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Xanthones from *Hypericum chinense*

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Abstract

Six xanthones, 1,3,7-trihydroxy-2-(2-hydroxy-3-methyl-3-butenyl)-xanthone (**1**), 1,7-dihydroxy-2,3-[2″-(1-hydroxy-1-methylethyl)-dihydrofurano]-xanthone (**2**), 1,3,7-trihydroxy-5-methoxyxanthone (**3**), 1,7-dihydroxy-5,6-dimethoxyxanthone (**4**), 4,5-dihydroxy-2,3-dimethoxyxanthone (**5**), 1,3-dihydroxy-2,4-dimethoxyxanthone (**6**) and 21 known xanthones were isolated from the leaves and stems of *Hypericum chinense*. Their structures were established based on spectroscopic studies.

Keywords: *Hypericum chinense*; Clusiaceae; Xanthones

1. Introduction

The family Clusiaceae is a rich source of xanthones (Sultanbawa, 1980; Bennett and Lee, 1989). These xanthones show various bioactivities: e.g. anti-methicillin-resistant *Staphylococcus aureus* (MRSA) (Rukachaisirikul et al., 2003, 2005; Sukpondma et al., 2005), anti-vancomycin-resistant *Enterococci* (VRE) (Sakagami et al., 2005), anti-malarial (Ignatushchenko et al., 2000), tumor-promoting inhibition (Ito et al., 2003), selective cyclooxygenase-2 inhibition (Zou et al., 2005) and inhibitory effects on PAF-induced hypotension (Oku et al., 2005). The genus *Hypericum* belonging to Clusiaceae is distributed widely in temperate regions, and has been used for traditional medicines in various parts of the world. In Japan, *H. chinese* is used as a folk medicine for treatment of female disorders (Tanaka et al., 2005). Anti-bacterial acylphloroglucinols and spiro-lactones were also isolated from this species (Nagai and Tada, 1987; Tada and Nagai, 1989; Aramaki et al., 1995; Tanaka et al., 2005). In the course of our search for bioactive metabolites from plants, we became interested in the *Hypericum* plants and began to study their chemical constituents. As a part of this program, we have examined the MeOH extracts of the leaves and stems of this plant. As a result, six new and 21 known xanthones were isolated. In this paper, we report the isolation and the structure elucidation of these compounds.

2. Results and discussion

The MeOH extracts of *H. chinense* leaves were partitioned with *n*-hexane and H_2O. The *n*-hexane soluble fraction was repeatedly subjected to column chromatography to give one new (**1**) and five known (**9**, **10**, **25**, **26**, **27**) xanthones. In the same way, the MeOH extracts of *H. chinense* stems were partitioned with *n*-hexane, EtOAc, and H_2O. From the EtOAc soluble fraction, five new (**2**–**6**) and 18 known (**7**–**24**) xanthones were isolated.

Compound **1** had a molecular formula of $C_{18}H_{16}O_6$ on the basis of its HRFABMS analysis. The IR spectrum of **1** showed the presence of a hydroxyl group (3420 cm^{-1}), and a conjugated carbonyl group (1649 cm^{-1}). The ^1H NMR spectroscopic data revealed the presence of a hydrogen-bonded hydroxyl group [δ_H 13.45 (1H, *s*)], a pentasubstituted benzene ring [δ_H 6.41 (1H, *s*)], a 1,2,4-trisubstituted benzene ring [δ_H 7.57 (1H, *d*, $J = 2.9$ Hz), 7.41 (1H, *d*, $J = 9.0$ Hz), 7.36 (1H, *dd*, $J = 9.0$, 2.9 Hz)], a 2-hydroxy-3-methyl-3-butenyl group [δ_H 4.97, 4.76 (each 1H, *brs*),

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4.43 (1H, *dd*, $J = 7.9$, 3.6 Hz), 3.08 (1H, *dd*, $J = 14.4$, 3.6 Hz), 2.92 (1H, *dd*, $J = 14.4$, 7.9 Hz), 1.84 (3H, *s*)]. The ^{13}C NMR spectrum showed the presence of one conjugated carbonyl carbon, 12 aromatic carbons, and five other carbons. From these data, **1** was considered as a xanthone derivative having a side-chain of 2-hydroxy-3-methyl-3-butenyl group. The positions of the hydroxyl groups and the side-chain were determined by long-range correlations as shown in Fig. 2 in its HMBC spectrum. Thus, **1** was elucidated as 1,3,7-trihydroxy-2-(2-hydroxy-3-methyl-3-butenyl)-xanthone (Fig. 1). Because no Cotton effects were observed in its CD spectrum, **1** was considered to be a racemate.

Compound **2** had absorption bands of a hydroxyl group (3363 cm^{-1}), and a conjugated carbonyl group (1666 cm^{-1}) in its IR spectrum. The ^1H and ^{13}C NMR spectroscopic data of **2** were similar to those of **1** except for the side-chain, C-1–4, and 4a. The side-chain was deduced as 2,3-dihydroxy-2-methylbutane by the following analysis of its ^1H and ^{13}C NMR spectroscopic data: δ_H 4.85 (1H, *dd*, $J = 9.4$, 7.6 Hz), 3.19 (1H, *dd*, $J = 14.8$, 7.6 Hz), 3.17 (1H, *dd*, $J = 14.8$, 9.4 Hz), 1.30, 1.25 (each 3H, *s*); δ_C 92.5, 71.0, 26.4, 25.5, 25.0. The long-range correlations between H_2-1′ and C-2, and OH-1 and C-2 in its HMBC spectrum indicated that the side-chain was located at C-2. The down-field carbon signal of C-2′ (δ_C 92.5) revealed the presence of a dihydrofuran ring. This was supported by the molecular formula $C_{18}H_{16}O_6$. Thus, **2** was determined as 1,7-dihydroxy-2,3-[2″-(1-hydroxy-1-methylethyl)-dihydrofurano]-xanthone (Fig. 1).

Compound **3** had a molecular formula of $C_{14}H_{10}O_6$ based on its HREIMS analysis. The ^1H NMR spectrum showed the presence of a hydrogen-bonded hydroxyl group [δ_H 13.63 (1H, *s*)], four *meta*-coupled aromatic protons [δ_H 7.65, 7.19 (each 1H, *d*, $J = 2.4$ Hz), 6.76, 6.69 (each 1H, *d*, $J = 2.0$ Hz)], and a methoxyl group [δ_H 3.81 (3H, *s*)]. In its ^{13}C NMR spectrum, the presence of a conjugated carbonyl carbon, 12 aromatic carbons and a methoxyl group was observed. From these data, **3** was regarded as a tetraoxygenated xanthone derivative having one methoxyl group. Based on the long-range correlation between OH-1 (δ_H 13.63) and C-2 (δ_C 99.1), H-8 (δ_H 7.65) and C-9 (δ_C 180.8) in its HMBC spectrum, and the NOE correlation between H-6 (δ_H 7.19) and OMe-5 (δ_H 3.81) in its NOESY spectrum, three hydroxyl groups could be placed on C-1, -3, -7, and a methoxyl group on C-5. Thus, **3** was determined as 1,3,7-trihydroxy-5-methoxyxanthone (Fig. 1).

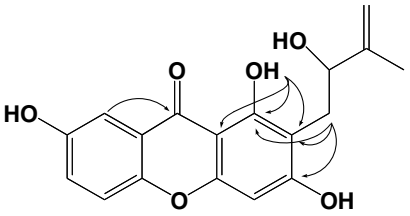
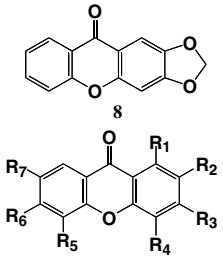


Fig. 2. Key long-range correlations of **1**.



	R_1	R_2	R_3	R_4	R_5	R_6	R_7
11	H	OH	H	H	OH	H	H
13	OH	OMe	OH	H	H	H	H
15	H	OMe	OH	OMe	H	H	H
17	OH	H	OH	H	OH	OMe	H
20	OH	H	H	H	OH	OMe	OMe
23	OH	H	OH	H	OH	OMe	OMe

Fig. 3. Structures of compounds **8**, **11**, **13**, **15**, **17**, **20**, **23**.

The molecular formula of **4** was determined as $C_{15}H_{12}O_6$ by its HREIMS analysis. The signals of a hydrogen-bonded hydroxyl group [δ_H 13.13 (1H, *s*)], four aromatic protons [δ_H 7.51 (1H, *dd*, $J = 8.4$, 8.4 Hz), 6.82 (1H, *d*, $J = 8.4$ Hz), 6.78 (1H, *s*), 6.75 (1H, *d*, $J = 8.4$ Hz)], and two methoxyl groups [δ_H 4.03, 4.02 (each 3H, *s*)] were exhibited in its ^1H NMR spectrum. The ^{13}C NMR spectrum showed the presence of a conjugated carbonyl carbon, 12 aromatic carbons, and two methoxyl carbons. These data meant that **4** was a xanthone derivative having two hydroxyl groups and two methoxyl groups. The ^{13}C NMR chemical shifts of **4** were compared with those of 7-hydroxy-5,6-dimethoxyxanthone (Morel et al.,

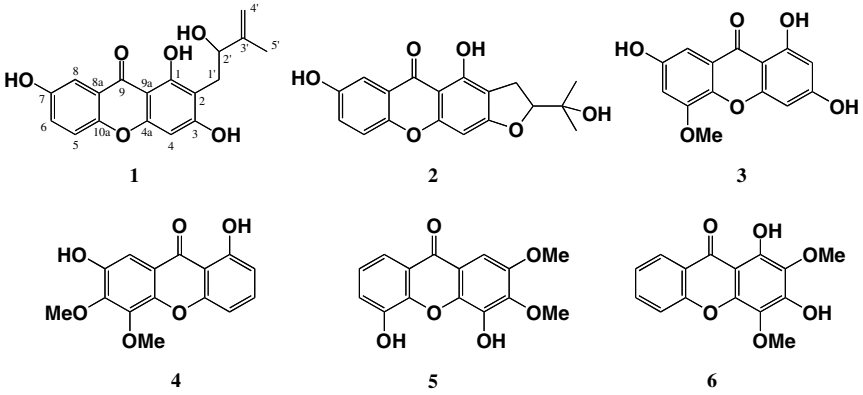


Fig. 1. New xanthones from *H. chinense*.

2000), and both of them showed good agreement on C-10a, 5–8, and 8a. The signal of a hydrogen-bonded hydroxyl group [δ_H 13.13 (1H, *s*)] in its ^{1}H NMR spectrum clearly showed that the hydroxyl group was at C-1. Thus, **4** was elucidated as 1,7-dihydroxy-5,6-dimethoxyxanthone (Fig. 1).

The ^{13}C NMR spectroscopic data of **5**, $C_{15}H_{12}O_6$, showed 15 carbons including one conjugated carbonyl, 12 aromatic, and two methoxyl carbons. Comparison of the ^{13}C NMR chemical shifts of **5** with those of 3,5-dihydroxy-1,2-dimethoxyxanthone (**22**) (Morel et al., 2002) showed good agreement on C-10a, 5–8, and 8a. So, one hydroxyl group could be placed on C-5. The positions of two methoxyl groups and the other hydroxyl group were determined by the following correlations: H-1 with C-2, -3, -4a, and -9a, OMe-2 with C-2, OMe-3 with C-3 in its HMBC spectrum; H-1 with OMe-2 in its NOESY spectrum. Thus, the structure of **5** was decided as 4,5-dihydroxy-2,3-dimethoxyxanthone (Fig. 1).

Compound **6**, $C_{15}H_{12}O_6$, showed the signals of a hydrogen-bonded hydroxyl group, a 1,2-disubstituted benzene ring, and two methoxyl groups in its ^{1}H NMR spectrum. The ^{13}C NMR spectroscopic data of **6** was compared with that of 3,6,8-trihydroxy-5,7-dimethoxy-1-methylxanthone (Mulholland et al., 2004). As a result, the chemical shifts of C-1 – 4, 4a, and 9a in **6** showed good agreement with that of C-10a, 5–8, and 8a in 3,6,8-trihydroxy-5,7-dimethoxy-1-methylxanthone. On the basis of these data, the structure of **6** was decided as 1,3-dihydroxy-2,4-dimethoxyxanthone (Fig. 1).

The following known compounds were identified (Fig. 3) by comparison with the literature data: 2-hydroxyxanthone (**7**) (Westerman et al., 1977), 2-hydroxy-1-methoxyxanthone (**9**) (Morel et al., 2000), 1,7-dihydroxyxanthone (**10**) (Yang et al., 2001), 2,5-dihydroxyxanthone (**11**) (Cardona et al., 1985), 2,7-dihydroxyxanthone (**12**) (Tosa et al., 1997), 1,3-dihydroxy-2-methoxyxanthone (**13**) (Delle Monache et al., 1983), 2,5-dihydroxy-1-methoxyxanthone (**14**) (Minami et al., 1996), 3-hydroxy-2,4-dimethoxyxanthone (**15**) (Cardona et al., 1986, 1990), 1,3,5,6-tetrahydroxyxanthone (**16**) (Sia et al., 1995), 1,3,5-trihydroxy-6-methoxyxanthone (**17**) (Chaudhuri and Ghosal, 1971), 1,3,6-trihydroxy-5-methoxyxanthone (**18**) (Ghosal et al., 1973; Zhang et al., 2002), 1,3,6,7-tetrahydroxyxanthone (**19**) (Noro et al., 1984), 1,5-dihydroxy-6,7-dimethoxyxanthone (**20**) (Quillinan and Scheinmann, 1975), 1,6-dihydroxy-7,8-dimethoxyxanthone (**21**) (Marston et al., 1993), 3,5-dihydroxy-1,2-dimethoxyxanthone (**22**) (Morel et al., 2002), 1,3,5-trihydroxy-6,7-dimethoxyxanthone (**23**) (Ghosal et al., 1977), 1,3,7-trihydroxy-5,6-dimethoxyxanthone (**24**) (Westerman et al., 1977), 1,7-dihydroxy-6-methoxyxanthone (**25**) (Tosa et al., 1997), toxyloxanthone B (**26**) (Tanaka et al., 2004), 1,3,7-trihydroxy-2-(3-methylbut-2-enyl)-xanthone (**27**) (Garcia Cortez et al., 1998).

2,3-Methylenedioxyxanthone (**8**) was previously reported from *Hypericum mysorense* (Balachandran et al., 1988). Our analysis of the NMR spectroscopic data including HMBC and HSQC spectrum for **8** allowed the reassignment of the ^{13}C NMR chemical shifts of **8** as shown in Table 2. Also, the ^{13}C NMR spectroscopic data for compounds **11**, **13**, **15**, **17**, **20**, **23** were assigned as shown in Table 2 since these data have not been reported previously.

3. Experimental

3.1. General experimental procedures

NMR experiments were run on a Bruker ARX-400 instrument, ^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz, using TMS as int. stand. MS was obtained on a JEOL JMSD-300 instrument, and a Waters LCT Premier. Chromatography column: silica gel 60 (Merck, 63–210 μm), Sephadex LH-20 (Pharmacia), and Toyopearl HW-40 (TOSOH); HPLC: GPC (Shodex H-2001, 2002, $CHCl_3$; Asahipak, GS-310 2G, MeOH), silica gel (YMC-Pack SIL-06 SH-043-5-06, 250 × 20 mm), ODS (YMC-R-ODS-5, Yamamura). IR spectra were recorded on a 1720 Infrared Fourier Transform spectrometer (Perkin–Elmer). Optical rotations were measured with a JASCO DIP-370 digital polarimeter.

3.2. Plant material

The aerial parts of *Hypericum chinense* were collected in October 2002 in Tokushima Prefecture, Japan, and leaves and stems were separated. Herbarium specimens were deposited in the botanical garden of the University of Tokushima (Specimen Number: UTP98008).

3.3. Extraction and isolation of compounds from the leaves of *H. chinense*

The leaves of *H. chinense* (1.48 kg, dried) were crushed and extracted (3 × 18 L) with MeOH at 60 °C for 4 h. The MeOH extracts were concentrated in vacuo to give a residue (633 g), which was partitioned between *n*-hexane and H_2O. The *n*-hexane soluble fraction (92.6 g) was subjected to a silica gel CC eluted with solvents of increasing polarity *n*-hexane–EtOAc–MeOH to give 12 fractions (fr. 1–12). Fr. 2 (13.2 g) was loaded on a Toyopearl HW-40 column eluted with $CHCl_3$–MeOH (2:1) to give four fractions (fr. 2. 1–4). Fr. 2. 3 was purified by a silica gel HPLC with *n*-hexane–EtOAc (4:1) and a GPC on HPLC with $CHCl_3$ to give **10** (85 mg). Fr. 7 (590 mg) was applied on a Sephadex LH-20 column with MeOH and purified by a GPC on HPLC with MeOH to give **9** (10 mg). Fr. 8 (2.2 g) was subjected to a Toyopearl HW-40 column ($CHCl_3$–MeOH, 1:1) to give seven fractions (fr. 8. 1–7). Fr. 8. 5 was recrystallized from MeOH to give **25** (4 mg) and residue. The residue was applied on a silica gel CC with solvents of increasing polarity $CHCl_3$–MeOH, and purified by a GPC on HPLC (MeOH) to give **1** (11 mg), **26** (14 mg), and **27** (39 mg).

3.4. Extraction and isolation of compounds from the stems of *H. chinense*

The stems of *H. chinense* (4.54 kg, dried) were crushed and extracted (3 × 18 L) with MeOH at 60 °C for 4 h. The MeOH extracts were concentrated in vacuo to give a residue (548 g), which was partitioned between *n*-hexane, EtOAc, and H_2O. The EtOAc soluble fraction (96.8 g) was subjected to a silica gel CC eluted with solvents of increasing polarity *n*-hexane–EtOAc–MeOH to give 13 fractions (fr. 1–13). Fr. 4 (435 mg) was separated by a Toyopearl HW-40 column to give three fractions (fr. 4. 1–3). Fr. 4. 2 was purified by a preparative TLC (CHC_3–MeOH, 99:1) to give **8** (9 mg). Fr. 4. 3 was applied to a silica gel HPLC with $CHCl_3$–MeOH (98:2) to give **10** (54 mg) and **13** (56 mg). Fr. 5 (5.44 g) was subjected to a Toyopearl HW-40 column ($CHCl_3$–MeOH, 1:1) to give four fractions (fr. 5. 1–4). Fr. 5. 4 was applied to a silica gel CC eluted with solvents of increasing polarity ($CHCl_3$–MeOH) to give five fractions (fr. 5. 4. 1–5). Fr. 5. 4. 2 was purified by a GPC on HPLC (MeOH) to give **4** (21 mg). Fr. 5. 4. 3 was applied to a silica gel HPLC ($CHCl_3$–MeOH, 99:1) and a GPC on HPLC (MeOH) to give **6** (17 mg), **9** (8 mg), **20** (6 mg), and **21** (15 mg). Fr. 5. 4. 4 was loaded on a silica gel HPLC ($CHCl_3$–MeOH, 99:1), and purified by a preparative TLC ($CHCl_3$–acetone, 4:1) to give **7** (13 mg). Fr. 8 (2.2 g) was subjected to a silica gel CC eluted with solvents of increasing polarity ($CHCl_3$–MeOH) to give seven fractions (fr. 8. 1–7). Fr. 8. 2 was applied to a Toyopearl HW-40 column with $CHCl_3$–MeOH (2:1) and a Sephadex LH-20 column with MeOH to give **15** (169 mg). Fr. 8. 3 was subjected to a Toyopearl HW-40 column ($CHCl_3$–MeOH, 1:1), and purified by a GPC on HPLC eluted with MeOH to give **5** (4 mg). Fr. 8. 4 was loaded on a Toyopearl HW-40 column with $CHCl_3$–MeOH (1:1) to give five fractions (fr. 8. 4. 1–5). Fr. 8. 4. 5 was applied to a GPC on HPLC eluted with MeOH to give **3** (14 mg), **14** (18 mg), **24** (19 mg), and nine fractions (fr. 8. 4. 5. 1–9). Fr. 8. 4. 5. 4 was separated by a preparative TLC with $CHCl_3$–MeOH–H_2O (85:15:0.1) to give **22** (6 mg). Fr. 8. 4. 5. 6 was subjected to an ODS-HPLC (MeOH–H_2O, 7:3) to give **2** (2 mg), **11** (10 mg), and **12** (9 mg). Fr. 8. 4. 5. 7 was purified by a preparative TLC with $CHCl_3$–MeOH–H_2O (85:15:0.1) to give **18** (6 mg). Fr. 8. 4. 5. 8 was purified by an ODS-HPLC (MeOH–H_2O, 7:3) to give **23** (24 mg). Fr. 8. 4. 5. 9 was applied to a preparative TLC with $CHCl_3$–MeOH–H_2O (9:1:0.1) to give **17** (10 mg). Fr. 9 was subjected to a Sephadex LH-20 column eluted with MeOH, and purified by a GPC on HPLC with MeOH to give **16** (44 mg) and **19** (7 mg).

3.5. 1,3,7-Trihydroxy-2-(2-hydroxy-3-methyl-3-butenyl)-xanthone (*1*)

Yellow needle. $[\alpha]_D$: +0.5° (*c* 0.4 MeOH); IR (KBr) ν_{MAX} cm^{-1}: 3420, 1649, 1614, 1577, 1471, 1452, 1409, 1337, 1214, 1089; HRFABMS: *m*/*z* 327.0883 $[M-H]^-$ (calcd for $C_{18}H_{15}O_6$, 327.0869); ^1H NMR (acetone-d_6): δ_H 13.45 (1H, *s*, OH-1), 7.57 (1H, *d*, *J* = 2.9 Hz, H-8), 7.41 (1H, *d*, *J* = 9.0 Hz, H-5), 7.36 (1H, *dd*, *J* = 9.0, 2.9 Hz, H-6), 6.41 (1H, *s*, H-4), 4.97 (1H, *brs*, H-4′a), 4.76 (1H, *brs*, H-4′b), 4.43 (1H, *dd*, *J* = 7.9, 3.6 Hz, H-2′), 3.08 (1H, *dd*, *J* = 14.4, 3.6 Hz, H-1′a), 2.92 (1H, *dd*, *J* = 14.4, 7.9 Hz, H-1′b), 1.84 (3H, *s*, H_3-5′); for ^{13}C NMR (acetone-d_6) spectrum, see Table 1.

3.6. 1,7-Dihydroxy-2,3-[2″-(1-hydroxy-1-methylethyl)-dihydrofurano]-xanthone (*2*)

Yellow powder. $[\alpha]_D$: −4.3° (*c* 0.2 MeOH); IR (KBr) ν_{MAX} cm^{-1}: 3363, 2976, 2841, 1666, 1612, 1587, 1481, 1360, 1286, 1128, 1159, 1088; HREIMS: *m*/*z* 328.0939, $[M]^+$ (calcd for $C_{18}H_{16}O_6$, 328.0947); ^1H NMR (acetone-d_6): δ_H 13.17 (1H, *s*, OH-1), 7.57 (1H, *d*, *J* = 2.0 Hz, H-8), 7.44 (1H, *d*, *J* = 9.2 Hz, H-5), 7.35 (1H, *dd*, *J* = 9.2, 2.0 Hz, H-6), 6.36 (1H, *s*, H-4), 4.85 (1H, *dd*, *J* = 9.4, 7.6 Hz, H-2′), 3.19 (1H, *d*, *J* = 14.8, 7.6 Hz, H-1′a), 3.17 (1H, *d*, *J* = 14.8, 9.4 Hz, H-1′b), 1.30 (3H, *s*, H_3-4′), 1.25 (3H, *s*, H_3-5′); for ^{13}C NMR (acetone-d_6) spectrum, see Table 1.

3.7. 1,3,7-trihydroxy-5-methoxyxanthone (*3*)

Yellow powder. IR (KBr) ν_{MAX} cm^{-1}: 3270, 1653, 1591, 1152, 1444, 1379, 1308, 1265, 1188, 1158, 1107; HREIMS: *m*/*z* 274.0461, $[M]^+$ (calcd for $C_{14}H_{10}O_6$, 274.0477); ^1H

Table 1
^{13}C NMR spectroscopic data (δ_C) for xanthones (**1**–**6**)

Position	**1**[a]	**2**[a]	**3**[b]	**4**[c]	**5**[b]	**6**[a]
1	161.8	158.0	164.3	162.0	96.7	150.8
2	109.0	108.6	99.1	110.6	151.0	131.2
3	165.7	168.4	167.2	135.9	143.2	152.3
4	95.0	88.9	94.7	106.2	141.6	128.1
4a	157.2	158.7	158.5	155.5	143.2	145.2
10a	150.7	150.3	140.7	154.6[d]	147.0	156.3
5	119.7	119.2	150.2	152.3	148.3	118.2
6	124.9	124.5	107.3	137.5	120.5	135.8
7	154.7	154.4	155.5	155.5[d]	123.6[e]	124.6
8	109.3	108.7	99.8	99.1	116.3	125.7
8a	121.7	121.3	122.2	109.2	123.6	120.3
9	181.2	180.8	180.8	181.4	176.9	181.5
9a	103.2	103.6	103.3	108.7	118.2	100.5
1′	30.0	26.4	–	–	–	–
2′	76.5	92.5	–	–	–	–
3′	148.2	71.0	–	–	–	–
4′	110.4	25.0	–	–	–	–
5′	18.3	25.5	–	–	–	–
2-OMe	–	–	–	–	55.9	60.3
3-OMe	–	–	–	–	60.8	–
4-OMe	–	–	–	–	–	61.2
5-OMe	–	–	56.1	62.0	–	–
6-OMe	–	–	–	61.7	–	–

[a] Measured in acetone-d_6.
[b] Measured in pyridine-d_5.
[c] Measured in $CDCl_3$.
[d] Interchangeable.
[e] Overlapped with solvent.

Table 2
^{13}C NMR spectroscopic data (δ_C) for known xanthones (**8**, **11**, **13**, **15**, **17**, **20**, **23**)

Position	**8**[a]	**11**[b]	**13**[a]	**15**[c]	**17**[b]	**20**[a]	**23**[b]
1	103.1	110.0	153.2	101.1	164.7	161.7	164.3
2	145.2	155.5	129.5	147.3	99.7	110.3	99.1
3	153.6	125.1	156.3	148.9[d]	169.4	136.3	167.0
4	97.8	119.7	93.3	136.3	95.5	107.1	94.7
4a	153.6	150.0[e]	153.3	147.1[d]	159.1	156.1	158.7
10a	155.9	146.9	156.0	156.3	146.7	140.9	142.9
5	117.5	148.5	117.5	118.3	136.9	137.8	141.2
6	133.9	120.7	134.9	134.2	153.4	141.6	143.4
7	123.8	124.1	123.9	124.0	108.7	149.4	150.9
8	126.4	116.0	125.6	126.6	115.2	96.8	96.0
8a	121.2	123.0	120.0	122.0	116.2	116.6	116.7
9	175.8	177.4	181.3	175.7	180.8	181.4	180.6
9a	116.3	123.0	103.9	113.9	102.3	108.5	103.2
Dioxymethylene	102.3	–	–	–	–	–	–
2-OMe	–	–	60.8	56.0	–	–	–
4-OMe	–	–	–	61.1	–	–	–
6-OMe	–	–	–	–	56.4	61.4	60.7
7-OMe	–	–	–	–	–	56.1	55.9

[a] Measured in $CDCl_3$.
[b] Measured in pyridine-d_5.
[c] Measured in acetone-d_6.
[d] Interchangeable.
[e] Overlapped with solvent.

NMR (pyridine-d_5): δ_H 13.63 (1H, *s*, OH-1), 7.65 (1H, *d*, $J = 2.4$ Hz, H-8), 7.19 (1H, *d*, $J = 2.4$ Hz, H-6), 6.76 (1H, *d*, $J = 2.0$ Hz, H-4), 6.69 (1H, *d*, $J = 2.0$, H-2), 3.81 (3H, *s*, OMe-5); for ^{13}C NMR (pyridine-d_5) spectrum, see Table 1.

3.8. 1,7-Dihydroxy-5,6-dimethoxyxanthone (*4*)

Pearl white needle. IR (KBr) ν_{MAX} cm^{-1}: 3303, 1644, 1602, 1477, 1429, 1271, 1236, 1155, 1090, 1055, 1010; HREIMS: *m/z* 288.0621, $[M]^+$ (calcd for $C_{15}H_{12}O_6$, 288.0634); ^1H NMR ($CDCl_3$): δ_H 13.13 (1H, *s*, OH-1), 7.51 (1H, *dd*, $J = 8.4$, 8.4 Hz, H-3), 6.82 (1H, *d*, $J = 8.4$ Hz, H-4), 6.78 (1H, *s*, H-8), 6.75 (1H, *d*, $J = 8.4$ Hz, H-2), 4.03 (3H, *s*, OMe-6), 4.02 (3H, *s*, OMe-5); for ^{13}C NMR ($CDCl_3$) spectrum, see Table 1.

3.9. 4,5-Dihydroxy-2,3-dimethoxyxanthone (*5*)

Yellow powder. IR (KBr) ν_{MAX} cm^{-1}: 3255, 1639, 1589, 1469, 1292, 1265, 1211, 1136, 1091; HREIMS: *m/z* 288.0621 $[M]^+$ (calcd for $C_{15}H_{12}O_6$, 288.0634); ^1H NMR (pyridine-d_5): δ_H 8.15 (1H, *d*, $J = 8.0$ Hz, H-8), 7.59 (1H, *s*, H-1), 7.52 (1H, *d*, $J = 8.0$, H-6), 7.28 (1H, *dd*, $J = 8.0$, 8.0 Hz, H-7), 3.92 (3H, *s*, OMe-3), 3.76 (3H, *s*, OMe-2); for ^{13}C NMR (pyridine-d_5) spectrum, see Table 1.

3.10. 1,3-Dihydroxy-2,4-dimethoxyxanthone (*6*)

Yellow powder. IR (KBr) ν_{MAX} cm^{-1}: 3361, 1651, 1616, 1589, 1569, 1467, 1355, 1132, 1037; HREIMS: *m/z* 288.0638 $[M]^+$ (calcd for $C_{15}H_{12}O_6$, 288.0634); ^1H NMR (acetone-d_6): δ_H 12.82 (1H, *s*, OH-1), 8.22 (1H, *d*, $J = 8.0$ Hz, H-8), 7.87 (1H, *dd*, $J = 8.4$, 8.0 Hz, H-6), 7.63 (1H, *d*, $J = 8.4$ Hz, H-5), 7.48 (1H, *dd*, $J = 8.0$, 8.0 Hz, H-7), 3.95 (3H, *s*, OMe-4), 3.89 (3H, *s*, OMe-2); for ^{13}C NMR (acetone-d_6) spectrum, see Table 1.

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