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Three New Xanthones from *Polygala crotalarioides*

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Abstract: Three new xanthones, 3, 6-dihydroxy-1, 2, 7-trimethoxyxanthone **1**, 1, 3, 6-trihydroxy-2, 7, 8-trimethoxyxanthone **2**, and 3, 6-dihydroxy-1, 2, 7, 8-tetramethoxyxanthone **3**, were isolated from the roots of *Polygala crotalarioides*. Their structures were elucidated by spectral and chemical methods.

Keywords: *Polygala crotalarioides*, chemical constituents, xanthones.

Polygala crotalarioides Buch. Ham. (Polygalaceae) is known to be a folk tonic medicine used in Yunnan Wa nationality[1]. Its bioactivities attracted us to investigate its chemical constituents. Three new xanthones were isolated from the roots of *Polygala crotalarioides* by us. Their structural elucidation was reported in this paper.

Compound **1** was obtained as yellow needles, mp 194-196°C. The molecular formula was assigned as $C_{16}H_{14}O_7$ on the basis of HREI-MS (*m/z* 318.0610 $[M]^+$, calcd. for $C_{16}H_{14}O_7$, 318.0622). Its ^{13}C NMR spectral data indicated that **1** was a pentasubstituted xanthone, with two hydroxyl and three methoxyl groups. The carbonyl carbon signal in the ^{13}C NMR spectrum at δ 174.5 indicated a non-chelated carbonyl, meaning there was no hydroxyl group attached at position 1 and 8[2]. The UV spectrum (in MeOH) of **1** showed absorptions at 205, 241, 316 nm. On addition of NaOAc, the spectrum exhibited a bathochromic shift, indicating the presence of a hydroxyl group at position 3 or 6[3]. In the xanthone skeletons, δ value of the di-*ortho* substituted methoxy groups in the ^{13}C NMR spectra are more than 60 ppm, otherwise, it will be less than 60 ppm[2]. Thus, three methoxy groups at δ_C 62.4, 61.3 and 55.2 in compound **1** indicated that two of the methoxy groups were di-*ortho* substituted, and one was not di-*ortho* substituted. In the ^1H NMR spectrum, **1** showed signals at δ 7.98 (s, 1H), 7.15 (s, 1H) and 7.01 (s, 1H) indicating the protons at positions 8, 5, 4, respectively. In the ROESY spectrum, there was a correlation between H–8 (δ 7.98) and a three-proton singlet at δ 3.75, requiring the presence of 7-subsituted methoxy group. The oxygenation 1, 2, 3 was also confirmed by the low value chemical shift (δ_C 139.8) for C-2 in the ^{13}C NMR spectrum[4]. On the basis of the above evidence, the structure of **1** was elucidated as 3, 6-dihydroxy-1, 2, 7-trimethoxyxanthone.

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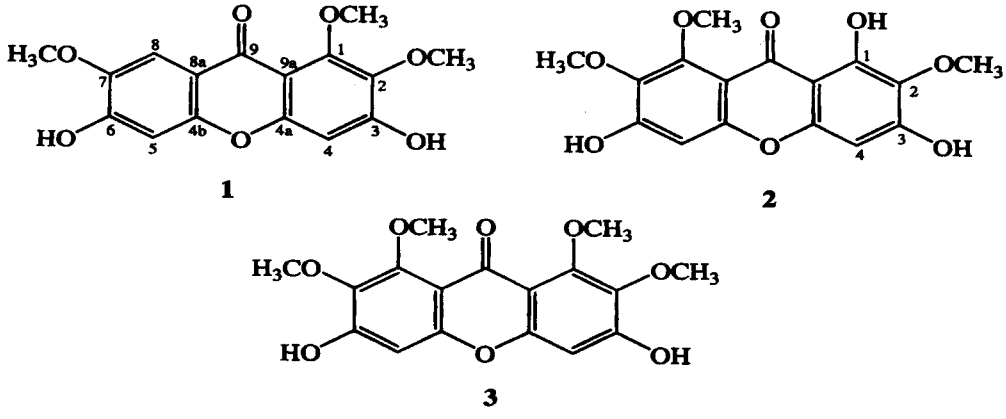
Figure 1 Structures of compounds **1**, **2** and **3**



Compound **2**, amorphous yellow powders, mp 245-247°C, was analyzed for $C_{16}H_{14}O_8$ by HREI-MS (*m/z* 334.0735 $[M]^+$, calcd. for $C_{16}H_{14}O_8$, 334.0729). Its ^{13}C NMR spectral data indicated that **2** was a hexasubstituted xanthone, with three hydroxyl and three methoxyl groups. The signal at δ_C 179.6 indicated a free hydroxyl group at C-1 or C-8, chelated with the carbonyl group [2]. Its UV spectrum showed absorptions at 209, 242, 322 nm. On addition of NaOAc, the spectrum exhibited a bathochromic shift indicating the presence of a hydroxyl group at position 3 or 6[3]. The signals in the ^{13}C NMR spectrum at δ 61.8, 60.9 and 60.1 indicated that all of the methoxy groups were di-*ortho* substituted. In the ^1H NMR spectrum, **2** showed signals at δ 6.38 (s, 1H) and 6.70 (s, 1H), assignable to the protons at positions 4, 5, respectively. Hence, the structure of **2** was concluded to be 1, 3, 6-trihydroxy-2, 7, 8-trimethoxyxanthone.

Table 1 ^1H and ^{13}C NMR data for comopounds **1**, **2** and **3** (400 MHz, C_5D_5N, δ ppm)

	1		2		3	
C	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	155.2 s		153.2 s		154.3 s	
2	139.8 s		130.5 s		139.7 s	
3	158.0 s		154.5 s		157.9 s	
4	100.7 d	7.01, s	93.2 d	6.38, s	100.1 d	6.95, s
4a	155.3 s		157.5 s		154.4 s	
4b	155.0 s		153.6 s		154.4 s	
5	103.5 d	7.15, s	99.5 d	6.70, s	100.1 d	6.95, s
6	152.2 s		157.9 s		157.9 s	
7	148.8 s		138.8 s		139.7 s	
8	107.0 d	7.98, s	151.6 s		154.3 s	
8a	115.4 s		106.9 s		111.0 s	
9	174.5 s		179.6 s		174.5 s	
9a	110.3 s		102.2 s		111.0 s	
OMe-1	62.4 q	4.25, s			62.2 q	4.21, s
OMe-2	61.3 q	3.94, s	59.9 q	3.75, s	61.3 q	3.92, s
OMe-7	55.2 q	3.75, s	60.9 q	3.81, s	61.3 q	3.92, s
OMe-8			61.8 q	3.87, s	62.2 q	4.21, s
OH-1				13.6, s		

Compound **3** was obtained as yellow needles, mp 260-262°C, $C_{17}H_{16}O_8$ (*m/z* 348.0349 $[M]^+$, calcd. for $C_{17}H_{16}O_8$, 348.0361). Its ^{13}C NMR spectral data indicated that **3** was a symmetrical xanthone, with two hydroxyl and four methoxyl groups. The signal at δ_C 174.5 indicated a non-chelated carbonyl, meaning there was no hydroxyl group attached at position 1 and 8 [2]. The UV spectrum showed absorptions at 208, 241, 325 nm. On addition of NaOAc, the spectrum also exhibited a bathochromic shift, indicating the presence of a hydroxyl group at position 3 or 6 [3]. The signals in the ^{13}C NMR spectrum at δ 61.3 and 62.2 indicated that these methoxy groups were di-*ortho* substituted. In the ^1H NMR spectrum, there was only one singlet of aromatic protons appeared at δ 6.95, assignable to the protons at positions 4 and 5. Therefore, compound **3** was identified as 3, 6-dihydroxy-1, 2, 7, 8-tetramethoxyxanthone.

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