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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  $250-252^{\circ}$ C. The molecular formula was assigned as C<sub>15</sub>H<sub>10</sub>O<sub>8</sub> on the basis of HREIMS (*m/z* 318.0547). Its <sup>13</sup>C NMR spectral data were indicative of a hexasubstituted xanthone, having one methylenedioxy moiety ( $\delta$  103.4, t,  $-O-CH_2-O-$ ), one methoxyl and three hydroxyls. The carbonyl signal at  $\delta$  183.9 in the <sup>13</sup>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  $\delta$  61.3 in the <sup>13</sup>C NMR spectrum [2]. The  $\delta$  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 <sup>1</sup>H NMR spectrum of **1** showed two aromatic



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Figure 1. Structures of compounds 1 and 2.

proton singlets at  $\delta$  6.59 and 6.74, assignable to H-4 and H-5 respectively. The three-proton singlet at  $\delta$  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-methylene-dioxyxanthone.

Compound **2**, amorphous yellow powder, mp  $275-277^{\circ}$ C, was analyzed for C<sub>16</sub>H<sub>12</sub>O<sub>8</sub> by HREIM at *m/z* 332.0639 [M]<sup>+</sup>. Its <sup>13</sup>C NMR spectral data were also indicative of a hexasubstituted xanthone, having one methylenedioxy moiety ( $\delta$  103.2, t,  $-O-CH_2-O-$ ), two hydroxyls and two methoxyls. The signal at  $\delta_{\rm C}$  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 <sup>13</sup>C NMR spectrum at  $\delta$  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  $\delta$  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 <sup>1</sup>H NMR spectrum of **2** showed signals at  $\delta$  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

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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<sub>3</sub>–MeOH–H<sub>2</sub>O (7:3:0.5, v/v/v) to afford ten fractions. Fraction 7 was chromatograpyed on Si gel with CHCl<sub>3</sub>–MeOH (100:1) and resubjected to Si gel column chromatography eluting with petroleum ether–Me<sub>2</sub>CO (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)  $\lambda_{max}$  nm: 208, 255, 323; + NaOAc: 209, 254, 351. EIMS (*m/z*): 318 [M]<sup>+</sup> (55), 303 (67), 288 (100), 275 (58), 149 (16). HREIMS: 318.0547 [M]<sup>+</sup> (calcd for C<sub>15</sub>H<sub>10</sub>O<sub>8</sub>, 318.0591). <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$  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); <sup>13</sup>C NMR (100 MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$  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)  $\lambda_{max}$  nm: 210, 249, 322; + NaOAc: 206, 247, 358. EIMS (*m*/*z*): 332 [M]<sup>+</sup> (55), 303 (67), 288 (100), 275 (58), 149 (16). HREIMS: 332.0639 [M]<sup>(</sup> (calcd for C<sub>16</sub>H<sub>12</sub>O<sub>8</sub>, 332.0675). <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$  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<sub>3</sub>-8); <sup>13</sup>C NMR (100 MHz, C<sub>5</sub>D<sub>5</sub>N):  $\delta$  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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#### References

- [1] B.X. Xiang, P.F. Zhang, Y.H. Xiang. Gui Zhou Sci., 13, 24 (1995).
- [2] I. Miura, K. Hostettmann, K. Nakanishi. Nouv. J. Chim., 2, 653 (1978).
- [3] A.A. Lins Mesquita, D. De Barros Correa, O.R. Gottlieb. Anal. Chim. Acta, 42, 311 (1968).
- [4] T.R. Pinheiro, V.C. Filho, A.R.S. Santos. Phytochemistry, 48, 725 (1998).