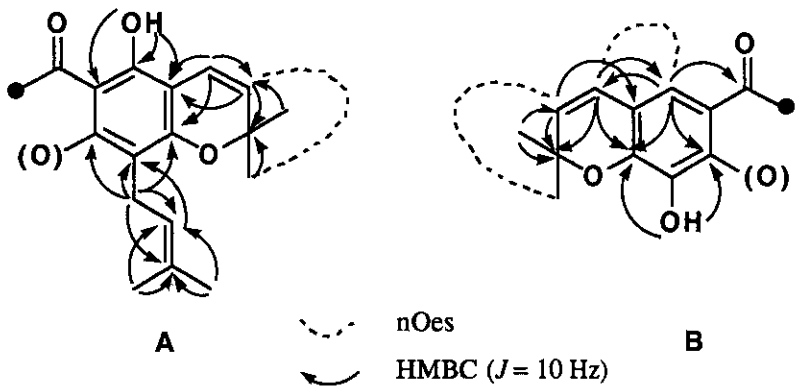


Figure 1 Partial structures (**A** and **B**), and nOes and HMBC spectrum of **1**

Table 1 NMR spectral data of xanthones (**1** - **3**)

	1[a]		2[a]		3	
No	δ_C	δ_H	δ_C	δ_H	δ_C[b]	δ_H[a]
1	156.7		156.8[c]		157.8	
2	103.6		105.1		104.8	
3	158.6		156.8[c]		160.5	
4	108.4		108.4[d]		95.5	6.36 (1H, s)
5	134.5		133.6		132.1	
6	146.6		151.5		144.5[f]	
7	119.2		126.8		117.8	
8	113.2	7.72 (1H, s)	117.1	7.56 (1H, s)	113.5	7.42 (1H, s)
9	181.5		181.5		180.2	
4a	155.0		154.9		156.9	
8a	115.2		113.7		114.7	
9a	105.1		108.4[d]		103.0	
10a	146.9		146.3		145.0[f]	
11	116.2	6.69 (1H, d, J = 9.8)	116.2	6.69 (1H, d, J = 10.3)	115.5	6.68 (1H, d, J = 10.0)
12	128.4	5.72 (1H, d, J = 9.8)	128.4	5.72 (1H, d, J = 10.3)	127.5	5.74 (1H, d, J = 10.0)
13	78.9		78.8		78.0[g]	
14, 15	28.5	1.49 (3H, s)	28.4	1.48 (3H, s)	28.4[h]	1.48[i] (3H, s)
16	22.0	3.53 (2H, br d)	21.8	3.56 (2H, d, J = 6.9)	121.4	6.85 (1H, d, J = 10.0)
17	123.3	5.33 (1H, m)	122.6	5.24 (1H, m)	131.0	5.90 (1H, d, J = 10.0)
18	131.8		132.1[e]		79.0[g]	
19	26.0	1.65 (3H, s)	26.0	1.65 (3H, s)	28.5[f]	1.50[i] (3H, s)
20	18.2	1.87 (3H, s)	18.1	1.85 (3H, s)	28.5	1.50 (3H, s)
21	122.1	6.57 (1H, d, J = 9.8)	28.8	3.45 (2H, d, J = 7.3)		
22	132.5	5.89 (1H, d, J = 9.8)	123.8	5.41 (1H, m)		
23	79.0		131.3[e]			
24	28.3	1.51 (3H, s)	26.6	1.75 (3H, s)		
25	28.3	1.51 (3H, s)	17.9	1.78 (3H, s)		
OH		8.34 (1H, br s)		8.75 (2H, br s)		
OH		13.45 (1H, s)		13.64 (1H, s)		

[a] Measured in acetone-d_6 (400 MHz), [b] Measured in $CDCl_3$ (400 MHz). [c-d] Overlapping. [e-g] Interchangeable.

Another partial structure of the xanthone was determined as follows. An nOe was observed between one of olefinic protons at δ 6.57 and the *peri*-proton at δ 7.42 which was additionally correlated to a carbonyl carbon at δ 181.5 in HMBC spectrum. Consequently another dimethylpyrene ring was also fused to the xanthone in a linear form. Furthermore an aromatic carbon at δ 146.6 caused cross peak both to the olefinic proton and the hydroxyl group at δ 8.34 in the HMBC spectrum (Figure 1). Considering these results, another partial structure of **1** is depicted as **B**, which was supported by the spectral identity to pyranojacareubin (**3**) isolated from *Reedia gardneriana* [12] (Table 1). Thus the total structure of caloxanthone I was characterized as **1**.

Caloxanthone J (**2**) was positive to $FeCl_3$ and had the molecular formula $C_{28}H_{28}O_6$ supported by the HR-EIMS (*m/z* 462.2025). The ^1H NMR spectrum closely resembled that of **1** except for the signals due to dimethylpyrene rings and showed the presence of another isoprenyl group [δ 1.75 (3H, s), 1.78 (3H, s), 3.45 (2H, br d) and 5.41 (1H, m)]. Three phenolic hydroxyl groups were exhibited at δ 8.75 (2H, br s) and δ 13.64 (1H, s). In the ^{13}C NMR spectrum, aromatic carbons with an *O*-function were observed at δ 133.6, 146.3, 151.5 and 154.9, 156.8 (C x 2), indicating that a xanthone of **2** was composed of a 1,2,3- and a 1,3,5-trioxygenated benzene ring as in the case of **1**. The chemical shift of methylene carbon on an isoprenyl group in phenolic compounds is generally observed at the range of δ 20.7-24.0 when both *ortho*-positions of the group are substituted, to the contrary, the shift is at δ 27.7−29.8 in the case that one of *ortho*-positions is substituted with an *O*-function.[11] In the present case, the chemical shift (δ 28.4) was applicable to the latter case. Then the isoprenyl group in **2** was located at C-7. An irradiation of the olefinic proton (δ 6.69) showed an enhancement of the chelated hydroxyl proton (δ 13.64) in the nOe spectrum (Figure 2), which supported that the dimethylpyrene ring was fused to the xanthone in a linear form and another isoprenyl group was located at C-4 such as **1**. On the basis of these results, the structure of caloxanthone J was concluded to be **2**.

Caloxanthone K (**10**) had the molecular formula $C_{19}H_{16}O_6$ supported by the HR-EIMS (*m/z* 340.0936). The UV and IR spectrum indicated that **10** is a xanthone derivative.[10] The presence of a methoxyl group [δ 3.90 (3H, s)], two *ortho*-coupled protons [δ 6.93 and 7.61 (1H each, d, J = 8.8 Hz)] and an isolated aromatic proton [δ 6.61 (1H, s)] was shown in the ^1H NMR spectrum. The presence of a dimethylpyrene ring was also exhibited by the ^1H NMR spectrum [δ 1.47 (6H, s), 5.83 and 6.72 (1H each, d, J = 10.0 Hz)], which was substantiated by observation of a base peak at *m/z* 325 [M^+ - 15] in the EIMS. The chemical shifts due to the *ortho*-coupled protons in the ^1H NMR spectrum preferably implied that **10** was a 5,6-dihydroxyxanthone, which was supported by comparison of the ^1H and ^{13}C NMR spectral data between **10** and **18** [1,5,6-trihyroxyxanthone]. An nOe was observed between the methoxyl proton at δ 3.90 and one of

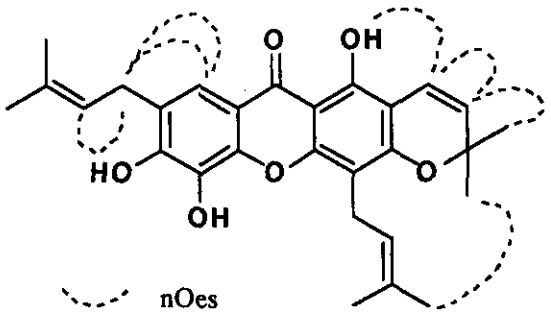


Figure 2 nOes in DIFNOE spectrum of **2**

Table 2 NMR spectral data of xanthones (**10** - **12**)

	10		**11**		**12**	
No	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	159.2[a)]		158.7		154.9	
2	110.7[b)]		105.1[c)]		132.0	
3	159.1[a)]		161.0		154.0	
4	100.8	6.61 (1H, s)	95.5	6.34 (1H, br s)	95.2[g)]	6.45 (1H, s)
5	132.6		113.9[d)]	6.99 (1H, br s)	95.2[g)]	6.38 (1H, d, J = 2.0)
6	150.8		146.9		99.4	
7	113.1	6.93 (1H, d, J = 8.8)	133.4		164.0	6.24 (1H, d, J = 2.0)
8	116.3	7.61 (1H, d, J = 8.8)	114.6[d)]	7.63 (1H, br s)	115.8	
9	174.3		181.3		184.6	
4a	157.0		157.9		159.5[e)]	
8a	112.7[b)]		117.3		102.5[f)]	
9a	117.0		103.5[c)]		102.0[f)]	
10a	145.8		152.5		159.0[e)]	
11	117.7	6.72 (1H, d, J = 10.0)	115.8	6.68 (1H, d, J = 10.0)		
12	130.9	5.83 (1H, d, J = 10.0)	128.6	5.73 (1H, d, J = 10.0)		
13	78.3		78.9			
14,15	28.2	1.47 (3H, s)	28.4	1.47 (3H, s)		
OMe	62.6	3.90 (3H, s)			61.0	3.85 (3H, s)
OH-C-1				13.58 (1H, s)		12.12 (1H, s)
OH-C-8						11.94 (1H, s)

All protons and carbons were measured in acetone-d_6 (400 MHz). [a-f)] Overlapping. [g)] Interchangeable.

olefinic protons at δ 6.72. In addition, the chemical shift of the methoxyl group (δ 62.6) indicated that both *ortho*-positions of the methoxyl group were occupied with any substituent,[13] and the chemical shift of a carbonyl carbon (δ 174.3) showed that **10** had no chelated hydroxyl group. Therefore the structure of caloxanthone K was determined to be **10**. When **10** was treated with BCl_3, a demethylated compound (**10a**) was obtained.[14] The ^1H NMR spectrum of **10a** was well-agreed to that of jacareubin isolated from the wood of *Calophyllum austroindicum*.[10] Compound (**11**) reacted positively to $FeCl_3$. The $[M]^+$ shown at *m/z* 326.0782 in the HR-EIMS is corresponding to the molecular formula $C_{18}H_{14}O_6$. The ^1H NMR spectrum closely resembled that of **10a** except for the signals due to two *ortho*-coupled protons and showed the

presence of two *para*-coupled protons [δ 6.99 (1H, br s) and 7.63 (1H, br s)]. Three carbon atoms with an *O*-function were observed at δ 133.4, 146.9 and 152.5 in the ^{13}C NMR spectrum, indicated that a 1,2,4-trioxygenated benzene ring is composed of one side of the xanthone moiety. Compared the chemical shifts due to this moiety with those of a 6,7-dioxygenated xanthone such as 3-hydroxy-2-methoxyxanthone (= 6-hydroxy-7-methoxyxanthone) isolated from the stem bark of *Mammea acuminata*,[15] the oxygenation pattern of **11** was a 6,7-dioxygenated substitution. The structure was then concluded to be **11** which has been previously synthesized,[16] however, the occurrence of **11** is first reported as a natural product.

Compound (**12**), positive to $FeCl_3$ test, was a xanthone without C_5-unit and had the molecular formula of $C_{14}H_{10}O_7$. The chemical shifts of a carbonyl carbon (δ_C 184.6) showed that **12** had two chelated hydroxyl groups [δ 11.94 (1H, s), and 12.12 (1H, s)] at *peri*-positions.[13] Considering the presence of two *meta*-coupled protons at δ 6.24 and 6.38 (1H each, d, J = 2.0 Hz) and an isolated proton at δ 6.45 (s), the substitution of the xanthone was alternatively either 1,3,6,8-tetrahydroxy-2-methoxy- or 1,3,6,8-tetrahydroxy-4-methoxyxanthone. The chemical shifts of **12** in the ^1H and ^{13}C NMR spectrum compared with those of **16** (1,3-dihydroxy-2,5-dimethoxyxanthone) preferably supported that **12** had a 1,3-dihydroxy-2-methoxyl substitution. Therefore the structure of **12** was 1,3,6,8-tetrahydroxy-4-methoxyxanthone.

Other eleven xanthones isolated in the present experiment were characterized as pyranojacareubin (**3**), 1,5-dihydroxy-6-isoprenyl- (**4**), 1,3,5-trihydroxy-2-methoxy- (**5**), 1,3,5-trihydroxy- (**6**), 1,3,6-trihydroxy-5-methoxyxanthone (**7**), 6-deoxyjacareubin (**13**), 1,5-dihydroxy- (**14**), 3,8-dihydroxy-1,2-dimethoxy- (**15**), 1,3-dihydroxy-2,5-dimethoxy- (**16**), 1,3,7-trihydroxy- (**17**), and 1,5,6-trihydroxyxanthone (**18**), respectively. Two coumarins were also identified as apetalic acid (**8**) and isoapetalic acid (**9**). The respective structures were determined by the spectral analyses.

EXPERIMENTAL

General. The following instruments were used: EIMS spectra, JEOL JMS-D300 (70 eV) instrument; ^1H and ^{13}C NMR spectra, JEOL JNM EX-400 (TMS as internal standard); UV spectra, Shimadzu UV-2200 spectrophotometer (in methanol solution); IR spectra, PERKIN ELMER FT-IR spectrophotometer 1720X (on KBr pallet). The following adsorbents were used for purification; analytical TLC: Merck Kieselgel 60 F_{254}, column chromatography: Merck Kieselgel 60, Fuji Davison Silica gel BW-300, and Pharmacia Fine Chemicals AB Sephadex LH-20.

Plant material. Stem bark and root of *Calophyllum apetalum* were collected at Tamil Nadu, India, in August, 1995. The voucher specimens are deposited in the Herbarium of Gifu Pharmaceutical University.

Extraction and isolation. The dried and ground stem bark (1 kg) of *C. apetalum* was extracted successively with benzene, acetone and 70% MeOH under reflux. After concentration, the extracts gave respective residues [90 g (benzene), 80 g (acetone) and 120 g (70% MeOH)]. The benzene extract was suspended into MeOH and partitioned with *n*-hexane. The MeOH soluble extract (43 g) was subjected to chromatography on silica gel column eluted with a mixture of benzene-acetone increasing polarity to give six fractions (^{BB}F. 1 - 6). ^{BB}F. 2 (10 : 1) was further subjected to column chromatography on Sephadex LH-20 (MeOH) to give three fractions (^{BB}F. 2-1- 2-6). Compounds (**8**) (30 mg) and (**9**) (35 mg) were obtained from ^{BB}F. 2-2. ^{BB}F. 2-3 was further separated by vacuum liquid chromatography (VLC) on silica gel eluted with an *n*-hexane-EtOAc system to give seven fractions (^{BB}F. 2-3A - 2-3G). Compounds (**1**) (10 mg), (**2**) (5 mg), (**3**) (8 mg) and (**4**) (2 mg) were obtained from ^{BB}F. 2-3B (20 : 1), and ^{BB}F. 2-3C (15 : 1), ^{BB}F. 2-3D (10 : 1), respectively. The acetone extract (57 g) was also subjected to silica gel column eluted with a mixture of benzene-acetone increasing polarity to give eight fractions (^{BA}F. 1 - 8). ^{BA}F. 6 was further purified by PTLC ($CHCl_3$-acetone = 10 : 1) to give (**5**) (16 mg), (**6**) (12 mg) and (7) (7 mg).

The dried and ground root (1.2 kg) of *C. apetalum* was extracted in same manners as the stem bark to give benzene (25 g), acetone (30 g) and 70% MeOH extract (50 g) after concentration. The benzene extract (22 g) was subjected to silica gel column eluted with a benzene-acetone system to give five fractions. The third fraction was further subjected to silica gel column eluted with an *n*-hexane-EtOAc system to give five fractions (^{RB}F. A - E). Compounds (**13**) (8 mg) and (**14**) (12 mg) were obtained in a pure form after recrystallization (benzene-acetone) from ^{RB}F. B (5 : 1) and ^{RB}F. C (5 : 1), respectively. Compounds (**15**) (10 mg) and (**16**) (12 mg) were obtained from ^{RB}F. D (5 : 1). The acetone extract (57 g) was separated by silica gel column chromatography eluted with a benzene-acetone system to give seven fractions (^{RA}F. 1 - 7). The second fraction (^{RA}F. 2) was further purified by VLC ($CHCl_3$-MeOH = 15 : 1) and PTLC (benzene-EtOAc = 5 : 1) to give (**12**) (4 mg) and (**17**) (8 mg). Compounds (**10**) (5 mg), (**11**) (8 mg) and (**18**) (5 mg) were obtained from ^{RA}F. 4 (3 : 1) and ^{RA}F. 5 (1 : 1), respectively.

Caloxanthone I (1) : A yellow amorphous powder; HR-EIMS: $[M]^+$ *m/z* 460.1878 (Calcd 460.1886 for $C_{28}H_{28}O_6$); EIMS *m/z* (rel. int.): 460 (M^+, 52), 445 (100), 417 (17), 405 (10), 230 (4), 215 (11), 187 (5); UV λ (nm): 239, 253 sh, 263 sh, 293 sh, 299, 347; IR ν (cm^{-1}): 3440, 2969, 2927, 2859, 1646, 1607, 1578; the ^1H and ^{13}C NMR spectral data are listed in Table 1.

Caloxanthone J (2) : A yellow amorphous powder; HR-EIMS $[M]^+$ *m/z* 462.2025 (Calcd 462.2041 for $C_{28}H_{30}O_6$); EIMS *m/z* (rel. int.): 462 (M^+, 53), 447 (100), 445 (22), 419 (17), 407 (12), 391 (15), 363 (5), 335 (5), 215 (3), 188 (3), 165 (2), 115 (1), 69 (1); UV λ (nm): 204, 224 sh, 238, 283 sh, 288, 335; IR ν (cm^{-1}): 3426, 2971, 2928, 1651, 1627, 1606; the ^1H and ^{13}C NMR spectral data are shown in Table 1.

Caloxanthone K(10) : A yellow amorphous powder; HR-EIMS $[M]^+$ *m/z* 340.0936 (Calcd 340.0942 for $C_{19}H_{16}O_6$); EIMS *m/z* (rel. int.): 340 (M^+, 41), 325 (100), 295 (8), 288 (5), 273 (10), 259 (7), 231 (7); UV λ (nm): 257sh, 300 sh, 268, 350 sh; IR ν (cm^{-1}): 2975, 2930, 1654, 1637, 1605; the ^1H and ^{13}C NMR spectral data are shown in Table 2.

Demethylation of 10: To a solution of dry CH_2Cl_2 (30 mL) containing **10** (2 mg) added BCl_3 (0.5 mL) at -25°C. The reaction mixture was left at room temperature for 3 h and evaporated under reduced pressure. The residue was purified by PTLC (*n*-hexane-EtOAc-MeOH = 8 : 2 : 1) to give **10a** (1 mg).Compound (**10a**) (jacareubin): A pale yellow amorphous powder; EIMS *m/z* (rel. int.): 326 (M^+, 18), 311 (100), 156 (7), 78 (9), 63 (9); UV λ (nm): 207, 232 sh, 240, 257 sh, 277, 283 sh, 303 sh, 331; IR ν (cm^{-1}): 3460, 3120, 2970, 1650, 1615, 1585; ^1H NMR (400 MHz, acetone-d_6) δ: 1.48 (6H, s, H-14, 15), 5.74 (1H, d, *J* = 10.0 Hz, H-12), 6.35 (1H, s, H-4), 6.69 (1H, d, *J* = 10.0 Hz, H-11), 6.99 (1H, d, *J* = 8.8 Hz, H-7), 7.64 (1H, d, *J* = 8.8 Hz, H-8), 8.92 (2H, br s, OH-C-5 and -6), 13.56 (1H, s, OH-C-1).

Compound (11) : A yellow amorphous powder; HR-EIMS $[M]^+$ *m/z* 326.0782 (Calcd 326.0786 for $C_{18}H_{14}O_6$); EIMS *m/z* (rel. int.): 326 (M^+, 23), 311 (100), 156 (8); UV λ (nm): 240, 276, 285 sh, 303 sh, 332; IR ν (cm^{-1}): 3468, 2975, 2927, 1654, 1618, 1585; the ^1H and ^{13}C NMR spectral data are shown in Table 2.

Compound (12) : A pale yellow amorphous powder; HR-EIMS $[M]^+$ *m/z* 290.0439 (Calcd 290.0425 for $C_{14}H_{10}O_7$); EIMS *m/z* (rel. int.): 290 (M^+, 80), 275 (62), 272 (17), 261 (13), 247 (100), 218 (6), 190 (5), 163 (6), 153 (10), 163 (6), 153 (10), 136 (6), 109 (6), 93 (5); UV λ (nm): 209, 236, 253, 270 sh, 327; IR ν (cm^{-1}): 3377, 2853, 1646, 1606, 1572; the ^1H and ^{13}C NMR spectral data are listed in Table 2.

Compound (18) : A yellow amorphous powder; HR-EIMS $[M]^+$ *m/z* 244.0382 (Calcd 244.0372 for $C_{13}H_8O_5$); EIMS *m/z* (rel. int.): 244 (M^+, 100), 243 (2), 216 (4), 215 (3), 187 (5), 131 (2), 108 (5); UV λ (nm): 207, 248, 286, 326; IR ν (cm^{-1}): 3392, 1650, 1610, 1582; ^1H NMR (400 MHz, acetone-d_6) δ: 6.75 (1H, br d, H-2), 6.98 (1H, br d, H-4), 7.03 (1H, d, *J* = 8.8 Hz, H-7), 7.65 (1H, t, *J* = 8.3 Hz, H-3), 7.68 (1H, d, *J* = 8.8 Hz, H-8), 9.05 (2H, br s, OH-C-5 and -6), 12.93 (1H, s, OH-C-1); ^{13}C NMR (100 MHz, acetone-d_6) δ: 107.7 (C-4), 109.0 (C-9a), 111.1 (C-2), 114.2 (C-7), 115.0 (C-8a), 117.8 (C-8), 133.4 (C-

5), 137.5 (C-3), 147.3 (C-10a), 152.8 (C-6), 157.2 (C-4a), 163.1 (C-1), 182.7 (C-9).

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