

## Two New Xanthenes from *Polygala crotalarioides*

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**Abstract:** Two new xanthenes, 1, 6, 8-trihydroxy-2, 3-methylenedioxyxanthone **1** and 1, 4-dihydroxy-6, 7-methylenedioxyxanthone **2**, were isolated from the roots of *Polygala crotalarioides*. Their structures were elucidated by spectroscopic and chemical methods.

**Keyword:** *Polygala crotalarioides*, Polygalaceae, xanthenes.

The interest in xanthenes has been increased recently as a class of natural products with a broad spectrum of biological activities. The discovery of the antidiabetic activity of some xanthenes from Swertiaceae has prompted us to undertake a more broadly search for novel xanthenes from the plants of Polygalaceae<sup>1</sup>. During our studies, two new xanthenes (**1**) and (**2**) (**Figure 1**) were isolated from the roots of *Polygala crotalarioides*. Their structural elucidation was reported in this paper. The phytochemical investigation of this plant has not been performed up to now.

Compound **1** was yellow needles, mp 280-282°C. The EI-MS of **1** gave a molecular ion peak [M]<sup>+</sup> at *m/z* 288 and its <sup>13</sup>C NMR spectrum including DEPT spectral data of compound **1** were indicative of a pentasubstituted xanthone, having one methylenedioxy moiety ( $\delta$  103.4, t, -O-CH<sub>2</sub>-O-) and three hydroxyl groups. The HREI-MS of compound **1** (*m/z* 288.0263, calcd. 288.027) gave its molecular formula C<sub>14</sub>H<sub>8</sub>O<sub>7</sub>. The IR and UV spectra also showed the characteristic absorption of xanthone. The carbonyl carbon signal in the <sup>13</sup>C NMR spectrum at  $\delta$  184.5 ppm indicated a double chelated carbonyl, meaning two hydroxyls attached at position C-1 and C-8<sup>2</sup>. This was accorded with the absence of proton signal in down field of <sup>1</sup>H NMR spectra. The three singlets of aromatic protons (sometimes *meta* coupling also is singlet peak) showed only *meta* substituted requiring the presence of 6-substituted hydroxyl. The oxygenation 1, 2, 3, rather than 1, 2, 4 or 1, 3, 4, of the another aromatic ring was deduced by the low value chemical shift ( $\delta$  131.2) for C-2 in the <sup>13</sup>C NMR spectrum<sup>3</sup>. Therefore, compound **1** was identified as 1, 6, 8-trihydroxy-2, 3-methylenedioxyxanthone. That is a new natural product.

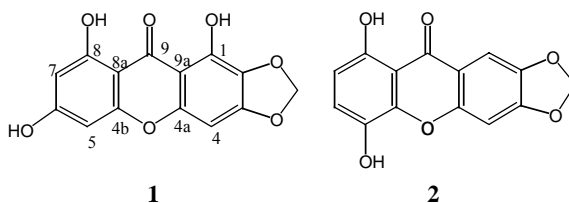
Compound **2**, amorphous yellow powder, mp 234-236°C; the EI-MS ([M]<sup>+</sup> at *m/z* 272) and <sup>13</sup>C NMR including DEPT spectral data of compound **2** indicated the existence

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of a tetrasubstituted xanthone, including one methylenedioxy moiety ( $\delta$  103.1, t, -O-CH<sub>2</sub>-O-) and two hydroxyl groups; the HREI-MS of compound **2** ( $m/z$  272.0323, 272.0321) gave its molecular formula C<sub>14</sub>H<sub>8</sub>O<sub>6</sub>. The IR and UV spectra also showed the characteristic absorption of xanthone. The signal at  $\delta$  181.8 indicated a free hydroxyl group at C-1 or C-8, chelated with the carbonyl group<sup>2</sup>. The down field singlet at  $\delta$  7.97 of H-8 in <sup>1</sup>H NMR spectrum suggested that the position of *ortho* and *meta* of C-8 were substituted, and the di-*ortho* substituted (C-6 and C-7) group must be methylenedioxy. The *ortho*-coupled AB system at  $\delta$  7.43 (d, 1H,  $J=8.4$  Hz, H-3) and  $\delta$  7.53 (d, 1H,  $J=8.4$  Hz, H-2), showed another hydroxyl group should be substituted at C-4 position. The absence of the NaOAc-induced shift in the UV spectrum also confirmed above inferences<sup>4</sup>. Hence, the structure of compound **2** was determined as 1,4-dihydroxy-6,7-methylenedioxyxanthone, it is also a new natural product.

**Figure 1** structures of compound **1** and **2**



**Table 1** <sup>1</sup>H and <sup>13</sup>C NMR data for compound **1** and **2** (400MHz, C<sub>5</sub>D<sub>5</sub>N,  $\delta$ ppm)

C	<b>1</b>		<b>2</b>	
	$\delta_c$	$\delta_H$	$\delta_c$	$\delta_H$
1	154.5 s		108.7 d	7.97, s
2	131.2 s		155.5 s	
3	159.0 s		157.5 s	
4	89.9 d	6.59, s	89.4 d	6.65, s
4a	153.8 s		155.5 s	
4b	156.0 s		143.4 s	
5	95.1 d	6.62, s	150.8 s	
6	167.8 s		119.3 d	7.43, d, $J=8.4$ Hz
7	99.8 d	6.68, s	125.3 d	7.53, d, $J=8.4$ Hz
8	163.4 s		155.5 s	
8a	104.8 s		105.5 s	
9	184.5 s		181.8 s	
9a	102.0 s		121.0 s	
OCH <sub>2</sub> O	103.4 t	6.12, s	103.1 t	6.11, s

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