



Xanthones from *Polygala caudata*

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Abstract

A new xanthone-*O*-glycoside, polycaudoside A, together with 2'-benzoylmangiferin, 1-methoxy-7-hydroxyxanthone, 1,2,8-trihydroxyxanthone, euxanthone, gentisein, wubangzside A, wubangzside B, 1,3-dihydroxy-2-methoxyxanthone, lancerin and neolancerin, stigmaterol, stigmastrol-3-*O*- β -D-glucoside, *p*-hydroxybenzoic acid, dihydroquercetin and quercetin were isolated from the roots of *Polygala caudata*. Their structures were established on the basis of chemical studies and spectral evidence, including 2D NMR analyses. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: *Polygala caudata*; Polygalaceae; Roots; Xanthones; Steroids; Flavonoids

1. Introduction

The roots of *Polygala caudata* Reld et Wils are used for the treatment of cough and hepatitis and as an expectorant and sedative agent under the name 'Wubangzi' in Chinese traditional medicine. Five xanthones, euxanthone, wubangzside A [euxanthone-7-*O*- β -D-apiofuranosyl-(1-2)- β -D-glucopyranoside], wubangzside B (euxanthone-7-*O*- β -D-glucopyranoside), mangiferin (1,3,6,7-tetrahydroxyxanthone-2-*C*- β -D-glucopyranoside) and wubangzside C (1,3,7-trihydroxyxanthone-2,4-*C*-di- β -D-glucopyranoside) were isolated from this plant by Pan and Mao (1984, 1985). In the course of our ethnopharmacological investigations on the *Polygala* species in China, we have now isolated a new xanthone-*O*-glycoside, polycaudoside A, together with 2'-benzoylmangiferin, 7-hydroxy-1-methoxyxanthone, 1,2,8-trihydroxyxanthone, euxanthone, gentisein (1,3,7-trihydroxyxanthone), wubangzside A and B, 1,3-dihydroxy-2-methoxyxanthone, lancerin (1,3,7-trihydroxyxanthone-4-*C*- β -D-glucopyranoside) and neolancerin (1,3,7-trihydroxyxanthone-2-*C*- β -

D-glucopyranoside), stigmaterol, stigmaterol-3-*O*-D-glucoside, *p*-hydroxybenzoic acid, dihydroquercetin and quercetin.

2. Results and discussion

Column chromatography combined with semi-preparative HPLC of the EtOAc-soluble fraction of *P. caudata* yielded a new xanthone-*O*-glycoside, along with fifteen known compounds.

Compound **1** was obtained as yellow needles, m.p. 175–177°C. Its molecular formula was elucidated as C₂₅H₂₈O₁₃ by analysis of its FAB-MS and NMR spectra and confirmed with HREIMS of the aglycone (C₁₃H₈O₄, found: 228.0413, calcd: 228.0422). Its UV spectrum (in MeOH) showed absorption maxima at 376, 286, 256 and 233 nm. With the addition of sodium acetate, the spectrum showed no bathochromic shift, which indicated that there were no 3- or 6-hydroxy groups in the molecule (Lins Mosquito, DeBerros Correa, Gottlieb & Magalhaes, 1986; Zhou, Liu, Blaskó & Cordell, 1989). The bathochromic shifts with aluminum chloride and aluminum chloride/hydrochloric acid were observed, indicating the presence of a

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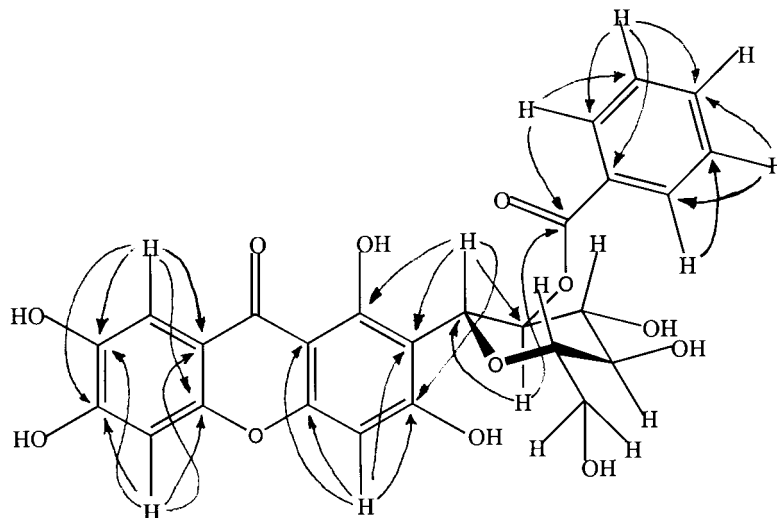


Fig. 1. Long-range correlations observed in HMBC spectrum of **2** (DMSO- d_6 + D_2O).

chelated hydroxy group in position 1 or 8 (Lins Mosquito et al., 1986; Zhou et al., 1989). In the IR spectrum, absorption characteristics of a xanthone were observed at 1650 cm^{-1} (conjugated carbonyl), as well as 1610 , 1580 and 1450 cm^{-1} (aromatic moieties). The FAB mass spectrum of **1** showed $(M+H)^+$ at m/z 537 and fragments at m/z 391 $(M-146+H)^+$ and 229 $(M-146-162+H)^+$, suggesting that there were two sugar moieties in the molecule. The nature of the sugar units was identified to be β -D-glucose and α -L-rhamnose by means of co-TLC after acid hydrolysis (Zhao, Li & He, 1987).

In the ^1H NMR spectrum, the singlet at δ 12.53 (1H, brs) was assigned to the signal of hydroxy group at C-1 (Pan & Mao, 1984). The signals at δ 7.07 (1H, d, $J=8.4\text{ Hz}$), 7.73 (1H, dd, $J=8.4\text{ Hz}$, 8.4 Hz) and 6.81 (1H, d, $J=8.4\text{ Hz}$) were assigned to the protons at C-2, 3 and 4 (Pan & Mao, 1984). The signals at δ 7.52 (1H, dd, $J=9.2\text{ Hz}$, 2.7 Hz) and 7.68 (2H, m) were ascribed to the protons at C-6, 5 and 8 (Pan & Mao, 1984). Thus, the aglycone of **1** was identified to be euxanthone, which was confirmed by co-TLC with an authentic sample after acid hydrolysis (Zhao et al., 1987).

In the ^{13}C NMR spectrum of **1**, the signal at δ 76.9 could be assigned to C-2 of the inner glucose, which showed a down-field shift by $\Delta 3\text{ ppm}$ on comparison with the corresponding signal (δ 73.3) of a known compound wubangzside B, indicating that the terminal rhamnose was attached to the C-2 position of the inner glucose by glycosylation, which was supported by the upfield shift ($\Delta 2.9\text{ ppm}$) of the glucose C-1 signal (δ 98.6) on comparison with the corresponding signal of wubangzside B (δ 101.5). On the above evidence, the structure of compound **1** was elucidated

to be 1,7-dihydroxyxanthone-7-*O*- α -L-rhamnopyranosyl-(1-2)- β -D-glucopyranoside and named as polycaudoside A.

Compound **2** was obtained as yellow amorphous powder, m.p. $162\text{--}164^\circ\text{C}$. Its molecular formula was determined to be $\text{C}_{26}\text{H}_{22}\text{O}_{12}$ by means of elemental analysis (found: C, 59.22, H, 4.14. calcd. $\text{C}_{26}\text{H}_{22}\text{O}_{12}$: C, 59.30, H, 4.21). The FAB mass spectrum of **2** showed $(M+H)^+$ peak at m/z 527. The IR spectrum of **2** showed the presence of hydroxyl group (3400 cm^{-1}), a chelated ketone (1640 cm^{-1}) and aromatic rings (1610 , 1600 and 1580 cm^{-1}). The UV spectrum of **2** in MeOH showed absorptions at 364, 315, 258 and 231 nm, indicating a hydroxy-substituted xanthone (Pan & Mao, 1985; Lins Mosquito et al., 1986; Zhou et al., 1989). A bathochromic shift with sodium acetate was observed, indicating the presence of free hydroxy group(s) at position 3 and/or 6. The bathochromic shift with aluminum chloride indicated the presence of a chelated hydroxyl group in position 1 or 8 (Lins Mosquito et al., 1986; Zhou et al., 1989). The reaction was reversed upon addition of hydrochloric acid suggesting the presence of *ortho*-hydroxy groups in the molecule (Massias, Carbonnier & Molho, 1981).

^1H NMR analysis of **2** suggested the presence of a chelated hydroxyl group (δ 13.78) and eight aromatic protons. Among aromatic protons three singlets (δ 6.29, 6.80 and 7.35) were assigned to the protons at C-4, 5 and 8 positions of the xanthone (Markham & Woolhouse, 1983; Murakami, Tanaka, Wasa, Saiki & Chen, 1986). The remaining five aromatic protons appeared as an $\text{A}_2\text{B}_2\text{M}$ system, centered at δ 7.78 (2H), 7.53 (2H) and 7.39 (1H), which were ascribable to the H-2, 6, H-3, 5 and H-4 signals of a benzoyl group in the molecule, respectively. The appearance of

the benzoyl group was further illustrated by the presence of the characteristic ketone absorption at 1720 cm^{-1} in the IR spectrum and the signals at δ 130.3 (B-1), 129.0 (B-2, 6), 128.4 (B-3, 5), 132.8 (B-4) and 164.7 (C=O) in the ^{13}C NMR spectrum. The signals integrating for six protons at δ 5.76 (1H, dd, $J=9.5\text{ Hz}$, 8.6 Hz), 3.79 (1H, dd, $J=11.7\text{ Hz}$, 1.6 Hz), 3.63 (1H, dd, $J=8.6\text{ Hz}$, 8.6 Hz), 3.55 (1H, dd, $J=11.7\text{ Hz}$, 5.3 Hz), 3.39 (1H, m), 3.37 (1H, m) and a doublet ($J=9.5\text{ Hz}$) at δ 5.02 were assigned to the aliphatic protons and the anomeric proton of the β -linked sugar moiety.

The site of the sugar linkage to the aglycone in **2** was considered to be at the C-2 position of 1,3,6,7-tetrahydroxyxanthone since the C-2 signal appeared at δ 105.7 in the ^{13}C NMR spectrum (Frahm & Chaudhuri, 1979), which was further confirmed by the appearance of the crosspeaks of the anomeric proton of the glucose at δ 5.02 (d, $J=9.5\text{ Hz}$) with the carbons at δ 161.7 (C-1), 105.7 (C-2) and 163.7 (C-3) in the long-range heteronuclear multiple-bond correlation (HMBC) spectrum (see Fig. 1. for correlations). The hexose substituent at C-2 gave a pattern of ^{13}C NMR signals similar to that exhibited by the C-linked glucose in the mangiferin (Markham & Woolhouse, 1983; Murakami et al., 1986), but the signal of glucose C-2 appeared at δ 73.1, which shifted to the downfield by $\Delta 2.5\text{ ppm}$ compared with the corresponding signal of mangiferin (δ 70.6). Meanwhile the signals of C-1 (70.8) and C-3 (76.4) of the glucose showed an upfield shift by $\Delta 2.6$ and 2.8 ppm , respectively, compared with the corresponding signals (δ 73.4, 79.2) of mangiferin (Markham & Woolhouse, 1983; Murakami et al., 1986). This suggested that the benzoyl group was attached to the C-2 position of the glucose by means of esterification, which was further supported by the appearance of the cross-peaks of the proton at glucose C-2 (δ 5.76) and the protons at benzoyl group C-2 and 6 (δ 7.76) with the carbonyl carbon (δ 164.7) of the benzoyl group in the HMBC spectrum (Fig. 1). Thus, the structure of **2** could be elucidated to be 1,3,6,7-tetrahydroxyxanthone-2- C - β -D-(2'-benzoyl)-glucopyranoside. This compound was previously reported as a mixture with 4'- and 6'-isomers by Markham and Wallace (1980).

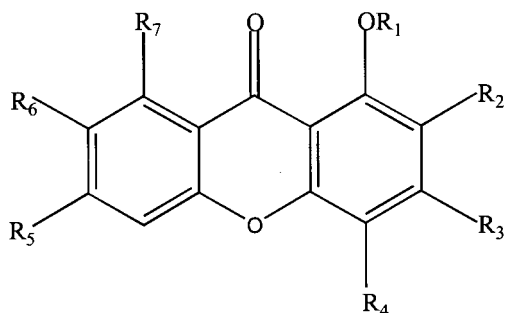
Compound **3** was obtained as needle-shaped crystals with m.p. $239\text{--}240^\circ\text{C}$. Its molecular formula was determined to be $\text{C}_{14}\text{H}_{10}\text{O}_4$ by means of HREIMS (found: 242.0563, calcd: 24.0579). It showed UV absorption maxima at 373, 283, 254 and 204 nm in MeOH as well as remaining unchanged on the addition of sodium acetate, aluminum chloride and aluminum chloride/hydrochloric acid, suggesting no hydroxy group in positions 1, 3, 6 or 8. The ^1H NMR spectrum of **3** showed signals at δ 7.45 (1H, d, $J=8.9\text{ Hz}$), 7.42 (1H, d, $J=3.0\text{ Hz}$) and 7.25 (1H, dd, $J=8.9\text{ Hz}$, 3.0 Hz), which were assigned to the protons at positions 6, 5

and 8 of the xanthone skeleton, respectively. The signals at δ 7.71 (1H, dd, $J=8.3\text{ Hz}$, 8.3 Hz), 7.11 (1H, dd, $J=8.3\text{ Hz}$, 0.7 Hz) and 6.95 (1H, d, $J=8.3\text{ Hz}$) were ascribable to the protons at positions 3, 4 and 2. The three-proton singlet at δ 3.91 was due to the methoxy group at position 1, which was further supported by the appearance of upfield shift ($\Delta 6.7\text{ ppm}$) of the carbonyl carbon signal (δ 174.7) on comparison with the corresponding signal (δ 181.4) of euxanthone due to the absence of the chelated hydroxy group at the C-1 position (Rocha et al., 1994). The hydroxy group at the C-7 position appeared at δ 9.92(s). Thus the structure of **3** was established to be 7-hydroxy-1-methoxyxanthone.

Compound **4** was obtained as yellow needles, m.p. $228\text{--}230^\circ\text{C}$. Its molecular formula was determined to be $\text{C}_{13}\text{H}_8\text{O}_5$ by means of HREIMS (found: 244.0347, calcd: 244.0372). The UV spectrum of **4** in MeOH showed absorption maxima at 335, 264, 240 and 202 nm. On addition of sodium acetate, the spectrum exhibited no bathochromic shift which demonstrated the absence of hydroxy group at C-3 or 6 position (Lins Mosquito et al., 1986; Zhou et al., 1989). The spectrum showed bathochromic shift with aluminum chloride indicating the presence of chelated hydroxy group(s) at position 1 and/or 8 (Lins Mosquito et al., 1986; Zhou et al., 1989). The reversion of the reaction upon the addition of hydrochloric acid suggested the presence of ortho dihydroxy groups in the molecule. In the ^1H NMR spectrum of **4**, the hydroxy group signals were observed at δ 11.77 (s, chelated OH), 11.56 (s, chelated OH) and 9.50 (s). Associated with this substitution pattern was an AB system at δ 6.97 (d, $J=8.9\text{ Hz}$) and 7.36 (d, $J=8.9\text{ Hz}$), attributable to a *ortho*-dihydroxy substituted benzene ring and an ABM system at δ 7.02 (d, $J=8.4\text{ Hz}$), 7.73 (dd, $J=8.4\text{ Hz}$, 8.4 Hz) and 6.80 (d, $J=8.4\text{ Hz}$), ascribable to *mono*-hydroxysubstituted benzene ring, indicating the presence of chelated hydroxy group at C-8 position. Hence **4** was identified as 1,2,8-trihydroxyxanthone, previously synthesized by Locksley and Murray (1970) and Gottlieb, Magalhaes, and Stefani (1966).

In addition, twelve known compounds, euthanone (Pan & Mao, 1984), gentisein (Atkinson, Gupta & Lewis, 1969; Lewis & Reary, 1970), wubangzicide A (Pan & Mao, 1984), wubangzicide B (Pan & Mao, 1984), 1,3-dihydroxy-2-methoxyxanthone (Monache, Mac-Quakae, Monache, Bettolo & Alves De Lima, 1983), lancerin (Lin, Chang, Arisawa, Shimizu & Morita, 1982), neolancerin (Schaufelberger & Hostettmann, 1988), stigmaterol (Mao et al., 1996), stigmaterol-3- O -D-glucoside (Pan & Mao, 1984), *p*-hydroxybenzoic acid (Mao et al., 1996), dihydroquercetin (Markham & Ternai, 1976) and quercetin (Wagner, Chari & Sonnenbichlen, 1976) were isolated from the extract. They were identified by comparison

of their m.p. and spectral data (UV, IR, NMR and MS) with those in the literature.



	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇
1	H	H	H	H	H	O-Glc ² Rha	H
2	H	2'-Benzoyl-Glc	OH	H	OH	OH	H
3	Me	H	H	H	H	OH	H
4	H	OH	H	H	H	H	OH

3. Experimental

M.p.'s uncorr. ¹H and ¹³C NMR spectra were measured on Bruker ARX-400, Joel AM-270 and Joel 400 spectrometers with TMS as the internal standard and DMSO-d₆ as the solvent. 2D NMR experiments were carried out on Bruker ARX-400 spectrometer. EI and FAB mass spectra were obtained on a Finnigan SSQ710 mass spectrometer.

3.1. Plant material

Dried and cut roots of *P. caudata* were obtained from the Guizhou Province, China, in August 1997. A voucher specimen was deposited in the Herbarium of Institute of Medicinal Plant Development, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing, China.

3.2. Extraction and separation

Dried and cut roots (3 kg) were extracted three times with 80% EtOH. The comb. extracts were concd. in vacuo to a residue, which was suspended in H₂O (2.5 l) and shaken with CHCl₃, EtOAc and *n*-BuOH (1 l × 5), respectively. The EtOAc part (27.8 g, yield 0.93%) was chromatographed over Si gel (150 g) eluted with CHCl₃-MeOH in gradient to give 10 frs. Fr. 10 (3.35 g, 0.11%) was subjected to Si gel chromatography eluted with CHCl₃-MeOH (5:1) to give 2 subfrs. Subfr. 2 was subjected to semi-preparative HPLC (HP 1050 system with UV and FLUOR detec-

tors, SUPELCO Rp-18 column) eluted with MeOH-H₂O (55:45) to give **1** (12 mg, 0.0004%).

Fr. 8 (5.95 g, 0.198%) was rechromatographed on Si gel with CHCl₃-MeOH (100:6) as the eluent to give 4 subfrs. Subfr. 2 was subjected to Sephadex LH-20 chromatography eluted with MeOH to yield 2 subfrs. (A and B). Subfr. B was purified with semi-preparative HPLC with MeOH-H₂O (60:40) as mobile phase to give **2** (400 mg, 0.013%).

Fr. 1 (7.39 g, 0.25%) was subjected to a Si gel column eluted with CHCl₃-MeOH in gradient to give subfrs. 1–4. Subfr. 4 was rechromatographed on a Sephadex LH-20 column with MeOH as the eluent to yield **3** (356 mg, 0.012%). Subfr. 1 was rechromatographed on a Si gel column eluted with *n*-hexane-CHCl₃ in a gradient to give subfr. A–C. Subfr. B was subjected to Sephadex LH-20 chromatography eluted with MeOH to give **4** (85 mg, 0.0028%).

Euxanthone (3048 mg, 0.1%), gentisein (157 mg, 0.0052%), 1,3-dihydroxy-2-methoxyxanthone (23 mg, 0.00077%) and stigmasterol (60 mg, 0.002%) from fr. 1; wubangzicide A (450 mg, 0.015%) from fr. 8; wubangzicide B (34 mg, 0.0011%), stigmasterol-3-*O*-D-glucoside (280 mg, 0.093%), dihydroquercetin (5 mg, 0.00017%) and quercetin (8 mg, 0.00026%) from fr. 5; lancerin (121 mg, 0.004%) and neolancerin (5 mg, 0.00017%) from fr. 10, *p*-hydroxybenzoic acid (5 mg, 0.00017%) from fr. 3 were obtained by chromatography over Si gel and purified by means of Sephadex LH-20 chromatography and/or semipreparative HPLC.

3.3. Acid hydrolysis

Sample solution was applied to 1 cm from the bottom edge of an HPTLC Si gel plate (5 × 10 cm) and hydrolysed with HCl vapor for 40 min at 50–60°C and the plate developed in 9 ml of the lower layer of a mixt. of CHCl₃-MeOH-H₂O (15:6:2) to which 1 ml of HOAc was added. The identification of the sugar was carried out by comparison with authentic sugar markers on the same plate (Zhao et al., 1987).

3.3.1. Polycaudoside A (**1**)

Yellow needles, m.p. 175–177°C. IR ν_{\max} (cm⁻¹): 3400, 3300 (OH), 1650 (α,β -unsaturated C=O), 1610, 1580, 1450 (aromatic ring). UV λ_{\max} nm: 376, 286, 256, 233; + NaOAc: 377, 286, 257; + AlCl₃: 437, 308, 276, 233, 202; + AlCl₃/HCl: 438, 307, 275, 233, 202. FAB-MS m/z : 537 (M+H)⁺, 391 (M-rhamnosyl+H)⁺, 229 (M-rhamnosyl-glucosyl+H, aglycone+H)⁺. EIMS m/z (%): 228 (100, aglycone), 200 (10). ¹H NMR (270 MHz, DMSO-d₆): δ 12.53 (1H, brs, OH-1), 7.73 (1H, dd, *J*=8.4 Hz, 8.4 Hz, H-3), 7.68 (2H, m, H-5, 8), 7.52 (1H, dd, *J*=9.2 Hz, 2.7 Hz, H-6), 7.07 (1H, d, *J*=8.4 Hz, H-2), 6.81 (1H, d,

$J=8.4$ Hz, H-4), 5.19 (1H, d, $J=7.3$ Hz, Glc-H-1), 4.71 (1H, brs, Rha-H-1), 1.20 (3H, d, $J=6.2$ Hz, Rha-H-6). ^{13}C NMR (100 MHz, DMSO- d_6): 160.9 (C-1), 109.5 (C-2), 137.4 (C-3), 107.2 (C-4), 119.6 (C-5), 125.6 (C-6), 153.4 (C-7), 110.0 (C-8), 181.3 (C-9), 155.8 (C-4a), 120.4 (C-8a), 108.0 (C-9a), 150.9 (C-10a), 98.6 (Glc-1), 76.9 (Glc-2), 76.6 (Glc-3), 69.6 (Glc-4), 77.1 (Glc-5), 60.4 (Glc-6), 100.5 (Rha-1), 70.4 (Rha-2), 70.5 (Rha-3), 71.8 (Rha-4), 68.3 (Rha-5), 18.0 (Rha-6).

3.3.2. 2'-Benzoylmangiferin (2)

Yellow amorphous powder. M.p. 164–166°C. IR $\nu_{\text{max}}(\text{cm}^{-1})$: 3400 (OH), 1720 (C=O), 1640 (α,β -unsaturated C=O), 1610, 1600, 1580 (aromatic rings). UV λ_{max} : 364, 315, 258, 231; +NaOAc: 380, 261, 233; + AlCl_3 : 417, 357, 268, 234; + AlCl_3/HCl : 404, 339, 264, 232, 203. FAB-MS m/z : 527 ($\text{M}+\text{H}^+$). EIMS m/z (%): 284 (15), 273 (8), 260 (25), 244 (22), 228 (6), 122 (75), 105 (55), 77 (43), 51 (32), and 45 (100). ^1H NMR (400 MHz, DMSO- d_6 + D_2O): δ 13.78 (1H, s, OH-1), 7.35 (1H, s, H-8), 6.80 (1H, s, H-5), 6.29 (1H, s, H-4), 7.78 (2H, dd, $J=7.1$ Hz, 1.7 Hz, B-H-2, 6), 7.53 (1H, ddd, $J=7.1$ Hz, 7.1 Hz, 1.7 Hz, B-H-4), 7.39 (2H, ddd, $J=7.1$ Hz, 7.1 Hz, 1.7 Hz, B-H-3, 5), 5.76 (1H, dd, $J=9.5$ Hz, 8.6 Hz, Glc-H-2), 5.02 (1H, d, $J=9.5$ Hz, Glc-H-1), 3.79 (1H, dd, $J=11.7$ Hz, 1.6 Hz, Glc-H-6a), 3.63 (1H, dd, $J=8.6$ Hz, 8.6 Hz, Glc-H-3), 3.55 (1H, dd, $J=11.7$ Hz, 5.3 Hz, Glc-H-6b), 3.39 (1H, m, Glc-H-4), 3.37 (1H, m, Glc-H-5). ^{13}C NMR (100 MHz, DMSO- d_6 + D_2O): 161.7 (C-1), 105.7 (C-2), 163.7 (C-3), 93.3 (C-4), 102.6 (C-5), 154.3 (C-6), 143.8 (C-7), 108.1 (C-8), 179.1 (C-9), 156.5 (C-4a), 111.7 (C-8a), 101.1 (C-9a), 150.9 (C-10a), 70.8 (Glc-1), 73.1 (Glc-2), 76.4 (Glc-3), 70.7 (Glc-4), 81.7 (Glc-5), 61.5 (Glc-6), 130.3 (Ben-1), 129.0 (Ben-2, 6), 128.4 (Ben-3, 5), 132.8 (Ben-4), 164.7 (Ben-CO).

3.3.3. 1-Methoxy-7-hydroxyxanthone (3)

Yellow needles from MeOH, m.p. 239–240°C. IR $\nu_{\text{max}}(\text{cm}^{-1})$: 3304 (OH), 2980, 2920 (CH_3), 1640 (α,β -unsaturated C=O), 1600, 1580, 1480 (aromatic ring). UV λ_{max} nm: 373, 283, 254, 242, 204; +NaOAc: 373, 282, 254, 243; + AlCl_3 : 373, 283, 254, 243, 203; + AlCl_3/HCl : 373, 283, 254, 243, 204. EIMS m/z (%): 243 ($\text{M}+1$, 100), 242 (15), 214 (1), 213 (9), 197 (3), 196 (10). ^1H NMR (400 MHz, DMSO- d_6): 9.92 (1H, s, OH-7), 7.71 (1H, dd, $J=8.3$ Hz, 8.3 Hz, H-3), 7.45 (1H, d, $J=8.9$ Hz, H-5), 7.42 (1H, d, $J=3.0$ Hz, H-8), 7.25 (1H, dd, $J=8.9$ Hz, 3.0 Hz, H-6), 7.11 (1H, dd, $J=8.3$ Hz, 0.7 Hz, H-4), 6.95 (1H, d, $J=8.3$ Hz, H-2), 3.91 (3H, s, OMe-1). ^{13}C NMR (100 MHz, DMSO- d_6): 160.1 (C-1), 109.6 (C-2), 135.3 (C-3), 105.8 (C-4), 118.7 (C-5), 123.6 (C-6), 153.8 (C-7), 108.8 (C-8), 174.7 (C-9), 157.4 (C-4a), 123.0 (C-8a), 111.1 (C-9a), 147.9 (C-10a), 56.1 (C-OMe).

3.3.4. 1,2,8-Trihydroxyxanthone (4)

Yellow needles from MeOH, m.p. 228–230°C. IR $\nu_{\text{max}}(\text{cm}^{-1})$: 3400, 3300 (OH), 1650 (α,β -unsaturated C=O), 1600, 1580, 1450 (aromatic ring). UV λ_{max} nm: 335, 264, 240, 202; +NaOAc: 335, 264, 217, 196; + AlCl_3 : 381, 289, 270, 250, 202; + AlCl_3/HCl : 317, 282, 266, 240. EIMS m/z (%): 244 (100), 216 (12), 198 (12). ^1H NMR (400 MHz, DMSO- d_6): δ 11.77 (1H, s, OH-8), 11.56 (1H, s, OH-1), 9.50 (1H, brs, OH-2), 7.73 (1H, dd, $J=8.4$ Hz, 8.4 Hz, H-6), 7.36 (1H, d, $J=8.9$ Hz, H-4), 7.02 (1H, d, $J=8.4$ Hz, H-5), 6.97 (1H, d, $J=8.9$ Hz, H-3), 6.80 (1H, d, $J=8.4$ Hz, H-7). ^{13}C NMR (100 MHz, DMSO- d_6): 148.2 (C-1), 140.4 (C-2), 124.9 (C-3), 107.9 (C-4), 106.4 (C-5), 138.0 (C-6), 110.0 (C-7), 160.4 (C-8), 185.9 (C-9), 107.3 (C-4a), 156.1 (C-8a), 146.8 (C-9a) and 107.1 (C-10a).

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