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Oxanthrone *C*-glycosides and epoxynaphthoquinol from the roots of *Rumex japonicus*

Lili Jiang, Shuwei Zhang, Lijiang Xuan *

State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Shanghai Institutes for Biological Sciences, Chinese Academy of Science, 555 Zuchongzhi Road, Zhangjiang Hi-Tech Park, Shanghai 201203, PR China

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Abstract

Five oxanthrone *C*-glycosides, namely rumejaposide A–E, and an epoxynaphthoquinol, together with eight known compounds, 2,6-dihydroxy benzoic acid, 4-hydroxy benzoic acid, epicatechin, 4-hydroxy-3-methoxy benzoic acid, 2,6-dimethoxy-4-hydroxyl benzoic acid, rutin, emodin and 2-acetyl-1,8-dihydroxy-3-methyl-6-methoxynaphthalene, were isolated from the roots of *Rumex japonicus*. The structures of the oxanthrone *C*-glycosides were elucidated by application of spectroscopic methods as (10*R*)10-*C*-β-glucopyranosyl-1,8,10-trihydroxy-2-carboxyl-3-methyl-9(10*H*)-anthracenone, (10*S*)10-*C*-β-glucopyranosyl-1,8,10-trihydroxy-2-carboxyl-3- methyl-9(10*H*)-anthracenone, (10*R*)10-*C*-β-glucopyranosyl-1,6,8,10-tetrahydroxy-2-carboxyl-3-methyl-9(10*H*)-anthracenone, (10*R*)10-*C*-β-glucopyranosyl-1,6,8,10-tetrahydroxy-3-hydroxymethyl-9(10*H*)-anthracenone, and (10*R*)10-*C*-β-glucopyranosyl-1,6,8,10-tetrahydroxy-3-methyl-9(10*H*)-anthracenone. Absolute configurations for each compound were deduced by analyses of CD spectra and comparison with those known similar compounds. The structure of epoxynaphthoquinol was elucidated by spectroscopic methods as 3-acetyl-2-methyl-1,4,5-trihydroxy-2,3-epoxynaphthoquinol, and its relative configuration was determined by a 2D-ROESY experiment.

Keywords: *Rumex japonicus*; Polygonaceae; Oxanthrone *C*-glycosides; Epoxynaphthoquinol

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1. Introduction

The genus Rumex, belonging to the Polygonaceae, is characterized by a high percentage of anthraquinone derivatives (Midiwo and Rukunga, 1985; Demirezer, 1994). Previous studies of the genus have led to the isolation of emodin, chrysophanol, physcione, emodin-1,6-dimethylether, xanthorin-5-methylether, aloe-emodin, emodin-1-*O*-β-D-glucoside, emodin-8-*O*-β-D-glucoside, physcione-8-*O*-β-D-glucoside, chrysophanol-8-*O*-β-D-glucoside (Xu et al., 2004; Erturk et al., 2001; Zaghloul and El-Fattah, 1999; Yuan et al., 2000) and an anthraquinoid-*C*-glycoside, chrysaloin (Masood et al., 1982). It is well known that anthraquinones contribute to the bioactivities within this genus, especially as to the anti-microorganic, purgative and anti-inflammatory activities (Xu et al., 2004; Muller et al., 1989). As part of our phytochemical research of the Polygonaceae (Xiao et al., 2000, 2002, 2003a,b), the water-soluble constituents of *Rumex japonicus* were investigated in this study, with five new oxanthrone *C*-glycosides, namely rumejaposide A–E (**1**–**5**) and a new epoxynaphthoquinol, 3-acetyl-2-methyl-1,4,5-trihydroxy-2,3-epoxynaphthoquinol (**6**) isolated. In addition, the known compounds, 2,6-dihydroxy benzoic acid (**7**), 4-hydroxy benzoic acid (**8**), epicatechin (**9**), 4-hydroxy-3-methoxy benzoic acid (**10**), 2,6-dimethoxy-4-hydroxyl benzoic acid (**11**), rutin (**12**), emodin (**13**) and 2-acetyl-1,8-dihydroxy-3-methyl-6-methoxynaphthalene (**14**), were obtained as well. In this paper, we describe the isolation and structure elucidation of the six new compounds.

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* Corresponding author. Tel./fax: +86 21 50272221.
E-mail address: ljxuan@mail.shcnc.ac.cn (L. Xuan).

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2. Results and discussion

The water-soluble part of the aqueous acetone (70:30 v/v) extract was subjected to reversed-phase column chromatography on different stationary phases to yield six new natural products (**1**–**6**) and eight known compounds. The structures of the new compounds were elucidated on the basis of UV, IR, CD, MS and NMR spectroscopic analyses, and by comparison of their spectroscopic data with those reported in the literature.

Compounds **1** and **2** were obtained as yellow amorphous powders. Their molecular formulae were elucidated as $C_{22}H_{22}O_{11}$ from the positive quasi-molecular ion peak in the HRESIMS at *m*/*z* 485.1047 $[M+Na]^+$ (calc. 485.1060) for compound **1** and at *m*/*z* 463.1242 $[M+H]^+$ (calc. 463.1240) for compound **2**. Analyses of their UV, IR, ^1H and ^{13}C NMR spectra showed them to be closely related to one another (Tables 1 and 2). The UV spectra of **1** and **2** showed maximum absorptions at 270, 307, and 364 nm, characteristic of a highly conjugated system (Harding et al., 1999), which was confirmed by the presence of IR absorption maxima indicating the presence of hydroxyl (3396 cm^{-1}), chelated carbonyl (1616 cm^{-1}) and chelated carboxyl (1710 cm^{-1}) functional groups, respectively. The ^{13}C NMR spectrum, including a DEPT experiment, showed 22 carbon atoms comprising 1 methyl (δ 22.0), 1 oxymethylene (δ 63.4), 4 aromatic methines, 5 sp^3 oxymethines, and 11 quaternary carbons, of which 2 were carbonyls. The ^1H NMR spectra showed two different aromatic proton spin systems: three *ortho*-coupled aromatic protons at δ 7.34 (1H, *d*, $J = 7.6$ Hz, H-5), δ 7.56 (1H, *dd*, $J = 7.8$, 8.2 Hz, H-6) and δ 6.98 (1H, *d*, $J = 8.3$ Hz, H-7), and a pentasubstituted aromatic ring at δ 7.31, (1H, *s*, H-4). The ^1H and ^{13}C NMR chemical shifts of **1** and **2** (Tables 1 and 2) were assigned using a combination of COSY, HMQC, and HMBC spectroscopic analyses that allowed an unambiguous identification of the oxanthrone and sugar moieties. The attachment of the carboxyl group to C-2 of the aglycone was established by the following HMBC correlations: H-4 (δ 7.31) with C-10 (δ 76.2) and C-2 (δ 125.4), CH_3-3 (δ 2.48) with C-2 (δ 125.4), C-3 (δ 146.7) and C-4 (δ 122.5), respectively. In the ^1H NMR spectrum, the anomeric proton appeared at δ 3.47 (1H, *d*, $J = 9.5$ Hz, H-1′) indicating a β-configuration at C-1′. The upfield shift of the anomeric carbon signal (δ 86.0) and the HMBC correlations from the anomeric proton to the quaternary carbon at δ 76.2 (C-10) indicated that the sugar moiety was connected to the aglycone at C-10 to form an oxanthrone *C*-glycoside. Compound **1** differs from **2** only in the stereochemical disposition at the C-10 quaternary carbon center. The CD spectra (Fig. 3) of rumejaposide A (**1**) and B (**2**) showed opposite Cotton effects in the

Table 2
^{13}C NMR spectroscopic data for compounds **1**–**5** in D_2O[a]

	1	**2**	**3**	**4**	**5**
1	159.4	160.7	160.1	162.8	161.4
1a	116.0	117.3	117.4	116.7	114.2
2	125.4	130.8	133.3	116.3	118.5
3	146.7	148.9	145.9	150.6	149.2
4	122.5	124.0	124.1	118.1	121.2
4a	148.2	148.9	147.5	151.2	148.4
5	120.7	122.7	111.9	109.0	108.9
5a	146.9	148.9	150.9	146.8	145.4
6	138.9	140.5	167.2	166.3	164.2
7	119.2	121.2	106.6	104.1	103.8
8	162.3	164.2	166.8	165.5	164.2
8a	117.1	119.7	112.7	110.9	109.9
9	194.2	196.3	194.5	192.7	191.6
10	76.2	78.2	77.8	76.7	75.1
2-COOH	173.8	177.8	179.6		
$3-CH_3$	22.0	23.8	23.7		22.8
$3-CH_2OH$				65.1	
1′	86.0	88.0	88.6	86.2	86.0
2′	73.4	75.4	75.4	73.4	72.4
3′	79.6	81.6	81.6	79.7	78.8
4′	71.6	73.5	73.6	71.7	75.1
5′	81.9	83.8	83.8	81.9	80.9
6′	63.4	65.3	65.4	63.5	62.6

[a] Spectra taken at 400 MHz for **1**, **2**, **4**, and **5** and 300 MHz for **3**.

Table 1
^1H NMR spectroscopic data for compounds **1**–**5** in D_2O[a]

	1	**2**	**3**	**4**	**5**
2				6.89 (1H, *s*)	6.66 (1H, *s*)
4	7.31 (1H, *s*)	7.36 (1H, *s*)	7.17 (1H, *s*)	7.32 (1H, *s*)	7.04 (1H, *s*)
5	7.34 (1H, *d*, 7.6)	7.31 (1H, *d*, 7.7)	6.53 (1H, *br*, *s*)	6.92 (1H, *d*, 1.95)	6.71 (1H, *s*)
6	7.56 (1H, *dd*, 7.8, 8.2)	7.60 (1H, *dd*, 7.9, 8.0)			
7	6.98 (1H, *d*, 8.3)	7.00 (1H, *d*, 8.2)	6.24 (1H, *d*, 1.1)	6.33 (1H, *d*, 1.96)	6.29 (1H, *s*)
$3-CH_3$	2.48 (3H, *s*)	2.46 (3H, *s*)	2.36 (3H, *s*)		2.33 (3H, *s*)
$3-CH_2OH$				4.69 (2H, *s*)	
1′	3.47 (1H, *d*, 9.5)	3.47 (1H, *d*, 9.6)	3.40 (1H, *d*, 9.6)	3.38 (1H, *d*, 9.4)	3.40 (1H, *d*, 9.6)
2′	2.72 (1H, *dd*, 9.5, 9.0)	2.73 (1H, *dd*, 9.2, 9.1)	2.54 (1H, *dd*, 9.3, 9.2)	2.84 (1H, *dd*, 10.2, 9.2)	2.59 (1H, *dd*, 9.2, 9.2)
3′	3.27 (1H, *dd*, 9.0, 9.2)	3.28 (1H, *dd*, 9.0, 9.6)	3.15 (1H, *dd*, 8.7, 9.0)	3.27 (1H, *dd*, 9.0, 8.9)	3.17 (1H, *dd*, 8.9, 8.8)
4′	2.96 (1H, *dd*, 9.4, 9.7)	2.97 (1H, *dd*, 9.6, 9.4)	2.89 (1H, *dd*, 9.4, 9.3)	2.89 (1H, *dd*, 9.4, 9.6)	2.93 (1H, *dd*, 9.4, 9.4)
5′	3.18 (1H, *ddd*, 9.8, 6.3, 1.6)	3.18 (1H, *ddd*, 9.8, 6.3, 1.9)	3.15 (1H, *d*, 8.7, 9.0)	3.09 (1H, *ddd*, 9.6, 6.3, 1.8)	3.14 (1H, *dd*, 7.6, 6.8)
6′	3.58 (1H, *dd*, 6.4, 12.0)	3.55 (1H, *dd*, 6.3, 12.3)	3.50 (1H, *dd*, 12.2, 6.7)	3.47 (1H, *dd*, 6.3, 12.1)	3.54 (1H, *dd*, 12.2, 6.4)
	3.74 (1H, *dd*, 11.9, 1.3)	3.74 (1H, *dd*, 12.3, 2.2)	3.72 (1H, *d*, 11.4)	3.66 (1H, *d*, 10.4)	3.74 (1H, *d*, 12.7)

[a] Spectra taken at 400 MHz for **1**, **2**, **4**, and **5** and 300 MHz for **3**.