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SIX XANTHONES FROM *CALOPHYLLUM AUSTROINDICUM*

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Key Word Index—*Calophyllum austroindicum*; Guttiferae; xanthone; caloxanthone F; caloxanthone G; caloxanthone H; 6-hydroxy-1,3,5-trimethoxyxanthone; 3,6-dihydroxy-1,5-dimethoxyxanthone; 1,3,6-trihydroxy-5,7-dimethoxyxanthone.

Abstract—Six new xanthones, caloxanthone F, G, H, 6-hydroxy-1,3,5-trimethoxy-, 3,6-dihydroxy-1,5-dimethoxy- and 1,3,6-trihydroxy-5,7-dimethoxyxanthone, were isolated from the stem wood of *Calophyllum austroindicum*, in addition to eight known xanthones. From the bark, four known xanthones, a coumarin, apetallic acid, and (−)-epicatechin were isolated. These structures were determined by analysis of NMR spectral data including 2D techniques. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The genus *Calophyllum* belongs to the same subfamily as *Mammea* and *Mesua* [1]. Plants in this subfamily are a rich source of xanthones [2], coumarins [3] and biflavonoids [4]. Recently the bioactivities of various xanthones (antihypoglycaemic [5], antiplatelet [6], antimicrobacterial [7], etc.) and coumarins (anti-HIV activity [8, 9]) have been reported. In a continuation of search for biologically active principles in Guttiferaeous plants [10–13], the chemical constituents of *C. austroindicum* Kosterm ex P. F. Stevens were examined. We report here on the isolation and characterization of six new xanthones along with 14 known compounds.

RESULTS AND DISCUSSION

Trunk of *C. austroindicum* collected in India was divided into bark and wood. Each part was air-dried, ground and extracted successively with benzene, acetone and 70% MeOH. The benzene extract of the wood was repeatedly chromatographed on silica gel and Sephadex LH-20 to give compound **1**, and the known xanthones [6-deoxyjacareubin (**7**), jacareubin (**8**), guanandin (**9**), dehydrocycloguanandin (**10**), 1,3,5-trihydroxy-2-isoprenyl- (**11**), 1,7-dihydroxy- (**13**)and 1-hydroxy-7-methoxyxanthone (**14**)]. From an acetone extract of the wood, **2–6** and 1,3,5,6-tetrahydroxy-2-isoprenylxanthone were isolated. The benzene and an acetone extract of the bark were chromatographed repeatedly in the same manner to give the known thwaitesixanthone (**15**), 2-methoxy- (**16**), 4-hydroxy- (**17**) and 2-hydroxyxanthone (**18**), a coumarin, apetallic acid (**19**) and (−)-epicatechin (**20**).

Compound **1**, caloxanthone F, $[\alpha]_D$ −6°, gave positive Gibb's and $FeCl_3$ tests. The HR-EI-mass spectrum showed the molecular ion at *m/z* 312.1009 which corresponds to $C_{18}H_{16}O_5$. The IR spectrum exhibited strong bands due to hydroxyls (3460 cm^{-1}) and a conjugated carbonyl group (1645 cm^{-1}). Its UV absorptions closely resembled those of 1,5-dihydroxyxanthone [14]. The ^1H NMR spectrum showed the presence of two *ortho*-coupled protons [δ 7.29 and 7.68 (1H each, *d*, J = 8.1 Hz)], a 1,2,3-trisubstituted benzene ring [δ 6.77 and 7.01 (1H each, *dd*, J = 8.3, 1.0 Hz), 7.70 (1H, *t*, J = 8.3 Hz)] and a chelated hydroxyl group [δ 12.77 (1H, *s*)]. In the HMBC spectrum (Fig. 1), the chelated hydroxyl group caused three cross peaks with three aromatic carbons at δ 109.3, 111.1 and 163.1, respectively, one of which (δ 111.1) was further correlated to the proton at δ 6.77 assignable to H-2 in the CH COSY spectrum. In the HMBC spectrum, one of the *ortho*-coupled protons (δ 7.68) was correlated to the carbonyl carbon at δ 183.0. These results indicated that **1** was a 1-hydroxy-5,6-disubstituted xanthone. The ^1H NMR spectrum further showed the presence of two methyls adjacent to an oxygen-function (δ 1.28 and 1.38), an oxygenated methine proton [δ 4.91 (1H, *dd*, J = 9.8, 8.3 Hz)] and a hydroxyl group [δ 3.84 (1H, *br s*)], in addition to two methylene protons [δ 3.39 (1H, *dd*, J = 16.8, 9.8 Hz) and 3.51 (1H, *dd*, J = 16.8, 8.3 Hz)]. In the HMBC spectrum of **1** (Fig. 1), the methyl protons (δ 1.28 and 1.38) were correlated to the methine carbon with an oxygen-function (δ 92.4) and a quaternary carbon with an oxygen-function (δ 71.5). The latter carbon was further correlated to one of the

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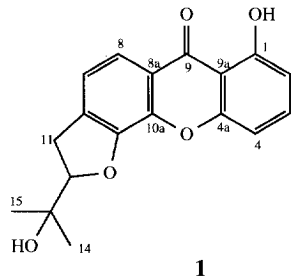

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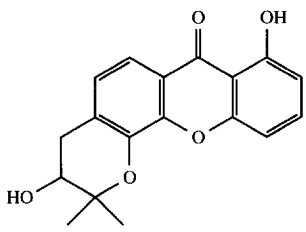

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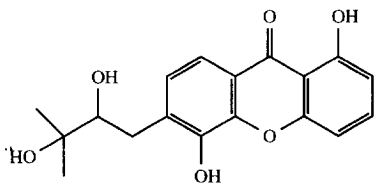

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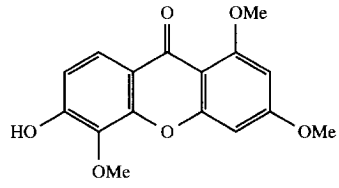

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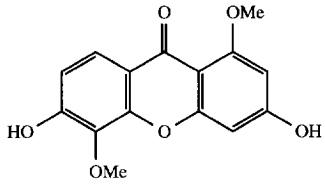

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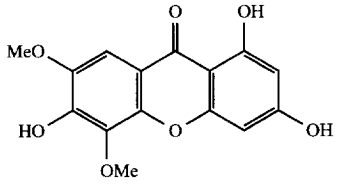

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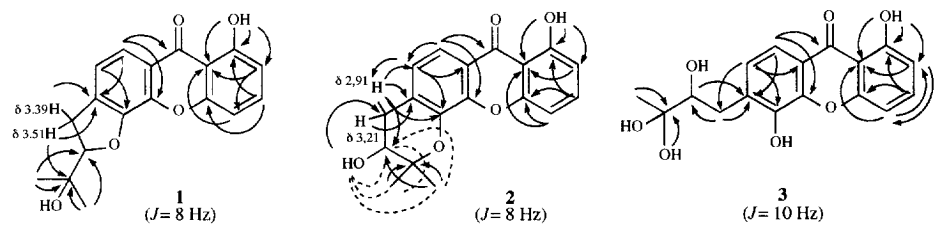
methylene protons at δ 3.51. These results and the MS spectral data suggested that a possible partial structure of **1** was either **A** or **B** (Fig. 2). Because NOEs were observed between the above two methyl protons and the methylene proton at δ 3.39 (Fig. 2), **A** was preferable to **B** as a partial structure of **1**. There remained to be determined the orientation of a dihydrofuran ring. In the HMBC spectrum, the methylene protons of the dihydrofuran ring caused a cross peak to the quaternary carbon at δ 137.3 which was also correlated to one of the *ortho*-coupled protons at C-8 (δ 7.68), supporting that the furan ring was formed through the hydroxyl group at C-5 of the xanthone. The structure of caloxanthone F was thus characterized as **1**, which was supported by the other correlations in the HMBC spectrum and NOEs. Assignment of the ^{13}C NMR spectral data are shown in Table 1.

Compound **2**, caloxanthone G, $[\alpha]_D$ $-33°$, gave positive Gibb's and $FeCl_3$ tests. The HR-EI-mass spectrum showed the molecular ion at m/z 312.0983 and the molecular formula to be $C_{18}H_{16}O_5$. Its UV spectrum and NMR spectral analysis including 2D technique suggested that **2** was also a 5-oxygenated 1-hydroxy-xanthone with a substituent at C-6 (Fig. 1). The ^1H NMR spectrum showed the presence of two methyls with an oxygen-function [δ 1.40 and 1.47 (3H each, *s*)], an oxygenated methine proton [δ 3.95 (1H, *dt*, $J = 7.3$, 5.4 Hz)] and the two methylene protons [δ 2.91 (1H, *dd*, $J = 7.6$, 7.3 Hz) and 3.21 (1H, *dd*, $J = 7.6$, 5.4 Hz)], in addition to a hydroxyl group [δ 4.39 (1H, *d*, $J = 5.4$ Hz)] which caused no cross peak in the CH COSY spectrum. In the HMBC spectrum of **2** (Fig. 1), the hydroxyl proton at δ 4.39 was correlated to a methylene carbon (δ 32.7) through ^3J. The methylene proton at δ 2.91 caused a cross peak with an oxymethine carbon (δ 69.0) which was also correlated to the two methyl protons. These results indicated that a possible partial structure of **2** was as shown in **B** (Fig. 2), which was also supported by the other correlations in the HMBC spectrum and NOE experiments (Fig. 1). The methylene proton at δ 2.91 was correlated to an aromatic carbon (δ 126.0) through ^3J in the HMBC spectrum, which was also correlated to one of the *ortho*-coupled proton (δ 7.16) in the CH COSY. These results indicated that the oxygen in the dimethylchromane ring originated from the hydroxyl group at C-5 of a xanthone skeleton. Thus the structure of caloxanthone G was characterized as **2**.

Compound **3**, $[\alpha]_D$ $+33°$, was positive to $FeCl_3$ and Gibb's reagent. HR-EI-mass spectrometry (m/z 330.1119) indicated the molecular formula of $C_{18}H_{18}O_6$. The UV and IR spectral features of **3** were



1 (J= 8 Hz) **2** (J= 8 Hz) **3** (J= 10 Hz)

Fig. 1. HMBC spectrum and NOE experiments for compounds **1**–**3**.

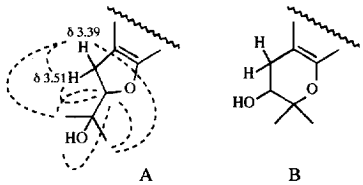


Fig. 2. Possible partial structure and NOE experiments for compound **1**. ----, NOE.

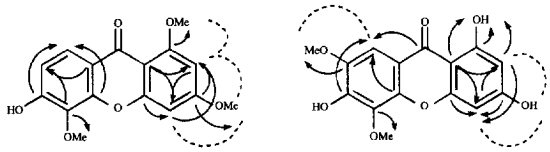


Fig. 3. COLOC ($J = 10$ Hz) spectrum and NOE experiments for compounds **4** and **6**. ⟶, COLOC; ----, NOE.

similar to those of **1** and **2** and the ^{1}H and ^{13}C NMR spectra were characteristic of a 5-oxygenated 1-hydroxy-xanthone with a substitutent at C-6. The ^{1}H NMR spectrum showed the presence of two methyl groups bearing an oxygen-function [δ 1.28 and 1.29 (3H each, *s*)], an oxymethine proton [δ 3.76 (1H, *dd*, $J = 9.5$, 2.0 Hz)] and two methylene protons [δ 2.89 (1H, *dd*, $J = 14.2$, 9.5 Hz) and 3.16 (1H, *dd*, $J = 14.2$, 2.0 Hz)], in addition to a hydroxyl group [δ 3.31 (1H, *br s*)]. Based on the above data, the C_5 unit in **3** was characterized as a 2,3-dihydroxy-3-methylbutyl chain. The structure of caloxantone H was concluded to be **3**, which was supported by the correlations in the HMBC spectrum (Fig. 1).

Compound **4** had the molecular formula $C_{16}H_{14}O_6$ (HR-EI mass spectrometry, *m/z* 302.0800). Its UV and IR spectra suggested that **4** was a xanthone. In the ^{1}H NMR spectrum, the presence of a hydroxyl group [δ 10.47 (1H, *br s*)] and three methoxyl groups [δ 3.85, 3.90 and 3.92 (3H each, *s*)] were indicated, in addition to two *meta*-coupled protons [δ 6.48 and 6.70 (1H each, *d*, $J = 2.0$ Hz)] and two *ortho*-coupled protons [δ 6.90 and 7.65 (1H each, *d*, $J = 8.8$ Hz)]. All protonated carbons were assigned by CH COSY (Table 1). In the COLOC spectrum (Fig. 3), the *meta*-coupled protons at δ 6.48 and 6.70 caused cross peaks with aromatic carbons with an oxygen-function at δ 164.3 and 158.9, respectively, suggesting the presence of a phloroglucinol-type benzene ring in **4**. NOEs were observed between one of the methoxyl groups at δ 3.92 and the *meta*-coupled protons (δ 6.48 and 6.70) (Fig. 3), and an NOE was found for the proton at δ 6.48 when the methoxyl group at δ 3.85 was irradiated. The partial structure in **4** was thus determined to be that of a 1,3-dimethoxyxanthone. Three aromatic carbons with an oxygen-function were observed at δ 134.0, 149.1 and 154.9 in the ^{13}C NMR spectrum, indicating the presence of a 1,2,3-trioxygenated benzene ring for another moiety of the xanthone. The chemical shift of a methoxyl group at δ 60.7 implied that both *ortho*-positions of the methoxyl group were substituted [15]. Thus a further partial structure of **4** was that of a 6-hydroxy-5-methoxyxanthone. Therefore, the total structure of **4** was determined to be 6-hydroxy-1,3,5-trimethoxyxanthone, which was supported by the other correlations in the COLOC spectrum.

Table 1. ^{13}C NMR spectral data of compounds **1–6**

C	1*	2*	3*	4†	5†	6†
1	163.1	162.8	163.0	161.3	161.7	162.5
2	111.1	107.9	111.0	95.4	95.6	97.9
3	137.9	137.7	137.9	164.3	163.2	164.8
4	107.8	110.9	108.0	93.2	95.0	93.8
5	148.5	143.0	145.5	134.0	133.9	134.9
6	137.3	128.8	135.8	154.9	154.8	147.1‡
7	121.3	126.0	127.7	113.3	113.1	146.0
8	117.9	115.9	116.0	121.0	121.0	99.5
9	183.0	183.1	183.4	172.3	172.8	178.7
4a	156.9	157.1	157.2	158.9	158.8	157.0
8a	121.4	120.4	120.7	116.0	115.6	111.1
9a	109.3	109.4	109.4	105.8	104.7	101.5
10a	142.2	147.0	146.7	149.1	149.0	145.6†
11	31.9	32.7	34.7			
12	92.4	69.0	80.3			
13	71.5	79.5	73.0			
14	25.8	21.3	25.6			
15	26.0	25.8	25.7			
OMe-C-1				56.0	55.8	
OMe-C-3				55.9		
OMe-C-5				60.7	60.6	60.9
OMe-C-7						56.0

*Measured in acetone-d_6.
†Measured in DMSO-d_6.
‡Signals interchangeable.

Compound **5** had the molecular formula $C_{15}H_{12}O_6$ (HR-EI-mass spectrometry, *m/z* 288.0648). Its UV absorptions closely resembled those of **4**, indicating that **5** was a 1,3,5,6-tetraoxygenated xanthone. The ^{1}H NMR spectrum showed the presence of two hydroxyls [δ 10.42 and 10.80 (1H each, *br s*)] and two methoxyl groups [δ 3.82 and 3.87 (3H each, *s*)], in addition to two *meta*-coupled protons [δ 6.36 and 6.44 (1H each, *d*, $J = 2.0$ Hz)] and two *ortho*-coupled protons [δ 6.87 and 7.63 (1H each, *d*, $J = 8.8$ Hz)]. A NOE was observed at one of the *meta*-coupled protons (δ 6.36) when the methoxyl group at δ 3.82 was irradiated, indicating that C-1 of the xanthone was substituted with a methoxyl group. The methoxyl carbons were observed at δ 55.8 and 60.6 in the ^{13}C NMR spectrum, the former was located at C-1 and the latter was at C-5. Thus structure of **5** was thus determined to be 3,6-dihydroxy-1,5-dimethoxyxanthone.

Compound **6** gave positive $FeCl_3$ and Gibb's tests. HR-EI-mass spectrometry (*m/z* 304.0595) gave the molecular formula $C_{15}H_{12}O_7$. Its UV spectrum was similar to those of 1,3,5,6-tetrahydroxy-7-methoxyxanthone, i.e. caloxanthone E [11]. The signals based on three hydroxyls [δ 10.30, 10.84 (1H each, *br s*) and 13.05 (1H, *s*, chelated)] and two methoxyl groups

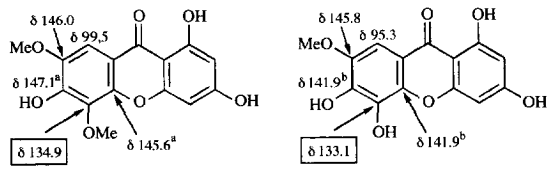


Fig. 4. Comparison of ^{13}C NMR spectral data between compound **6** and caloxanthone E. [a]Interchangeable; [b]overlapping.

[δ 3.90 and 3.91 (3H each, *s*)] were observed in the ^1H NMR spectrum, in addition to the signals of two *meta*-coupled protons [δ 6.18 and 6.39 (1H each, *d*, J = 2.0 Hz)] and an aromatic proton singlet (δ 7.26). All protonated carbons were assigned by CH COSY (Table 1). In the COLOC spectrum (Fig. 3), the chelated hydroxyl group caused a cross peak to the aromatic carbon at δ 97.9 which was also correlated to the *meta*-coupled proton at δ 6.18 in CH COSY. In the ^1H NMR spectrum, NOEs were observed between the hydroxyl group (δ 10.84) and the two *meta*-coupled protons. These results suggested that **6** was a 1,3-dihydroxyanthone derivative. In the COLOC spectrum (Fig. 3), the aromatic proton (δ 7.26) was correlated to a carbonyl carbon through ^3J, indicating that a *peri*-position of the carbonyl group (C-8) was not substituted. Furthermore, a NOE was observed at the aromatic proton (δ 7.26) when the methoxyl group at δ 3.90 was irradiated, suggesting a possible structure of **6** was either 1,3,6-trihydroxy-5,7-dimethoxyxanthone or 1,3,5-trihydroxy-6,7-dimethoxyxanthone. The methoxyl group at δ 3.91 caused a cross peak with an aromatic carbon with an oxygen-function at δ 134.9 in the COLOC spectrum. On comparison of the ^{13}C NMR spectral data of **6** with those of caloxanthone E [11] (Fig. 4), the aromatic carbon at δ 134.9 was assignable to C-5. The structure of **6** was thus determined to be 1,3,6-trihydroxy-5,7-dimethoyxanthone. Although **6** has already been synthesized [16], this is the first time it has been isolated from a natural source.

All of the known compounds isolated in this study (see above) were characterized by spectral methods.

EXPERIMENTAL

General experimental procedures. MS: JEOL JMS-D300 (70 eV); ^1H and ^{13}C NMR: JEOL JNM EX-400 (TMS as int. standard); IR: KBr pellets; UV: MeOH. Analytical TLC: Merck Kieselgel 60 F_{254}; CC: Merck Kieselgel 60, Fuji Davison Silica gel BW-300, and Pharmacia Fine Chemicals AB Sephadex LH-20.

Plant material. Trunk of *C. austroindicum* was collected in India in July, 1995. The voucher specimens are deposited in the Herbarium of Gifu Pharmaceutical University.

Extraction and isolation. The air-dried and ground wood of *C. austroindicum* (1 kg) was extracted under reflux with benzene (2 l × 12 hr × 3) (weight of extractive after solvent was removed: 12 g), Me_2CO (2 l × 12 hr × 3) (35 g), and 70% MeOH (2 l × 12 hr × 3) (40 g), successively. The benzene extract (10 g) was subjected to VLC on silica gel eluted with an *n*-hexane–EtOAc system to give nine fractions (frs 1–9). Compounds **8** (400 mg), **9** (40 mg) and **11** (50 mg) were obtained from fr. 7 (5:1), fr. 3 (10:1) and fr. 8 (3:1), respectively. Fr. 2 (20:1) was chromatographed on Sephadex LH-20 (Me_2CO) to give **10** (5 mg) and **14** (3 mg). Fr. 4 (10:1) was also purified by Sephadex LH-20 (Me_2CO) to give **7** (10 mg) and **13** (5 mg). Fr. 7 was further chromatographed on Sephadex LH-20 (Me_2CO) and prep. TLC (benzene-Me_2CO; 20:1) to give **1** (10 mg). The Me_2CO extract of the stem wood (25 g) was subjected to silica gel CC eluted with a benzene–Me_2CO system to give 11 frs (Fr. A–K). Compounds **2** (5 mg), **6** (10 mg) and **5** (1 mg) were obtained from fr. C (10:1), fr. H (3:1) and fr. I (2:1), respectively. Fr. H was further subjected to VLC with a $CHCl_3$–MeOH system to give **4** (5 mg) (from a 40:1 eluent), **3** (40 mg) (20:1) and **12** (5 mg) (5:1).

The air-dried, ground bark (1 kg) of *C. austroindicum* was extracted under reflux with benzene (2 l × 12 hr × 3) (32 g), Me_2CO (2 l × 12 hr × 3) (110 g), and 70% MeOH (2 l × 12 hr × 3) (95 g), successively. The benzene extract (20 g) was chromatographed on silica gel eluted with a benzene–Me_2CO system to give eight frs (Fr. 1–8). Compound **15** (20 mg) was obtained from fr. 1 (benzene 100%). Fraction 3 (benzene 100%) was further chromatographed on Sephadex LH-20 with Me_2CO to give three frs. The third fr. was further chromatographed on Sephadex LH-20 with Me_2CO to give three frs. The third fr. was purified by prep. TLC (*n*-hexane–EtOAc 20:1) to give **16** (3 mg). Fr. 5 (20:1) was chromatographed on Sephadex LH-20 (Me_2CO) to give four frs. The second fr. was repeatedly purified by Sephadex LH-20 CC (Me_2CO) to give **19** (500 mg). The fourth fr. was purified by prep. TLC (*n*-hexane–EtOAc–MeOH; 8:2:1) to give **17** (3 mg) and **18** (6 mg). Furthermore, the Me_2CO extract of the bark (60 g) was chromatographed on silica gel eluted with a benzene–Me_2CO system to give **20** (100 mg).

Compound **1** *(caloxanthone F).* A pale yellow amorphous, $[\alpha]_D^{20}$ −6° (*c* 0.09, MeOH), HR-EI-MS *m/z* 312.1009 for $C_{18}H_{16}O_5$ (calcd 312.1000). EI-MS *m/z* (rel. int.): 312 $[M]^+$ (59), 279 (9), 254 (67), 253 (100), 242 (8), 241 (8); IR ν_{max}^{KBr} cm^{-1}: 3460, 3000, 1645, 1605, 1595. UV λ_{max}^{MeOH} nm: 236 sh, 251, 272 sh, 290 sh, 320, 365; ^1H NMR (400 MHz, acetone-d_6): δ 1.28 and 1.38 (3H each, *s*, H-14 and 15), 3.39 (1H, *dd*, J = 16.8, 9.8 Hz, H-11), 3.51 (1H, *dd*, J = 16.8, 8.3 Hz, H-11), 3.84 (1H, *br s*, OH-C-13), 4.91 (1H, *dd*, J = 9.8, 8.3 Hz, H-12), 6.77 (1H, *dd*, J = 8.3, 1.0 Hz, H-2), 7.01 (1H, *dd*, J = 8.3, 1.0 Hz, H-4), 7.29 (1H, *d*, J = 8.1 Hz, H-7), 7.68 (1H, *d*, J = 8.1 Hz, H-8), 7.70 (1H, *t*, J = 8.1 Hz, H-3), 12.77 (1H, *s*, OH-C-1).

Compound **2** *(caloxanthone G).* A pale yellow amorphous, $[\alpha]_D^{20}$ −33° (*c* 0.09, MeOH), HR-EI-MS *m/z* 312.0983 for $C_{18}H_{16}O_5$ (calcd 312.1000). EI-MS

m/z (rel. int.): 312 $[M]^+$ (87), 279 (15), 254 (13), 253 (16), 242 (100), 213 (11); IR ν_{max}^{KBr} cm^{-1}: 3550, 3470, 3175, 1645, 1610, 1575; UV λ_{max}^{MeOH} nm: 235 sh, 251, 270 sh, 290 sh, 313, 367; ^1H NMR (400 MHz, acetone-d_6): δ 1.40, 1.47 (3H each, *s*, H-14, 15), 2.91 (1H, *dd*, $J = 7.6$, 7.3 Hz, H-11), 3.21 (1H, *dd*, $J = 7.6$, 5.4 Hz, H-11), 3.95 (1H, *dt*, $J = 7.3$, 5.4 Hz, H-12), 4.39 (1H, *d*, $J = 5.4$ Hz, OH-C-12), 6.77 (1H, *dd*, $J = 8.3$, 1.0 Hz, H-2), 7.04 (1H, *dd*, $J = 8.3$, 1.0 Hz, H-4), 7.16 (1H, *d*, $J = 8.3$ Hz, H-7), 7.66 (1H, *d*, $J = 8.3$ Hz, H-8), 7.69 (1H, *t*, $J = 8.3$ Hz, H-3), 12.74 (1H, *s*, OH-C-1).

Compound **3** *(caloxanthone H).* A pale yellow amorphous, $[\alpha]_D^{20}$ +33° (*c* 0.09, MeOH), HR-EI-MS *m/z* 330.1119 for $C_{18}H_{18}O_6$ (calcd 330.1103). EI-MS *m/z* (rel. int.): 330 $[M]^+$ (53), 312 (18), 304 (5), 279 (13), 271 (15), 263 (21), 242 (100), 241 (56), 229 (97), 213 (13), 197 (4), 139 (5), 128 (6); IR ν_{max}^{KBr} cm^{-1}: 3380, 2955, 1640, 1610, 1575; UV λ_{max}^{MeOH} nm: 237 sh, 251, 270 sh, 295 sh, 313, 367; ^1H NMR (400 MHz, acetone-d_6): δ 1.28, 1.29 (3H each, *s*, H-14, 15), 2.89 (1H, *dd*, $J = 14.2$, 9.5 Hz, H-11), 3.16 (1H, *dd*, $J = 14.2$, 2.0 Hz, H-11), 3.31 (1H, *br s*, OH), 3.76 (1H, *dd*, $J = 9.5$, 2.0 Hz, H-12), 6.77 (1H, *dd*, $J = 8.3$, 1.0 Hz, H-2), 7.03 (1H, *dd*, $J = 8.3$, 1.0 Hz, H-4), 7.30 (1H, *d*, $J = 7.8$ Hz, H-7), 7.66 (1H, *d*, $J = 7.8$ Hz, H-8), 7.69 (1H, *t*, $J = 7.8$ Hz, H-3), 12.76 (1H, *s*, OH-C-1).

Compound **4** (6-*hydroxy*-1,3,5-*trimethoxyxanthone*). A pale yellow amorphous, HR-EI-MS *m/z* 302.0800 for $C_{16}H_{14}O_6$ (calcd 302.0790). EI-MS *m/z* (rel. int.): 302 $[M]^+$ (100), 286 (12), 273 (34), 271 (15), 256 (26), 229 (32), 201 (11), 186 (7); IR ν_{max}^{KBr} cm^{-1}: 3430, 2910, 1640 sh, 1620, 1600 sh; UV λ_{max}^{MeOH} nm: 244, 283, 305, 315 sh; ^1H NMR (400 MHz, DMSO-d_6): δ 3.85 (3H, *s*, OMe-C-1), 3.90 (3H, *s*, OMe-C-5), 3.92 (3H, *s*, OMe-C-3), 6.48 (1H, *d*, $J = 2.0$ Hz, H-2), 6.70 (1H, *d*, $J = 2.0$ Hz, H-4), 6.90 (1H, *d*, $J = 8.8$ Hz, H-7), 7.65 (1H, *d*, $J = 8.8$ Hz, H-8), 10.47 (1H, *br s*, OH-C-6).

Compound **5** (3,6-*dihydroxy*-1,5-*dimethoxyxanthone*). A pale red amorphous, HR-EI-MS *m/z* 288.0648 for $C_{15}H_{12}O_6$ (calcd 288.0633). EI-MS *m/z* (rel. int.): 288 $[M]^+$ (100), 272 (16), 271 (18), 259 (38), 244 (22), 243 (23), 242 (33), 227 (11), 215 (29), 187 (14); IR ν_{max}^{KBr} cm^{-1}: 3520, 3080, 1645, 1620, 1575. UV λ_{max}^{MeOH} nm: 242, 287, 306, 315 sh; ^1H NMR (400 MHz, DMSO-d_6): δ 3.82 (3H, *s*, OMe-C-1), 3.87 (3H, *s*, OMe-C-5), 6.36 (1H, *d*, $J = 2.0$ Hz, H-2), 6.44 (1H, *d*, $J = 2.0$ Hz, H-4), 6.87 (1H, *d*, $J = 8.8$ Hz, H-7), 7.63 (1H, *d*, $J = 8.8$ Hz, H-8), 10.42, 10.80 (1H each, *br s*, OH-C-3, 6).

Compound **6** (1,3,6-*trihydroxy*-5,7-*dimethoxyxanthone*). A pale yellow amorphous, HR-EI-MS *m/z* 304.0595 for $C_{15}H_{12}O_7$ (calcd 304.0583). EI-MS *m/z* (rel. int.): 304 $[M]^+$ (100), 289 (11), 275 (5), 261 (10), 243 (14), 215 (7); IR ν_{max}^{KBr} cm^{-1}: 3380, 1660, 1605, 1595; UV λ_{max}^{MeOH} nm: 240 sh, 254, 279, 316, 358; ^1H NMR (400 MHz, DMSO-d_6): δ 3.90 (3H, *s*, OMe-C-7), 3.91 (3H, *s*, OMe-C-5), 6.18 (1H, *d*, $J = 2.0$ Hz, H-2), 6.39 (1H, *d*, $J = 2.0$ Hz, H-4), 7.26 (1H, *s*, H-8), 10.30 (1H, *br s*, OH-C-6), 10.84 (1H, *br s*, OH-C-3), 13.05 (1H, *s*, OH-C-1).

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