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XANTHONES FROM *POLYGALA TENUIFOLIA*

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Key Word Index—*Polygala tenuifolia*; Polygalaceae; xanthones; 3-hydroxy-2,8-dimethoxyxanthone; 7-hydroxy-1,2,3-trimethoxyxanthone; 3-hydroxy-1,2,7-trimethoxyxanthone, 1,7-dimethoxy-2,3-methylenedioxyxanthone; 6,8-dihydroxy-1,2,4-trimethoxyxanthone; 6,8-dihydroxy-1,2,3-trimethoxyxanthone.

Abstract—From the roots of *Polygala tenuifolia*, six new xanthones, 3-hydroxy-2,8-dimethoxyxanthone, 7-hydroxy-1,2,3-trimethoxyxanthone, 3-hydroxy-1,2,7-trimethoxyxanthone, 1,7-dimethoxy-2,3-methylenedioxyxanthone, 6,8-dihydroxy-1,2,4-trimethoxyxanthone, and 6,8-dihydroxy-1,2,3-trimethoxyxanthone, have been isolated along with seven known xanthones, 1,7-dihydroxyxanthone, 1,7-dimethoxyxanthone, 1-hydroxy-3,7-dimethoxyxanthone, 2,3,8-trimethoxyxanthone, 1,7-dihydroxy-2,3-dimethoxyxanthone, 1,6-dihydroxy-3,7-dimethoxyxanthone and 1,3,6,7-tetramethoxyxanthone. Their structures have been elucidated by chemical and spectroscopic evidence.

INTRODUCTION

Polygalae Radix, the root of *Polygala tenuifolia* has been used as an expectorant and sedative. It is also effective in inhibiting congestive oedema in rats [1]. Early investigations of the constituents of this species focused on the isolation of saponins [2], sapogenins [3], sugars [4] and alkaloids [5]. In 1977, Fujita and coworkers isolated five xanthones including three novel substances [6]. This paper describes the structural elucidation of xanthones isolated through the re-examination of the xanthone fraction of the plant [7, 8].

RESULTS AND DISCUSSION

Column chromatography combined with prep. TLC of the chloroform-soluble fraction yielded six new xanthones along with seven known xanthones.

Xanthone **1** was obtained as yellow needles, mp 261–262°. The molecular formula was assigned as $C_{15}H_{12}O_5$ on the basis of HR mass spectrometry (*m/z* 272.0680). The UV spectrum (in EtOH) of **1** showed absorptions at 215, 246, 285, 308 and 360 nm. On the addition of NaOAc, the spectrum exhibited a bathochromic shift demonstrating the presence of a hydroxy group at position 3 or 6. In the ^{1}H NMR spectrum, **1** shows signals at δ6.79 (1H, *dd*, J=1.4 and 7.4 Hz), 7.05 (1H, *dd*, J=1.4 and 7.4 Hz) and 7.56 (1H, *t*, J=7.4 Hz) assignable to the protons at positions 7, 5 and 6, respectively. The two one-proton singlets at δ7.67 and 6.93 are assigned to the protons at positions 1 and 4. The two three-proton singlets should be assigned to the methoxy groups at positions 2 and 8, respectively. The structure of **1** was thus established to be 3-hydroxy-2,8-dimethoxyxanthone.

Xanthone **2** was obtained as yellow needles, mp 241–242°, $C_{16}H_{14}O_6$ (*m/z* 302.0781). Its UV spectrum showed absorptions at 243, 255sh, 280, 311 and 360 nm. Although it remained unchanged on the addition of NaOAc, the UV spectrum showed a bathochromic shift on the addition of NaOMe. Thus, the hydroxy group in **2** does not occupy position 3 or 6. In the ^{1}H NMR spectrum, the one-proton singlet at δ6.93 is assignable to the proton at position 4. The signals at δ7.24 (1H, *dd*, J=2 and 9 Hz), 7.41 (1H, *d*, J=9 Hz) and 7.51 (1H, *d*, J=2 Hz) are assigned to the protons at positions 6, 5 and 8 of the xanthone skeleton, respectively. The three three-proton singlets at δ3.90, 4.01 and 4.10 are ascribable to the methoxy groups located at positions 1, 2 and 3 or 1, 3 and 7. Thus, the hydroxy group giving the signal at δ7.90 could be located at the 2 or 7 position. Acetylation of **2** with Ac_2O in pyridine gave the acetate **2a**. In the ^{1}H NMR spectrum of **2a**, the signals due to the protons only at positions 6 and 8 shifted to lower field by δ0.31 and 0.37, respectively. On the basis of the evidence so far described, the structure of **2** was established as 7-hydroxy-1,2,3-trimethoxyxanthone [7]. Recently, Mitsuhashi *et al.* also isolated xanthone **2** from a MeOH extract of *P. tenuifolia* purchased at a Tokyo market and determined the structure independently [9].

Xanthone **3** was obtained as yellow needles, mp 193–195°, $C_{16}H_{14}O_6$ (*m/z* 302.0790). The UV spectrum (in EtOH) of **3** showed absorptions at 235, 255, 282, 314 and 356 nm. On the addition of NaOAc, the spectrum showed a bathochromc shift indicating the presence of a hydroxy group at position 3 or 6. The ^{1}H NMR spectrum of **3** showed signals at δ7.28 (1H, *dd*, J=1.5 and 9 Hz), 7.32 (1H, *d*, J=9 Hz) and 7.68 (1H, *d*, J=1.5 Hz), which are assignable to the protons at positions 6, 5 and 8 of the xanthone skeleton, respectively. The signal at δ6.80 (1H, *s*) is ascribable to the proton at position 4. The three-proton singlets at δ3.91, 4.02 and 4.04 are due to the

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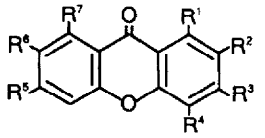


1. $R^2 = R^7 = OMe$, $R^1 = R^4 = R^5 = R^6 = H$, $R^3 = OH$

2. $R^1 = R^2 = R^3 = OMe$, $R^4 = R^5 = R^7 = H$, $R^6 = OH$

2a. $R^1 = R^2 = R^3 = OMe$, $R^4 = R^5 = R^7 = H$, $R^6 = OAc$

3. $R^1 = R^2 = R^6 = OMe$, $R^4 = R^5 = R^7 = H$, $R^3 = OH$

5. $R^1 = R^2 = R^4 = OMe$, $R^3 = R^6 = H$, $R^5 = R^7 = OH$

5a. $R^1 = R^2 = R^4 = OMe$, $R^3 = R^6 = H$, $R^5 = R^7 = OAc$

6. $R^1 = R^2 = R^3 = OMe$, $R^4 = R^6 = H$, $R^5 = R^7 = OH$

6a. $R^1 = R^2 = R^3 = OMe$, $R^4 = R^6 = H$, $R^5 = R^7 = OAc$

7. $R^2 = R^3 = R^4 = R^5 = R^7 = H$, $R^1 = R^6 = OH$

8. $R^2 = R^3 = R^4 = R^5 = R^7 = H$, $R^1 = R^6 = OMe$

9. $R^2 = R^3 = R^7 = OMe$, $R^1 = R^4 = R^5 = R^6 = H$

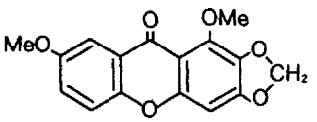
10. $R^3 = R^6 = OMe$, $R^2 = R^4 = R^5 = R^7 = H$, $R^1 = OH$

11. $R^2 = R^3 = OMe$, $R^4 = R^5 = R^7 = H$, $R^1 = R^6 = OH$

12. $R^3 = R^6 = OMe$, $R^2 = R^4 = R^7 = H$, $R^1 = R^5 = OH$

12a. $R^3 = R^6 = OMe$, $R^2 = R^4 = R^7 = H$, $R^1 = R^5 = OAc$

13. $R^1 = R^3 = R^5 = R^6 = OMe$, $R^2 = R^4 = R^7 = H$



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methoxy groups at positions 1, 2 and 7. On the basis of the above-described evidence, the structure of **3** was established to be 3-hydroxy-1,2,7-trimethoxyxanthone.

Xanthone **4**, fine yellow needles, mp 253–254°, was negative to the $FeCl_3$ test. The molecular formula was assigned as $C_{16}H_{12}O_6$ (*m/z* 300.0625). Its UV spectrum (in EtOH) showed absorptions at 245, 260 sh, 281, 317 and 360 nm. In the IR spectrum, absorptions characteristic of a xanthone were observed at 1640 cm^{-1} (conjugated carbonyl) as well as at 1610 and 1596 cm^{-1} (aromatic moieties). There was no hydroxy absorption in the IR spectrum. In the ^1H NMR spectrum, two methoxy signals were observed at δ3.89 and 4.15. The two-proton signal at δ6.06 is assigned to two protons of a methylenedioxy group. The signals at δ6.66 (1H, *s*), 7.22 (1H, *dd*, $J = 9$ and 3 Hz), 7.33 (1H, *d*, $J = 9$ Hz) and 7.67 (1H, *d*, $J = 3$ Hz) are assigned to the protons at positions 4, 6, 5 and 8, respectively. These data indicate that a methoxy group is located at position 7. In a long range C–H COSY spectrum ($^{2\text{ or }3}J_{CH} = 5$ Hz), the C-4 proton signal at δ6.66 was cross-coupled to the signals of C-2, C-3, C-4a and C-8b. The methylenedioxy proton signal at δ6.06 was cross-coupled to the signals of C-2 and C-3. A ^3J interaction was observed between the methoxy protons at δ4.15 and the carbon at position 1. These findings corroborate that the methylenedioxy group is located at positions 2 and 3 and that position 1 is substituted by a methoxy group. From these spectral data, the structure of **4** was established to be 1,7-dimethoxy-2,3-methylenedioxyxanthone.

Xanthone **5** was obtained as yellow needles, mp 239–240°. The molecular formula was assigned as $C_{16}H_{14}O_7$ on the basis of HR mass spectrometry (*m/z* 318.0736). The UV spectrum (in EtOH) of **5** showed absorptions at 240, 255, 277, 316 and 362 nm [10]. On the addition of NaOAc or $AlCl_3$, the spectrum showed a bathochromic shift indicating the presence of hydroxy groups at a position *peri* to the carbonyl group as well as position 3 or 6. The IR spectrum (KBr) showed absorption bands at 3250 (OH), 1661 (conj. CO) and 1593 cm^{-1} (aromatic ring). The ^1H NMR spectrum shows a hydrogen-bonded hydroxy signal at δ12.94 demonstrating the presence of a hydroxy group at a site *peri* to the carbonyl, that is, at position 8. Another hydroxy signal was observed at δ6.30 which disappeared on addition of D_2O. The signals at δ7.42 (1H, *s*), 6.36 and 6.52 (each 1H, *d*, $J = 2.2$ Hz) are ascribable to the protons at positions 3, 7 and 5, respectively. Singlets, each 3H, at δ3.90, 4.01 and 4.10 are due to three methoxy groups, which could be located at positions 1, 2 and 4 leaving positions 6 and 8 for the hydroxy groups. Acetylation of **5** with Ac_2O in pyridine gave the acetate **5a**. In the ^1H NMR spectrum of **5a**, the signals due to the protons only at positions 5 and 7 shifted remarkably to lower field by δ0.26. The lower-field shift is ascribable to the deshielding effect due to the acetylation of the hydroxy groups at positions 6 and 8 [11]. On the basis of the evidence described above, the structure of **5** was concluded to be 6,8-dihydroxy-1,2,4-trimethoxyxanthone.

Xanthone **6** was obtained as yellow needles, mp 164–166°, $C_{16}H_{14}O_7$ (*m/z* 318.0748). The UV spectrum (in EtOH) of **6** showed absorptions at 215, 240, 255 sh, 311 and 355 nm. The UV spectrum in the presence of NaOAc or $AlCl_3$ and NMR spectral behaviour of this compound, together with the lower-field shift of the aromatic proton signals in its acetate **6a**, are the same as those found in **5** and **5a**. These findings suggest that the hydroxy groups in **6** occupy similar positions on the xanthone skeleton. In the ^1H NMR spectrum of **6**, the one-proton singlet at δ6.75 appeared upfield by δ0.67, compared with the signal of the proton at position 3 of **5** at δ7.42. The singlet is thus assignable to the proton at position 4. Consequently, the three methoxy groups are located at positions 1, 2 and 3. The structure of **6** was concluded to be 6,8-dihydroxy-1,2,3-trimethoxyxanthone.

In addition to the six new xanthones described above, seven known xanthones, 1,7-dihydroxyxanthone (**7**) [12], 1,7-dimethoxyxanthone (**8**) [13], 1-hydroxy-3,7-dimethoxyxanthone (**9**) [14], 2,3,8-trimethoxyxanthone (**10**) [15], 1,7-dihydroxy-2,3-dimethoxyxanthone (**11**) [16], 1,6-dihydroxy-3,7-dimethoxyxanthone (**12**) [17] and 1,3,6,7-tetramethoxyxanthone (**13**) [18] were isolated from the same extract. They were identified by com-

parisons of their mp and spectral data (UV, IR, ^{1}H NMR and mass spectra) with those in the literature [12–18]. All of these xanthones have been isolated for the first time from this species.

EXPERIMENTAL

General. Mps uncorr. ^{1}H and ^{13}C NMR spectra were measured at 200 and 50 MHz, respectively. Longe range C–H COSY spectra were recorded at 10 Hz, delay time 50 msec. Solvents used for NMR measurements were TMS–$CDCl_3$ and TMS–CD_3OD.

Plant material. Dried and cut roots of *Polygala tenuifolia* Willd. were imported from China.

Extraction and separation. Dried and cut roots (30 kg) were refluxed twice with a mixt. of $CHCl_3$ and MeOH (90 l, 2:1) for 2 hr. After filtration, the comb. extracts were concd *in vacuo* to give a residue, which was dissolved in $CHCl_3$ (54 l). The $CHCl_3$ layer, washed with H_2O (×3), was concd *in vacuo* and the resultant residue dissolved in *n*-hexane (20 l). The hexane layer was extracted twice with MeOH–H_2O (9:1). The H_2O content of the aq. MeOH layer was increased to 20% and extracted with CCl_4. After raising the H_2O content to 35%, the aq. MeOH layer was extracted with $CHCl_3$. The comb. $CHCl_3$ extracts were concd to give a residue (230 g). An aliquot of the residue (15 g) was chromatographed on silica gel and eluted with *n*-hexane–EtOAc (2:3) to give xanthones **1**–**13**. These compounds were purified repeatedly by silica gel CC and prep. TLC (1 mm thickness) with the same solvent system. Yields: **1** (8 mg), **2** (11 mg), **3** (9 mg), **4** (25 mg), **5** (15 mg), **6** (10 mg), **7** (15 mg), **8** (18 mg), **9** (14 mg), **10** (20 mg), **11** (21 mg), **12** (12 mg) and **13** (13 mg).

3-*Hydroxy*-2,8-*dimethoxyxanthone* (**1**). Fine yellow needles (from EtOH), mp 261–262°. HR-MS *m/z*: 272.0680, calcd for $[M]^+$, $C_{15}H_{12}O_5$: 272.0685. This compound gave a blue fluorescence under UV light and coloured dark green with $FeCl_3$. UV λ_{max}^{EtOH} nm (log ε): 215 (3.68), 246 (3.71), 285 (3.91), 308 (3.76), 360 (3.92); +NaOAc: 230 (3.75), 280 sh (3.81), 268 (4.07). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3410 (OH), 1643 (CO), 1618, 1596, 1510 (aromatic). EI-MS *m/z* (rel. int.): 272 (100), 245 (57), 199 (12). ^{1}H NMR ($CDCl_3$): δ4.0 and 4.01 (each 3H, *s*, OMe), 6.37 (1H, *s*, *ex* D_2O, OH-3,), 6.79 (1H, *dd*, *J* = 7.4 and 1.4 Hz, H-7), 6.93 (1H, *s*, H-4), 7.05 (1H, *dd*, *J* = 7.4 and 1.4 Hz, H-5), 7.56 (1H, *t*, *J* = 7.4 Hz, H-6), 7.67 (1H, *s*, H-1).

7-*Hydroxy*-1,2,3-*trimethoxyxanthone* (**2**). Fine yellow needles (from EtOH), mp 241–242°. HR-MS *m/z*: 302.0781, calcd for $[M]^+$, $C_{16}H_{14}O_6$: 302.0790. This compound gave a positive $FeCl_3$ test and showed a blue fluorescence under UV light. UV λ_{max}^{EtOH} nm (log ε): 243 (4.04), 255 sh (3.85), 280 (4.41), 311 (4.33), 360 (4.09); +NaOMe: 218 (4.51), 290 (4.04), 320 sh (4.18), no change with NaOAc. EI-MS *m/z* (rel. int.): 302 $[M]^+$ (45), 287 (100), 259 (23), 143 (13), 97 (15), 69 (16). ^{1}H NMR (200 MHz, CD_3OD): δ3.85, 3.95 and 3.99 (each 3H, *s*, OMe), 6.93 (1H, *s*, H-4), 7.24 (1H, *dd*, *J* = 9.0 and 2.0 Hz, H-6), 7.41 (1H, *d*, *J* = 9 Hz, H-5), 7.51 (1H, *d*, *J* = 2.0 Hz, H-8), 7.90 (1H, *s*, *ex* D_2O, OH-7). On acetylation, **2** gave the acetate **2** as crystals, mp 82–83°. ^{1}H NMR (CD_3OD): δ2.33 (3H, *s*, Ac-7), 3.86, 3.96 and 4.01 (each 3H, OMe), 7.00 (1H, *s*, H-4), 7.53 (1H, *d*, *J* = 9.0 Hz, H-5), 7.55 (1H, *dd*, *J* = 9.0 and 2.0 Hz, H-6), 7.88 (1H, *d*, *J* = 2.0 Hz, H-8).

3-*Hydroxy*-1,2,7-*trimethoxyxanthone* (**3**). Fine yellow needles (from EtOH), mp 193–195°. HR-MS *m/z*: 302.0790, calcd for $[M]^+$, $C_{16}H_{14}O_6$: 302.0790. This compound gave a positive $FeCl_3$ test, and showed an orange-yellow fluorescence and UV light. UV λ_{max}^{EtOH} nm (log ε): 235 (4.10), 255 sh (4.02), 282 (3.63), 314 (3.68), 356 (3.65); +NaOAc: 236 (4.17), 360 (3.84). EI-MS *m/z* (rel. int.): 302 $[M]^+$ (31), 287 (100), 259 (19), 241 (12), 143 (11). ^{1}H NMR ($CDCl_3$): δ3.91, 4.02 and 4.40 (each 3H, *s*, OMe), 6.49 (1H, *s*, *ex* D_2O, OH-3), 6.80 (1H, *s*, H-4), 7.28 (1H, *dd*, *J* = 8.4 and 1.5 Hz, H-6), 7.32 (1H, *d*, *J* = 8.4 Hz, H-5), 7.68 (1H, *d*, *J* = 1.5 Hz, H-8).

1,7-*Dimethoxy*-2,3-*methylenedioxyxanthone* (**4**). Fine yellow needles (from EtOH), mp 253–254°. HR-MS *m/z*: 300.0625, calcd for $[M]^+$, $C_{16}H_{12}O_6$: 300.0634. This compound was negative to the $FeCl_3$ test but showed a blue fluorescence under UV light. UV λ_{max}^{EtOH} nm (log ε): 245 (4.65), 260 sh (4.59), 281 (4.34), 317 (4.34), 360 (4.22); no change with NaOAc, NaOMe, $AlCl_3$ or $AlCl_3$ + HCl. IR ν_{max}^{KBr} cm^{-1}: 1640 (CO), 1610, 1596 (aromatic ring), 930 (methylenedioxy). EI-MS *m/z* (rel. int.): 300 $[M]^+$ (100), 272 (65), 226 (53), 77 (53). ^{1}H NMR (200 MHz, $CDCl_3$): δ3.89 and 4.15 (each 3H, *s*, OMe), 6.06 (2H, *s*, OCH_2O), 6.66 (1H, *s*, H-4), 7.22 (1H, *dd*, *J* = 9.0 and 3.0 Hz, H-6), 7.33 (1H, *d*, *J* = 9.0 Hz, H-5), 7.67 (1H, *d*, *J* = 3.0 Hz, H-8). ^{13}C NMR ($CDCl_3$): δ142.1 (*s*, C-1), 134.2 (*s*, C-2), 153.7 (*s*, C-3), 93.1 (*d*, C-4), 154.9 (*s*, C-4a), 149.8 (*s*, C-4b), 118.5 (*d*, C-5), 123.7 (*d*, C-6), 156.1 (*s*, C-7), 106.0 (*d*, C-8), 122.7 (*s*, C-8a), 110.3 (*s*, C-8b), 175.5 (*s*, C-9), 102.1 (*t*, C-10), 61.1 (*s*, C-11), 55.9 (*s*, C-12).

6,8-*Dihydroxy*-1,2,4-*trimethoxyxanthone* (**5**). Fine yellow needles (from MeOH), mp 239–240°. HR-MS *m/z*: 318.0736, calcd for $[M]^+$, $C_{16}H_{14}O_7$: 318.0739. This compound was positive to the $FeCl_3$ test and gave an orange-yellow fluorescence under UV light. UV λ_{max}^{EtOH} nm (log ε): 240 (4.15), 255 (4.18), 277 (4.32), 316 (4.08), 362 (4.39); +NaOAc: 242 (4.20), 257 sh (4.12), 358 (4.13); +$AlCl_3$: 232 (4.16), 267 (4.18), 287 (4.36), 343 (4.62). IR ν_{max}^{KBr} cm^{-1}: 3250 (OH), 1661 (conj. CO), 1593 (aromatic ring). EI-MS *m/z* (rel. int.): 318 $[M]^+$ (100), 303 (12), 257 (16), 145 (8), 71 (9). ^{1}H NMR ($CDCl_3$): δ3.90, 4.01 and 4.10 (each 3H, *s*, OMe), 6.30 (1H, *s*, *ex* D_2O, OH-6), 6, 36 (1H, *d*, *J* = 2.2 Hz, H-7), 6.52 (1H, *d*, *J* = 2.2 Hz, H-5), 7.42 (1H, *s*, H-3), 12.94 (1H, *s*, *ex* D_2O, OH-8). Acetylation of **5** yielded 6,8-acetoxy-1,2,4-trimethoxyxanthone (**5a**), pale yellow crystals, mp 157–158°. ^{1}H NMR ($CDCl_3$): δ7.47 (1H, *s*, H-3), 6.88 and 6.62 (each 3H, *s*, OMe), 2.48 and 2.41 (each 3H, *s*, OAc).

6,8-*Dihydroxy*-1,2,3-*trimethoxyxanthone* (**6**). Fine yellow needles, mp 164–166°. HR-MS *m/z*: 318.0748, calcd for $[M]^+$, $C_{16}H_{14}O_7$: 318.0740. This compound showed an orange-yellow fluorescence under UV light and was positive to the $FeCl_3$ test. UV λ_{max}^{EtOH} nm (log ε): 215 (4.86), 240 (4.90), 255 sh (4.83), 311 (4.62), 355 (4.58); +$AlCl_3$: 235 (4.90), 253 (4.85), 273 sh (4.66), 315 (4.69). UV spectral change was not observed on addition of conc. HCl to an EtOH solution with $AlCl_3$ or on the addition of NaOAc to an EtOH solution. EI-MS *m/z* (rel. int.) 318 $[M]^+$ (52), 303 (100), 275 (15), 257 (7), 152 (16). ^{1}H NMR ($CDCl_3$): δ3.87 (3H, *s*, OMe), 4.01 (3H, *s*, OMe), 4.03 (3H, *s*, OMe), 6.31 (1H, *d*, *J* = 2.5 Hz, H-7), 6.33 (1H, *d*, *J* = 2.5 Hz, H-5), 6.49 (1H, *s*, *ex* D_2O, OH-6), 6.75 (1H, *s*, H-4), 13.34 (1H, *s*, *ex* D_2O, OH-8). Acetylation of **6** yielded 6,8-acetoxy-1,2,4-trimethoxyxanthone **6a** as pale yellow crystals from EtOH, mp 143–144°. ^{1}H NMR ($CDCl_3$): δ2.37 and 2.47 (each 3H, OAc), 3.89, 3.94, and 3.95 (each 3H, OMe), 6.56 (1H, *d*, *J* = 2.5 Hz, H-7), 6.72 (1H, *d*, *J* = 2.5 Hz, H-5), 6.90 (1H, *s*, H-4).

1,7-*Dihydroxyxanthone* (**7**). Yellowish fine needles (from EtOH), mp 226–229°. HR-MS *m/z*: 228.0429, calcd for $[M]^+$, $C_{13}H_8O_4$: 228.0423. This compound showed an orange-yellow fluorescence under a UV light and was positive to the $FeCl_3$ test. UV λ_{max}^{EtOH} nm (log ε): 234 (4.09), 260 (4.16), 285 (3.53); +NaOMe: 249 (4.25), 265 (4.11); +$AlCl_3$ (after 10 min); 235 (4.12), 277 (4.04), 308 (3.54). UV spectral change was not observed on the addition of NaOAc to an EtOH solution or on addition of HCl to a solution mixed with $AlCl_3$. EI-MS *m/z* (rel. int.): 228 $[M]^+$ (100), 200 (10), 171 (5), 144 (4), 115 (8), 63 (6). ^{1}H NMR (200 MHz, $CDCl_3$): δ5.01 (1H, *s*, *ex* D_2O, OH-7), 6.77 (1H, *dd*, *J* = 8.4 and 0.5 Hz, H-2), 6.95 (1H, *dd*, *J* = 8.4 and 0.5 Hz, H-4), 7.33 (1H, *dd*, *J* = 9.3 and 2.9 Hz, H-6), 7.41 (1H, *d*, *J* = 9.3 Hz, H-5), 7.59 (1H, *t*, *J*

= 8.8 Hz, H-3), 7.63 (1H, *d*, *J* = 2.9 Hz, H-8), 12.62 (1H, *s*, *ex* D_2O, OH-1). Workup of **7** (10 mg) with CH_2N_2–Et_2O gave 5 mg of 1,7-dimethoxyxanthone (**8**) as needles (from EtOH), mp 130–134°. This compound was identical with an authentic sample of **8** (mmp, TLC and ^1H NMR).

1,7-*Dimethoxyxanthone* (**8**). Needles (from EtOH), mp 148–149°. HR-MS *m/z*: 256.0742, calcd for $[M]^+$, $C_{16}H_{12}O_6$: 256.0736. This compound showed a blue fluorescence under a UV light and was negative to the $FeCl_3$ test. UV λ_{max}^{EtOH} nm (log ε): 241 (4.15), 257 (4.21), 283 (3.85), 305 sh (3.78), 370 (3.88). EI-MS *m/z* (rel. int.): 256 $[M]^+$ (100), 227 (60), 210 (38), 155 (15), 127 (10). ^1H NMR (200 MHz, $CDCl_3$): δ 3.91 and 4.02 (each 3H, *s*, OMe), 6.79 (1H, *d*, *J* = 8.4 Hz, H-2), 6.81 (1H, *t*, *J* = 8.4 Hz, H-3), 7.05 (1H, *d*, *J* = 8.4 Hz, H-4), 7.28 (1H, *dd*, *J* = 9.0 and 3.0 Hz, H-6), 7.39 (1H, *d*, *J* = 9.0 Hz, H-5), 7.69 (1H, *d*, *J* = 3.0 Hz, H-8).

2,3,8-*Trimethoxyxanthone* (**9**). Pale yellow needles (from EtOH), mp 184–187°. HR-MS *m/z*: 286.0843, calcd for $[M]^+$, $C_{16}H_{14}O_5$: 286.0841. This compound showing a blue fluorescence under a UV light was negative to the $FeCl_3$ test. EI-MS *m/z* (rel int.): 286 (71), 257 (37), 111 (26), 89 (40), 71 (60). ^1H NMR (200 MHz, $CDCl_3$): δ 3.98, 4.0 and 4.02 (each 3H, *s*, OMe), 6.75 (1H, *dd*, *J* = 1.5 and 7.5 Hz, H-7), 6.86 (1H, *s*, H-4), 7.05 (1H, *dd*, *J* = 7.5 and 1.5 Hz, H-5), 7.56 (1H, *t*, *J* = 7.5 Hz, H-6), 7.69 (1H, *s*, H-1).

1-*Hydroxy*-3,7-*dimethoxyxanthone* (**10**). Yellowish fine needles (from EtOH), mp 169–174°. HR-MS *m/z*: 272.0303, calcd for $[M]^+$, $C_{15}H_{12}O_5$ 272.0684. This compound showing an orange fluorescence under a UV light was positive to the $FeCl_3$ test. UV λ_{max}^{EtOH} nm (log ε): 235 (4.06), 258 (4.18), 303 (3.74); + NaOMe: 244 (3.98), 269 (4.16), 304 (3.63); + $AlCl_3$: 232 (4.07), 260 (3.83), 273 (4.08), 314 (3.83). UV spectral change was not observed on the addition of conc. HCl to a solution in EtOH with $AlCl_3$ or the addition of NaOAc to a solution in EtOH. EI-MS *m/z* (rel. int.): 272 $[M]^+$ (7), 258 (100), 229 (51), 201 (7), 129 (6), 69 (5). ^1H NMR (200 MHz, $CDCl_3$): δ 3.91 (6H, *s*, 2 × OMe), 6.35 (1H, *d*, *J* = 1.8 Hz, H-2), 6.42 (1H, *d*, *J* = 1.8 Hz, H-4), 7.44 (1H, *d*, *J* = 9 Hz, H-5), 7.26 (1H, *dd*, *J* = 3.0 and 9.0 Hz, H-6), 7.60 (1H, *d*, *J* = 3 Hz, H-8), 12.82 (1H, *s*, *ex* D_2O, OH-1).

1,7-*Dihydroxy*-2,3-*dimethoxyxanthone* (**11**). Yellowish fine needles (from EtOH), mp 245–246°. HR-MS *m/z*: 288.0639, calcd for $[M]^+$, $C_{15}H_{12}O_6$ 288.0564. This compound showing an orange-yellow fluorescence under UV light was positive to the $FeCl_3$ test. UV λ_{max}^{EtOH} nm (log ε): 240 (4.20), 262 (4.21), 300 (4.22); + NaOMe: 240 (4.04), 269 (4.37), 305 (4.77); + $AlCl_3$ (after 10 min): 235 (4.29), 270 (4.19), 320 (4.07); UV spectral change was not observed after addition of NaOAc to a solution in EtOH or the addition of conc. HCl to a solution in EtOH with $AlCl_3$. EI-MS *m/z* (rel. int.): 288 $[M]^+$ (99), 273 (100), 259 (15), 245 (57), 202 (18), 136 (14), 93 (6). ^1H NMR (200 MHz, CD_3OD): δ 3.92 and 3.98 (each 3H, *s*, OMe), 5.90 (1H, *s*, *ex* D_2O, OH-7), 6.56 (1H, *s*, H-4), 7.30 (1H, *dd*, *J* = 9.0 and 2.0 Hz, H-6), 7.43 (1H, *d*, *J* = 9.0 Hz, H-5), 7.50 (1H, *d*, *J* = 2.0 Hz, H-8), 12.62 (1H, *s*, *ex* D_2O, OH-1).

1,6-*Dihydroxy*-3,7-*dimethoxyxanthone* (**12**). Fine yellow needles (from EtOH), mp 262–264°. HR-MS *m/z* 228.0625, calcd for $[M]^+$, $C_{15}H_{12}O_6$: 288.0634. This compound showing an orange-yellow fluorescence under UV light was positive to the $FeCl_3$ test. UV λ_{max}^{EtOH} nm (log ε): 236 (4.63), 255 (4.65), 310 (4.25), 361 (4.31); + NaOAc: 270 (4.52). EI-MS *m/z*: 288 (100), 273 (21), 245 (22), 217 (9), 130 (8), 57 (13). ^1H NMR (200 MHz, $CDCl_3$): δ 3.89 and 4.02 (each 3H, *s*, OMe), 6.34 (1H, *d*, *J* = 1.8 Hz, H-2), 6.38 (1H, *br s*, *ex* D_2O, OH-6), 6.42 (1H, *d*, *J* = 1.8 Hz, H-4), 6.95 (1H, *s*, H-5), 7.59 (1H, *s*, H-8), 12.99 (1H, *s*, *ex* D_2O, OH-1). Acetylation of **12** gave 1,6-diacetoxy-3,7-dimethoxyxanthone (**12a**) as pale yellow needles (from $CHCl_3$–MeOH, 1 : 1), mp 215°. ^1H NMR (200 MHz, $CDCl_3$): δ 2.48 and 2.49 (each 3H, OAc), 3.65 and 3.92 (each 3H, OMe), 6.59 (1H, *d*, *J* = 1.8 Hz, H-2), 6.81 (1H, *d*, *J* = 1.8 Hz, H-4), 7.19 (1H, *s*, H-5), 7.71 (1H, *s*, H-8).

1,3,6,7-*Tetramethoxyxanthone* (**13**). Pale yellow needles (from EtOH), mp 165–166°. HR-MS *m/z*: 316.0937, calcd for $[M]^+$ $C_{17}H_{16}O_6$: 316.0946. This compound showing a blue fluorescence under UV light was negative to the $FeCl_3$ test. EI-MS *m/z* (rel. int.): 316 (100), 287 (44), 111 (34), 97 (58), 83 (56), 43 (56). ^1H NMR (200 MHz, $CDCl_3$): δ 3.91, 3.97, 3.99 and 4.0 (each 3H, *s*, OMe), 6.35 (1H, *d*, *J* = 2.2 Hz, H-2), 6.47 (1H, *d*, *J* = 2.2 Hz, H-4), 6.73 (1H, *s*, H-5), 7.65 (1H, *s*, H-8).

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