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TWO XANTHONES FROM *POLYGALA TENUIFOLIA*

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Key Word Index—*Polygala tenuifolia*; Polygalaceae; roots; xanthones; onjixanthone I; onjixanthone II.

Abstract—Two new xanthones, onjixanthones I and II, and four known xanthones, 1,6-dihydroxy-3,7-dimethoxyxanthone, 1,7-dihydroxy-3-methoxyxanthone, 1,6-dihydroxy-3,5,7-trimethoxyxanthone and 1-hydroxy-3,6,7-trimethoxyxanthone were isolated from roots of *Polygala tenuifolia*. The structures of these xanthones were established on the basis of chemical studies and spectral evidence including 2D NMR and NOE studies.

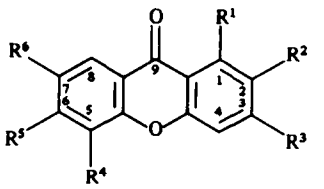
INTRODUCTION

The roots of *Polygala tenuifolia* are used as an expectorant, tonic and sedative agent under the names 'Onji' in Japan and 'Yuan zhi' in China. Eight xanthones, 1,2,3,7-tetramethoxyxanthone (**7**), 1,2,3,6,7-pentamethoxyxanthone (**8**), 6-hydroxy-1,2,3,7-tetramethoxyxanthone (**9**), 1,7-dihydroxyxanthone (**10**), 1,7-dimethoxyxanthone (**11**), 1,7-dihydroxy-2,3-dimethoxyxanthone (**12**), 1-hydroxy-3,7-dimethoxyxanthone, 1,7-dimethoxy-2,3-methylenedioxyxanthone have been isolated from this plant by Ito *et al.* [1] and Liu *et al.* [2]. In addition to these compounds, we have now isolated two new xanthones, onjixanthone I(**1**) and onjixanthone II(**2**), and four known xanthones, 1,6-dihydroxy-3,7-dimethoxyxanthone (**3**), 1,7-dihydroxy-3-methoxyxanthone (**4**), 1,6-dihydroxy-3,5,7-trimethoxyxanthone (**5**) and 1-hydroxy-3,6,7-trimethoxyxanthone (**6**).

RESULTS AND DISCUSSION

The methanolic extract of *P. tenuifolia* was separated into an ether soluble part, a *n*-BuOH soluble part and water soluble part. The ether soluble part was further fractionated by silica gel to give 12 xanthones (**1**–**12**). Compounds **7**–**12** were identified by comparison of mp, IR, UV, ^{1}H and ^{13}C NMR data [1–6]. Compounds **3**–**6** were identified as 1,6-dihydroxy-3,7-dimethoxyxanthone, 1,7-dihydroxy-3-methoxyxanthone, 1,6-dihydroxy-3,5,7-trimethoxyxanthone and 1-hydroxy-3,6,7-trimethoxyxanthone, respectively, by comparing their spectral data (UV, IR, mass, ^{1}H NMR (Table 1)) with the literature [7–10]. The structures of compounds **3**–**6** were also supported by ^{13}C NMR spectra and those of their acetates **3a**–**6a** (Table 2); carbon assignments were based on ^{1}H–^{13}C COSY and COLOC spectra and the literature values [4, 11, 12]. In the ^{13}C NMR spectra of compounds **3**–**6** and **3a**–**6a**, the replacement of a hydroxyl group by an acetoxyl group produced an upfield shift of 7.2–12.7 ppm at the *ipso* carbon.

Onjixanthone I(**1**) was obtained as yellow needles, mp 237–240°, $C_{16}H_{14}O_6$. Its UV spectrum (λ_{max} 241.4, 253.4, 279.6, 311.4 and 355.8 nm) was similar to that of 1,2,3,7-tetramethoxyxanthone (**7**) (λ_{max} 242, 256, 280, 310 and 355 nm) [1]. The ^{1}H NMR spectrum (Table 1) showed the presence of three methoxyl groups (δ3.88, 3.92 and 4.15) and a hydroxyl group (δ5.02). The downfield aromatic proton signal assignable to the H-8 signal showed *meta–para* coupling, indicating the presence of a C-7 substituent in **1**. Therefore, the *ortho–meta* coupled aromatic proton signal at δ7.55 and the *ortho–para* coupled aromatic proton signal at δ7.51 were assigned to H-6 and H-5, respectively. Methylation of **1** afforded a monomethyl ether, $C_{17}H_{16}O_6$, which was identified as 1,2,3,7-tetramethoxyxanthone (**7**) by direct comparison with an authentic sample. This indicated that **1** corresponds with a xanthone possessing one hydroxyl group and three methoxyl groups at the C-1, C-2, C-3 and C-7 positions, respectively.



1 R^1 = R^2 = R^3 = OMe, R^4 = R^5 = H, R^6 = OH
2 R^1 = R^3 = R^5 = OH, R^2 = R^6 = OMe, R^4 = H
2a R^1 = R^3 = R^5 = OCH_2Ph, R^2 = R^6 = OMe, R^4 = H
3 R^1 = R^5 = OH, R^3 = R^6 = OMe, R^2 = R^4 = H
3a R^1 = R^5 = OAc, R^3 = R^6 = OMe, R^2 = R^4 = H
4 R^1 = R^6 = OH, R^2 = R^4 = R^5 = H, R^3 = OMe
4a R^1 = R^6 = OAc, R^2 = R^4 = R^5 = H, R^3 = OMe
5 R^1 = R^5 = OH, R^2 = H, R^3 = R^4 = R^6 = OMe
5a R^1 = R^5 = OAc, R^2 = H, R^3 = R^4 = R^6 = OMe
6 R^1 = OH, R^2 = R^4 = H, R^3 = R^5 = R^6 = OMe
6a R^1 = OAc, R^2 = R^4 = H, R^3 = R^5 = R^6 = OMe
7 R^1 = R^2 = R^3 = R^6 = OMe, R^4 = R^5 = H
8 R^1 = R^2 = R^3 = R^5 = R^6 = OMe, R^4 = H
9 R^1 = R^2 = R^3 = R^6 = OMe, R^4 = H, R^5 = OH
10 R^1 = R^6 = OH, R^2 = R^3 = R^4 = R^5 = H
11 R^1 = R^6 = OMe, R^2 = R^3 = R^4 = R^5 = H
12 R^1 = R^6 = OH, R^2 = R^3 = OMe, R^4 = R^5 = H

Table 1. ^{1}H NMR spectral data of compounds **1**–**8**, **3a**, **4a**, **5a** and **6a** (in $CDCl_3$, 500 MHz)

Compound	1-Subst. *s*	H-2 *d*	H-4	H-5 *dd*	H-6 *dd*	H-8 *dd*	OMe *s*	OH *s*	Ac *s*
1*†	4.15 (OMe)	—	6.85 *s*	7.51 (8.9, 0.5)	7.55 (8.9, 2.9)	8.20 (2.9, 0.5)	3.88, 3.92	5.02	—
2*	14.09 (OH)	—	6.78 *s*	7.17 *s*	—	7.81 s	3.77, 4.00	—	—
3*	13.84 (OH)	6.54 (2.4)	6.61 *d* (2.4)	7.19 *s*	—	7.78 s	3.75, 3.76		
3a†	2.48 (Ac)	6.59 (2.4)	6.79 *d* (2.4)	7.18 *s*	—	7.71 s	3.91, 3.92	—	2.36
4‡	12.85 (OH)	6.37 (2.1)	6.60 *d* (2.1)	7.49 *d* (9.0)	7.32 (9.0, 3.0)	7.43 *d* (3.0)	3.88	10.05	—
4a	2.47 (Ac)	6.59 (2.5)	6.81 *d* (2.5)	7.42 (9.0, 0.9)	7.40 (9.0, 2.4)	7.91 (2.4, 0.9)	3.92	—	2.32
5*	13.80 (OH)	6.74 (2.4)	6.62 *d* (2.4)	—	—	7.64 s	3.76, 3.78, 4.13	—	—
5a†	2.48 (Ac)	6.61 (2.5)	6.87 *d* (2.5)	—	—	7.47 *s*	3.90, 3.93, 4.04	—	2.41
6	12.98 (OH)	6.33 (2.4)	6.37 *d* (2.4)	6.83 *s*		7.52 *s*	3.88, 3.98, 4.00		
6a	2.49 (Ac)	6.80 (2.2)	6.59 *d* (2.2)	6.85 *s*	—	7.58 *s*	3.92, 3.97, 4.00	—	
7	4.03 (OMe)	—	6.72 *s*	7.33 *d* (9.2)	7.24 (9.2, 2.9)	7.68 *d* (2.9)	3.90, 3.92, 3.98	—	—
8	4.03 (OMe)	—	6.70 *s*	6.82 *s*	—	7.65 *s*	3.92, 3.97, 3.98 4.00	—	—

*Compounds measured in pyridine-d_5.
†Assignments confirmed by NOESY.
‡Compound measured in DMSO-d_6.
J (in Hz) in parentheses.

The NOESY spectrum of **1** (in pyridine) showed appreciable NOE between the singlet aromatic proton (H-4) signal at δ6.85 and the methoxyl signal at δ3.88, which was assigned to the C-3 methoxyl signal; no NOE between each of three methoxyl signals and the H-6 and H-8 signals was observed. This indicated the presence of a hydroxyl group at the C-7 position in **1**. Furthermore, the presence of a C-7 hydroxyl group in **1** was supported by the ^{13}C NMR spectrum (Table 2). The C-4b, C-5, C-6, C-7, C-8 and C-8a shifts in the ^{13}C NMR spectrum of **1** are essentially the same as those of 1,7-dihydroxy-2,3-dimethoxyxanthone (**12**) which also has a C-7 hydroxyl group. From the above data, onjixanthone I was determined to be 7-hydroxy-1,2,3-trimethoxyxanthone (**1**).

Onjixanthone II(**2**) was obtained as yellow needles, 231–233°, $C_{15}H_{12}O_7$. The UV spectrum (λ_{max} 242.0, 256.6, 322.2 and 366.2 nm) was similar to that of 6-hydroxy-1,2,3,7-tetramethoxyxanthone (**9**) (λ_{max} 242.8, 274.6, 315.8 and 353.8sh nm). The ^{1}H NMR spectrum of **2** (Table 1) showed the presence of three singlet aromatic protons, two methoxyl groups and a chelated hydroxyl group (δ14.09), which was assigned to the C-1 hydroxyl group. Methylation of **2** afforded a methyl ether, $C_{18}H_{18}O_7$, which was identified as 1,2,3,6,7-pentamethoxyxanthone (**8**) by direct comparison with an authentic sample. This indicated that **2** is a xanthone possessing three hydroxyl and two methoxyl groups at the C-1, C-2, C-3, C-6 and C-7 positions, respectively, including the C-1 hydroxyl group.

It is reported by Chaudhuri *et al.* (4) that the δ value for a methoxyl carbon surrounded by two ortho substituents (OMe, O-aryl, CO-aryl) in the ^{13}C NMR spectrum of polymethoxyxanthone is shifted downfield to δ60–62. Therefore, the appearance of a downfield methoxyl signal at δ60.3 in the ^{13}C NMR spectrum of **2** (Table 2) indicated the presence of a C-2 methoxyl group. Finally, the substituents attaching to C-3, C-6 and C-7 of **2** were determined by the NOESY spectrum of the benzyl ether (**2a**) of **2**. This spectrum in $CDCl_3$ showed three cross peaks between the downfield aromatic proton (H-8) at δ7.69 and the methoxyl signal at δ3.99, the benzylmethylene signal at δ5.22 and the aromatic proton signal at δ6.74, and the benzylmethylene signal at δ5.26 and the aromatic proton signal at δ6.82. This indicated that **2** possesses hydroxyl groups at the C-3 and C-6 positions and a methoxyl group at the C-7 position. From the above results, onjixanthone II was determined to be 1,3,6-trihydroxy-2,7-dimethoxyxanthone (**2**).

EXPERIMENTAL

General. Mps: uncorr. IR: KBr discs. ^{1}H and ^{13}C NMR: TMS as an int. standard, chemical shifts expressed in ppm and coupling constants (*J*) in Hz. TLC: (analytical and prep.) on precoated Kieselgel 60 F_{254} plate.

2D-NOESY. 2D-NOE data were obtained from the NOESY (magnitude mode) using the standard DISNMR software package (Bruker): data were collected in 2K t_2 data with 4 scans and 512 t_1 increments. A mixing time of 1 sec was randomly modulated by ±2% in order to eliminate coherent magnetization transfer. Data were filtered through a shifted sinebell window filter (SSB2 = 0) and doubly transformed in a 2K × 1K data matrix with a digital resolution of 2.68 Hz per point in the w_2 and w_1 domain.

Plant material. Dried and cut roots of *P. tenuifolia* Willd. were purchased from Yamamoto-yakuhin Co., Ltd (Tokyo).

Extraction and isolation. Roots (4.8 kg) were extracted with MeOH (20 l × 3, 3 hr each) under reflux. The MeOH extract was concd under red. pres. (1084.8 g), dissolved in H_2O (45 l) and shaken successively with Et_2O, *n*-BuOH (3 l × 3, each). The Et_2O sol part (168.1 g, yield 3.5%) was chromatographed over 1 kg of silica gel with *n*-hexane–Me_2CO to give 8 frs. Fr. 5 (7.436 g) was

Table 2. ^{13}C NMR spectral data of compounds **1–6**, **3a**, **4a**, **5a**, and **6a** (125 MHz)

C	1*	2	3	3a*	4	4a*	5	5a*	6	6a
1	153.8	153.8[a]	163.8	151.5	162.4	151.6	163.7	151.5	163.2	151.5[a]
2	140.0	131.7	97.4	107.6	96.8	107.6	97.7	97.7	107.9	96.9
3	159.1	155.2	166.3	164.3	166.3	164.6	166.4	164.4	166.0	163.7
4	96.9	94.8	92.7	98.8	92.4	99.0	92.9	98.9	92.5	98.9
4a	155.0	159.4	158.4	159.0	157.3	158.9	151.8	158.7	157.2	158.8
4b	149.2	156.3	153.4[a]	149.8	149.0	152.9	147.1	144.3	152.4	151.3[a]
5	119.0	103.8	103.9	112.2	118.9	118.6	136.2	141.5	99.5	99.2
6	124.1	153.4[a]	156.5[a]	145.3	124.7	128.4	—†	138.5	155.6	155.0
7	155.5	146.8	147.0	148.6	154.0	146.8	147.3	149.0	146.7	146.8
8	110.1	105.3	105.4	107.2	107.9	118.6	100.4	101.2	104.6	105.4
8a	123.8	112.2	112.7	120.4	120.3	122.9	112.2	120.4	113.3	115.3
9	174.9	180.4	180.2	174.1	180.0	174.2	180.2	174.0	179.8	174.1
9a	110.8	103.1	103.8	108.8	102.7	108.9	103.7	108.8	103.5	108.9
OMe-1	62.2	—	—	—	—	—	—	—	—	—
OMe-2	61.4	60.3	—	—	—	—	—	—	—	—
OMe-3	56.4	—	55.9[b]	56.0[a]	56.0	56.0	55.9[a]	56.1	55.8[a]	55.9[b]
OMe-7	—	55.9	56.0[b]	56.5[a]	—	—	56.0[a]	56.5	56.5[a]	56.4[b]
Ac	—	—	—	169.6, 21.7	—	169.6, 21.2	—	169.6, 21.2	—	169.7, 21.3
				168.2, 20.7		169.3, 21.0		168.1, 20.5		

Spectra of **1**, **2**, **3**, and **5** measured in pyridine-d_5, **4** in DMSO-d_6, and **3a**, **4a**, **5a**, **6**, **6a**, **7**, and **8** in chloroform-*d*.

*Assignments confirmed by ^{1}H-^{13}C COSY and COLOC.

†Signal overlapped signals of pyridine-d_5.

[a,b]Assignments interchangeable.

rechromatographed on silica gel (5 cm i.d. × 20 cm) with $CHCl_3$–MeOH. The $CHCl_3$–MeOH (99:1) eluate (250 ml) was concd to give a residue (838 mg), which was purified by prep. TLC ($CHCl_3$–MeOH (30:1), R_f 0.45) to give **10** (10 mg). The $CHCl_3$–MeOH (49:1) eluate (200 ml) was concd to give a residue (1.81 g), which was purified by prep. TLC ($CHCl_3$–MeOH (30:1)) to give **6** (R_f 0.91, 15 mg), **7** (R_f 0.80, 33 mg). Fr. 6 (7.879 g) was chromatographed on silica gel (4 cm i.d. × 20 cm) with $CHCl_3$–MeOH. The $CHCl_3$ eluate (627 mg) was purified by prep. TLC ($CHCl_3$–MeOH (30:1)) to give **6** (R_f 0.91, 19 mg, total 34 mg) and a mixt. of **7** and **11** (R_f 0.80, 156 mg). The mixt of **7** and **11** was purified by prep. TLC (*n*-hexane–EtOAc (3:2)) to give **7** (R_f 0.43, 98 mg, total 152 mg) and **11** (R_f 0.30, 28 mg). The $CHCl_3$–MeOH (50:1) eluate (2977 mg) was purified by prep. TLC (*n*-hexane–Me_2CO (3:2), R_f 0.65) to give **4** (12 mg). Fr. 7 (4.415 g) was chromatographed on silica gel (4 cm i.d. × 23 cm) with $CHCl_3$–MeOH. The $CHCl_3$ eluate (319 mg) was purified by prep. TLC ($CHCl_3$–MeOH (30:1), R_f 0.78) to give **8** (46 mg). The $CHCl_3$–MeOH (99:1) eluate (624 mg) was purified by prep. TLC [C_6H_6 – Et_2O (1:1)] to give **3** (R_f 0.63, 15 mg) and **5** (R_f 0.55, 42 mg). The $CHCl_3$–MeOH (24:1) eluate (1.752 g) was rechromatographed on silica gel (3 cm i.d. × 22 cm) with *n*-hexane–Me_2CO. The *n*-hexane–Me_2CO (7:3) eluate (582 mg) was purified by prep. TLC [(i) *n*-hexane – Me_2CO (3:2), R_f 0.8; (ii) *n*-hexane–EtOAc (1:1), R_f 0.71] to give **12** (31 mg). The *n*-hexane–Me_2CO (3:2) eluate (472 mg) was purified by prep. TLC [*n*-hexane – EtOAc (1:1)] to give **1** (R_f 0.46, 8 mg) and **2** (R_f 0.52, 96 mg). The *n*-hexane–Me_2CO (1:1) eluate (335 mg) was purified by prep. TLC ($CHCl_3$–MeOH (30:1), R_f 0.50) to give **9** (85 mg).

Onjixanthone I (**1**). Yellow needles from CH_2Cl_2–EtOH, mp 237–240°. IR ν_{max}^{KBr} cm^{-1}: 3304 (OH), 1640 (C=O), 1616, 1590 (aromatic ring). UV λ_{max}^{EtOH} nm (log ε): 241.4 (4.28), 253.4 (4.24), 279.6 (3.90), 311.4 (3.89), 355.8 (3.62). EIMS *m/z* (rel. int.): 302 $[M]^+$ (32), 288 (18), 287 (100), 259 (43), 244 (25), 229 (22), 137 (23), 93 (25). High resolution MS *m/z*: 302.0788 (calc. for $C_{16}H_{14}O_6$: 302.0790).

Methylation of compound **1**. A mixt. of **1** (3 mg), Me_2SO_4 (0.05 ml) and K_2CO_3 (30 mg) in dry Me_2CO (1.5 ml) was stirred at 45° for 3 hr. After removal of inorganic salts by filtration, the filtrate was concd and purified by prep. TLC (*n*-hexane–EtOAc (3:2)) to give an amorphous powder, which was identified as 1,2,3,7-tetramethoxyxanthone (**7**) by direct comparison (EIMS, ^1H NMR and TLC) with an authentic sample.

Onjixanthone (**2**). Yellow needles from CH_2Cl_2–MeOH, mp 231–233° (Found: C, 59.00; H, 4.05. $C_{15}H_{12}O_7$ requires: C, 59.21; H, 3.98%). IR ν_{max}^{KBr} cm^{-1}: 3440, 3275 (OH), 1648 (C=O), 1612, 1572 (aromatic ring). UV λ_{max}^{EtOH} nm (log ε): 242.0 (4.45), 256.6 (4.40), 322.2 (4.32), 366.2 (4.15). EIMS *m/z* (rel. int.): 304 $(M)^+$ (71), 290 (14), 289 (75), 286 (24), 261 (100), 246 (34). High resolution MS *m/z*: 304.0582 (calc. for $C_{15}H_{12}O_7$: 304.0583).

Methylation of compound **2**. A mixt of **2** (10 mg), Me_2SO_4 (0.1 ml) and K_2CO_3 (50 ml) in dry Me_2CO (2 ml) was stirred at 50° for 3 hr. The reaction mixt. was dil. with Et_2O, washed with H_2O, and concd to give an amorphous powder (from CH_2Cl_2–EtOH) (7 mg), mp 181–183°. This was identified as 1,2,3,6,7-pentamethoxyxanthone (**8**) by direct comparison (IR, EIMS and ^1H NMR) with an authentic sample.

Benzylation of compound **2**. A mixt. of **2** (6 mg), $PhCH_2Cl$ (30 mg) and K_2CO_3 (30 mg) in DMF and H_2O (100:1) (1.5 ml) was stirred at 90° for 5 hr. The reaction mixt. was dil. with Et_2O, washed with H_2O and concd. The residue was purified by prep. TLC (*n*-hexane–Me_2CO (7:3)) to give an amorphous powder (**2a**) (6 mg). EIMS *m/z* (rel. int.): 574 $(M)^+$ (1.9), 484 (11), 469 (2.6), 393 (2.6), 105 (2.5), 91 (100). High resolution MS *m/z*: 574.1992 (calc. for $C_{36}H_{30}O_7$: 574.1991). ^1H NMR ($CDCl_3$): δ 3.88 (3H, *s*, OMe-2), 3.99 (3H, *s*, OMe-7), 5.18 (2H, *s*, $OCH_2C_6H_5$-1), 5.22 and 5.26 (each 2H, *s*, $OCH_2C_6H_5$-3 and -6), 6.74 and 6.82 (each 1H, *s*, H-4 and H-5), 7.69 (1H, *s*, H-8), 7.32–7.72 (15H, *m*, 3 × $OCH_2C_6\underline{H}_5$).

1,6-*Dihydroxy*-3,7-*dimethoxyxanthone* (**3**). Light yellow needles from EtOH, mp 262–264°. IR ν_{max}^{KBr} cm^{-1}: 3268 (OH), 1658 (C=O), 1600 (aromatic ring). UV λ_{max}^{EtOH} nm (log ε): 234.4 (4.39), 254.6 (4.38), 311.6 (4.00), 364.0 (4.05). EIMS *m/z* (rel. int.): 288 $(M)^+$ (100), 273 (24), 259 (28), 258 (19), 245 (44), 217 (18). High resolution MS *m/z*: 288.0638 (calc. for $C_{15}H_{12}O_6$: 288.0634).

Acetylation of compound **3**. Compound **3** (17 mg) was treated with Ac_2O (0.250 ml) and pyridine (0.4 ml) at room temp. overnight, dil. with H_2O and extracted with Et_2O. The dried Et_2O extract was purified by prep. TLC (C_6H_6–Et_2O (1:2)) to give **3a** (12 mg) as needles (from CH_2Cl_2–MeOH), mp 223.5–225.5°. IR ν_{max}^{KBr} cm^{-1}: 1768 (ester), 1656 (C=O), 1624, 1602 (aromatic ring). High resolution MS *m/z*: 372.0865 (calc. for $C_{19}H_{16}O_8$: 372.0845).

1,7-*Dihydroxy*-3-*methoxyxanthone* (**4**). Yellow needles from Me_2CO–EtOH, mp 273–275°. IR ν_{max}^{KBr} cm^{-1}: 3368 (OH), 1658 (C=O), 1610, 1584 (aromatic ring). UV λ_{max}^{EtOH} nm (log ε): 237.4 (4.27), 259.6 (4.40), 306.0 (3.97), 373.0 (3.63). EIMS *m/z* (rel. int.): 258 $(M)^+$ (100), 229 (78), 228 (22), 201 (12), 115 (9.9), 69 (12). High resolution MS *m/z*: 258.0526 (calc. for $C_{14}H_{10}O_5$: 258.0528).

Acetylation of **4**. Compound **4** (8 mg) was treated with Ac_2O (0.2 ml) and pyridine (0.4 ml) at room temp. overnight. The reaction mixt. was treated as described for acetylation of **3** to give **4a** (8 mg) as needles (from Et_2O–MeOH), mp 199–200°. IR ν_{max}^{KBr} cm^{-1}: 1764 (ester), 1650 (C=O), 1626, 1598 (aromatic ring). High resolution MS *m/z*: 342.0740 (calc. for $C_{18}H_{14}O_7$: 342.0739).

1,6-*Dihydroxy*-3,5,7-*trimethoxyxanthone* (**5**). Yellow needles from CH_2Cl_2–MeOH, mp 235–237° (Found: C, 60.23; H, 4.37. Calc. for $C_{16}H_{14}O_7$: C, 60.38; H, 4.43%). IR ν_{max}^{KBr} cm^{-1}: 3256 (OH), 1662 (C=O), 1596 (aromatic ring). UV λ_{max}^{EtOH} nm (log ε): 207.6 (4.38), 239 (sh 4.45), 255.2 (4.53), 279 (sh 3.97). EIMS *m/z* (rel. int.): 318 $(M)^+$ (100), 303 (14), 289 (13), 275 (15), 257 (20), 229 (12).

Acetylation of compound **5**. Compound **5** (20 mg) was treated with Ac_2O (0.2 ml) and pyridine (0.4 ml) at room temp. overnight. The reaction mixt. was treated as described for acetylation of **3** to give **5a** (17 mg) as needles (from Et_2O–MeOH), mp 174–176° (Found: C, 60.08; H, 4.44. Calc. for $C_{20}H_{18}O_9$: C, 59.70; H, 4.51%). IR ν_{max}^{KBr} cm^{-1}: 1770 (ester), 1632 (C=O), 1602 (aromatic ring). EIMS *m/z* (rel. int.): 402 $[M]^+$ (8.7), 360 (18), 319 (19), 318 (100), 303 (8.2), 289 (11), 257 (8.0).

1-*Hydroxy*-3,6,7-*trimethoxyxanthone* (**6**). Yellow needles from EtOH, mp 220–221°. IR ν_{max}^{KBr} nm^{-1}: 3420 (OH), 1666 (C=O), 1608, 1582 (aromatic ring). UV λ_{max}^{EtOH} nm (log ε): 204.2 (4.32), 239.4 (4.22), 256.2 (4.39), 308.2 (4.04), 359.6 (3.85). EIMS *m/z* (rel. int.): 302 $(M)^+$ (100), 287 (15), 273 (12), 259 (24), 231 (11), 216 (11). High resolution MS *m/z*: 302.0804 (calc. for $C_{16}H_{14}O_6$: 302.0790).

Acetylation of **6**. Compound **6** (19 mg) was treated with Ac_2O (0.25 ml) and pyridine (0.4 ml) at room temp. overnight. The reaction mixt. was treated as described for acetylation of **3** to give **6a** (17 mg) as needles (from CH_2Cl_2–EtOH), mp 214–216° (Found: C, 62.91; H, 4.73. Calc. for $C_{18}H_{16}O_7$: C, 62.79; H, 4.68). IR ν_{max}^{KBr} cm^{-1}: 1756, 1628 (C=O), 1614, 1598 (aromatic ring). EIMS *m/z* (rel. int.): 344 $(M)^+$ (17), 302 (100), 287 (13), 273 (14), 259 (16).

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REFERENCES

1. Ito, H., Taniguchi, H., Kita, T., Matsuki, Y., Tachikawa, E., and Fujita, T. (1977) *Phytochemistry* **16**, 1614.
2. Liu. T., Ueda, S., Fujita, T., and Takeda, Y. *Abstracts of Papers 2, The 110th Annual Meeting of Pharmaceutical Society of Japan, Sapporo*, August 1990, p. 228.
3. Govindachari, T. R., Pai, B. R., Subramaniam, P. S., Rao, U. R., and Muthukumaraswamy, N. (1967) *Tetrahedron* **23**, 243.
4. Chaudhuri, R. K., Zymalkowski, F. and Frahm, A. W. (1978) *Tetrahedron* **34**, 1837.
5. Sun, H.-F., Hu, B.-L., Fan, S.-F., and Ding, J.-Y. (1983) *Acta Botan. Sinica* **25**, 460.
6. Dreyer, D. L. and Bourell, J. H. (1981) *Phytochemistry* **20**, 493.
7. Bhardwaji, D. K., Jain, R. K., Jain, B. C., and Mehta, C. K. (1978) *Phytochemistry* **17**, 1440.
8. Atkinson, J. E., Gupta, P. and Lewis, J. R. (1969) *Tetrahedron* **24**, 1507.
9. Ghosal, S., Biswas, K., and Chaudhuri, R. K. (1977) *J. Chem. Soc., Perkin Trans I*, 1597.
10. Ghosal, S. and Chaudhuri, R. K. (1973) *Phytochemistry* **12**, 2035.
11. Frahm, A. W. and Chaudhuri, R. K. (1979) *Tetrahedron* **35**, 2035.
12. Westerman, P. W., Gunasekera, S. P., Uvais, M., Sultanbawa, S., and Kazlauskas, R. (1977) *Org. Magn. Reson.* **9**, 631.