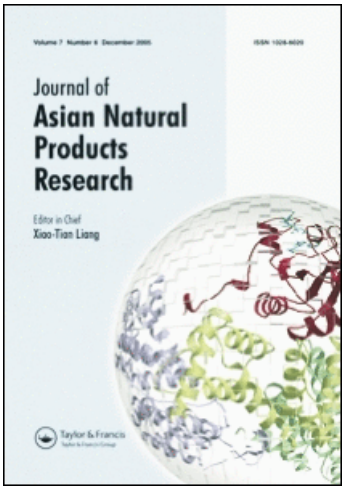

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Two new xanthones from *Polygala crotalarioides*

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Two new xanthones from *Polygala crotalarioides*

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Two new xanthones, 1,6,8-trihydroxy-7-methoxy-2,3-methylenedioxyxanthone (**1**) and 1,6-dihydroxy-7,8-dimethoxy-2,3-methylenedioxyxanthone (**2**), have been isolated from the roots of *Polygala crotalarioides*. Their structures were elucidated by spectral and chemical methods.

Keywords: *Polygala crotalarioides*; Polygalaceae; Xanthones; bioactivities

1. Introduction

Polygala crotalarioides Buch. Ham. (Polygalaceae) is known as a tonic folk medicine in Yunnan Wa nationality [1]. Its bioactivities attracted us to investigate its chemical constituents. During our studies on this plant, two new xanthones (**1** and **2**) were isolated from the roots of *Polygala crotalarioides*. The structural elucidation is reported in this paper (figure 1).

2. Results and discussion

Compound **1** was obtained as yellow needles, mp 250–252°C. The molecular formula was assigned as $C_{15}H_{10}O_8$ on the basis of HREIMS (*m*/*z* 318.0547). Its ^{13}C NMR spectral data were indicative of a hexasubstituted xanthone, having one methylenedioxy moiety (δ 103.4, t, $-O-CH_2-O-$), one methoxyl and three hydroxyls. The carbonyl signal at δ 183.9 in the ^{13}C NMR spectrum indicated a double-chelated carbonyl, meaning there were two hydroxyls attached at C-1 and C-8 [2]. The UV spectrum of **1** showed absorptions at 208, 255, 324 nm, which exhibited a bathochromic shift after addition of NaOAc, indicating the presence of a hydroxyl group at C-3 or C-6 [3]. The position of methoxy group in compound **1** was determined to be di-*ortho* substituted type based on the signal at δ 61.3 in the ^{13}C NMR spectrum [2]. The δ value of C-2 at 130.1 ppm showed that the oxygenation pattern was 1, 2, 3 rather than 1, 2, 4 or 1, 3, 4 type [4]. The ^1H NMR spectrum of **1** showed two aromatic

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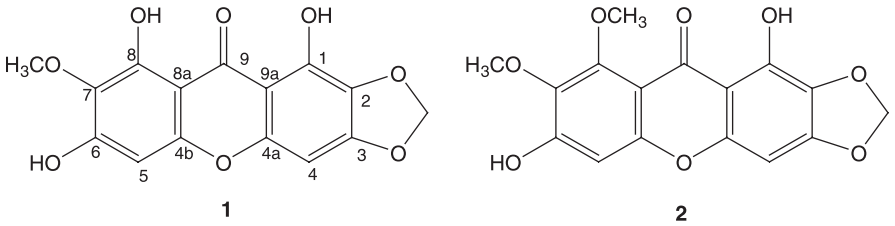

Figure 1. Structures of compounds **1** and **2**.

proton singlets at δ 6.59 and 6.74, assignable to H-4 and H-5 respectively. The three-proton singlet at δ 3.93 should be assigned to the methoxy group at C-7. On the basis of the above evidence, the structure of **1** was elucidated as 1,6,8-trihydroxy-7-methoxy-2,3-methylenedioxyxanthone.

Compound **2**, amorphous yellow powder, mp 275–277°C, was analyzed for $C_{16}H_{12}O_8$ by HREIM at *m/z* 332.0639 $[M]^+$. Its ^{13}C NMR spectral data were also indicative of a hexasubstituted xanthone, having one methylenedioxy moiety (δ 103.2, t, $-O-CH_2-O-$), two hydroxyls and two methoxyls. The signal at δ_C 181.2 indicated a free hydroxyl at C-1 or C-8, chelated with the carbonyl group [2]. As **1**, the NaOAc-induced shift was also observed in the UV spectrum of **2**, indicating the presence of a hydroxyl group at C-3 or C-6 [3]. The signals of two methoxyls in the ^{13}C NMR spectrum at δ 61.3 and 62.0 indicated that both were di-*ortho* substituted. In the ROESY spectrum, there was a correlation between the two methoxyl singlets at δ 3.90 and 4.12, requiring the presence of 7 and 8-subsituted methoxy groups. The methylenedioxy group at C-2 and C-3 was also confirmed by the spectral comparison with that of **1**. The ^1H NMR spectrum of **2** showed signals at δ 6.57 (1H, s) and 6.93 (1H, s), assignable to the protons at positions 4, 5, respectively. Hence, the structure of **2** was concluded to be 1,6-dihydroxy-7,8-dimethoxy-2,3-methylenedioxyxanthone.

3. Experimental

3.1 General experimental procedures

Melting point was measured on a Koffler melting point apparatus produced by Sichuan University (China) and is uncorrected. UV spectra were measured on a UV-210 spectrometer. EIMS and HR-EIMS were recorded on a VG Auto Spec-3000 mass spectrometer. NMR spectra were recorded in pyridine-d_5, on a Bruker AM-400 or DRX-500 instrument at room temperature, using TMS as an internal standard.

3.2 Plant material

The roots of *Polygala crotalarioides* were collected from Yun County, Yunnan Province, China, in May 2002. The plant was identified by Prof Shu-Kun Chen at Kunming Institute of Botany, the Chinese Academy of Sciences, where a voucher specimen (No. 0154671) is deposited.

3.3 Extraction and isolation

The dried roots (1 kg) of *P. crotalarioides* were extracted with 75% EtOH four times under reflux. After removal of the solvent *in vacuo*, the aqueous solution was passed through a

HPD-100 column and the absorbed materials were eluted with water, 75% aqueous ethanol and ethanol, successively. The 75% ethanol eluate was concentrated *in vacuo* to give a residue (96 g), which was chromatographed on a silica gel (200–300 mesh) column with $CHCl_3$–MeOH–H_2O (7:3:0.5, v/v/v) to afford ten fractions. Fraction 7 was chromatograpyed on Si gel with $CHCl_3$–MeOH (100:1) and resubjected to Si gel column chromatography eluting with petroleum ether–Me_2CO (4.5–1, v/v) to afford compounds **1** (6 mg), **2** (65 mg).

3.3.1 6,8-trihydroxy-7-methoxy-2,3-methylenedioxyxanthone (1). Yellow needles, mp 250–252°C. UV (MeOH) λ_{max} nm: 208, 255, 323; + NaOAc: 209, 254, 351. EIMS (*m*/*z*): 318 $[M]^+$ (55), 303 (67), 288 (100), 275 (58), 149 (16). HREIMS: 318.0547 $[M]^+$ (calcd for $C_{15}H_{10}O_8$, 318.0591). ^{1}H NMR (400 MHz, C_5D_5N): δ 6.74 (1H, s, H-5), 6.59 (1H, s, H-4), 6.12 (2H, s, –O–CH_2–O–), 3.93 (3H, s, OMe-7); ^{13}C NMR (100 MHz, C_5D_5N): δ 183.8 (s, C-9), 160.8 (s, C-3), 158.5(s, C-6), 158.4 (s, C-8), 155.7 (s, C-4b), 153.6 (s, C-1), 151.5 (s, C-4a), 143.1 (s, C-7), 130.1 (s, C-2), 104.1 (s, C-8a), 103.4 (t, –O–CH_2–O–), 101.6 (s, C-9a), 99.7 (d, C-5), 90.0 (d, C-4), 61.3(q, OMe-7).

3.3.2 6-dihydroxy-7,8-dimethoxy-2,3-methylenedioxyxanthone (2). Amorphous yellow powder, mp 275–277°C. UV (MeOH) λ_{max} nm: 210, 249, 322; + NaOAc: 206, 247, 358. EIMS (*m*/*z*): 332 $[M]^+$ (55), 303 (67), 288 (100), 275 (58), 149 (16). HREIMS: 332.0639 $[M]^($ (calcd for $C_{16}H_{12}O_8$, 332.0675). ^{1}H NMR (400 MHz, C_5D_5N): δ 6.93 (1H, s, H-5), 6.57 (1H, s, H-4), 6.10 (2H, s, –O–CH_2–O–), 3.90 (3H, s, OMe-7), 4.12 (3H, s, OCH_3-8); ^{13}C NMR (100 MHz, C_5D_5N): δ 181.2 (s, C-9), 159.7 (s, C-6), 159.5 (s, C-3),155.0 (s, C-4b), 154.9 (s, C-8), 153.9 (s, C-1), 152.6 (s, C-4a), 140.4 (s, C-7), 129.7 (s, C-2), 108.2 (s, C-8a), 105.8 (s, C-9a), 103.2 (t, –O–CH_2–O–), 100.5 (d, C-5), 88.9 (d, C-4), 61.3 (q, OMe-7), 62.0 (q, OMe-8).

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