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Two New Xanthone Glycosides from *Polygala tenuifolia*

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Abstract: Two new xanthone glycosides, polygalaxanthone IV and V were isolated from the roots of *Polygala tenuifolia* Willd. Their structures were established as 6-O-[α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl]-1-hydroxy-3, 7-dimethoxyxanthone (polygalaxanthone IV), and 6-O-[α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl]-1, 3-dihydroxy-7-methoxyxanthone (polygalaxanthone V), respectively, on the basis of chemical and spectral evidence.

Keywords: *Polygala tenuifolia*, xanthone glycosides, polygalaxanthone IV and V.

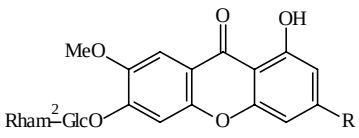
The roots of *Polygala tenuifolia* Willd, "yuanzhi" is a wellknown traditional Chinese medicine used as an expectorant, tonic, and sedative agents. It was reported that various xanthones, saponins and oligosaccharides had been isolated from this plant[1-6]. In order to search for new physiologically active components, a systematic chemical study was made on the roots of *Polygala tenuifolia* from the main production area, Shanxi Province. In this paper, we report the structure elucidation of two new xanthone glycosides named polygalaxanthone IV (**1**) and V (**2**), which are xanthone glycosides with rhamnose in the sugar moiety isolated from the genus *Polygala* for the first time.

Compound **1** was obtained as yellow powder, mp 273-275°C. The TOF-MS of **1** exhibited a quasi-molecular ion peak at *m/z* 597 $[M+H]^+$ and 619 $[M+Na]^+$, combining with the analysis of ^{13}C NMR spectrum, its molecular formulae was deduced to be $C_{27}H_{32}O_{15}$. Its UV spectrum in MeOH (λ_{max} 237, 256, 308 and 362 nm) is similar to that of 1, 6-dihydroxy-3, 7-dimethoxyxanthone (λ_{max} 234, 255, 312 and 364 nm)[1]. The IR spectrum of **1** showed the presence of hydroxyl groups (3407 cm^{-1}), a chelated ketone (1653 cm^{-1}), and aromatic rings (1612, 1580, 1478 cm^{-1}). The ^1H NMR spectrum showed a chelated hydroxyl signal at δ 13.00 (C-1-OH), two singlet aromatic protons at δ 7.45 and 7.29, two meta-coupled aromatic protons at δ 6.60 (d, 1H, J=2.1 Hz) and 6.37 (d, 1H, J=2.1 Hz), two anomeric proton signals at δ 5.42 (d, 1H, J=7.80 Hz) and 5.25 (s, 1H), and a methyl signal at δ 1.13 (d, 3H, J=5.7 Hz). In conjunction with a methyl carbon signal at δ 18.08 in the DEPT spectrum and the analysis of ^1H-^1HCOSY, it may be concluded that a methyl aldopentose sugar residue existed in this compound. On acid hydrolysis, **1** afforded glucose and rhamnose. The configuration of glucosyl residue was deduced to be β from the *J* value (7.8 Hz) of anomeric proton, and of rhamnosyl residue to be α by comparison of the ^{13}C NMR data[7]. In HMBC spectrum,

the rhamnose anomeric proton signal at δ 5.25 was correlated to C-2 (δ 75.1) of the glucosyl residue, and the glucosyl anomeric proton signal at δ 5.42 was correlated to C-6 signal of the aglycone (δ 152.8). Thus, **1** was determined to be 6-O-[α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl]-1-hydroxy-3, 7-dimethoxyxanthone.

Compound 2 was obtained as yellow powder, mp 232-235°C. Its UV and IR spectra were very similar to 1, but when adding NaOAC, the UV spectrum of 2 showed a bathochromic shift indicating the presence of a hydroxyl group at 3 or 6 position2. The TOF-MS of 2 showed a quasi-molecular ion peak at m/z 583 [M+H]+, 605 [M+Na]+ and 621 [M+K]+, 14 mass units lower than that of 1, and 13C NMR data were consistent with a formulae of C26H30O15. Comparing the NMR data with that of 1, an extra hydroxyl proton signal at δ 10.97 was presented in 1H NMR spectrum of 2, and a methyl carbon signal at δ 56.1 was disappeared in the DEPT spectrum of 2. All these data suggested that a hydroxyl group substituted a methoxyl group of **1** in **2**. The NMR signals of B ring and of the sugar moiety were almost the same as those of **1**, except that signals of A ring were a little different from those of **1**, which indicated that the hydroxyl group substituted the methoxyl at C-3, but not at C-6. Thus, **2** was identified as 6-O-[α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl-1, 3-dihydroxy-7-methoxyxanthone.

Figure 1 Structures of **1** and **2**



1 R=OMe

2 R=OH

Table 1 ^{13}C NMR data of **1** and **2** (DMSO-d_6, δ ppm)

	1	2		1	2
1	162.4	162.6	Glc-1	97.4	97.4
2	97.0	98.0	2	75.1	75.2
3	165.9	165.1	3	77.0	77.0
4	92.5	93.7	4	69.7	69.6
4a	157.3	157.4	5	77.6	77.6
4b	151.3	151.2	6	60.5	60.5
5	102.9	103.0	Rham-1	99.8	99.9
6	152.8	152.6	2	70.5	70.3
7	146.9	146.8	3	70.3	70.5
8	104.3	104.3	4	71.8	71.8
8a	113.2	113.2	5	68.4	68.4
8b	102.6	101.8	6	18.1	18.1
9	179.1	178.8			
OMe	55.8	55.8			
	56.1				

References

1. Y. Ikeya, K. Sugama, M. Okada, H. Mitsuhashi *et al*., *Phytochemistry*, **1991**, *30* (6), 2061.
2. T. Fujita, D. Y. Liu, S. Ueda, Y. Takeda, *Phytochemistry*, **1992**, *31* (11), 3997.
3. T. Miyase, Y. Iwata, A. Ueno, *Chem. Pharm. Bull*., **1991**, *40* (10), 741.
4. T. Miyase, Y. Iwata, A. Ueno, *Chem. Pharm. Bull*., **1991**, *39* (11), 3082.
5. S. Sakuma, J. Shojji, *Chem Pharm Bull*, **1981**, *21* (9), 2431.
6. S. Sakuma, J. Shojji, *Chem Pharm Bull*, **1981**, *30* (3), 810.
7. T. Miyase, H. Noguchi, X. M. Chen, *J. Nat. Prod*., **1999**, *62* (7), 993.

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