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

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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

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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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**.

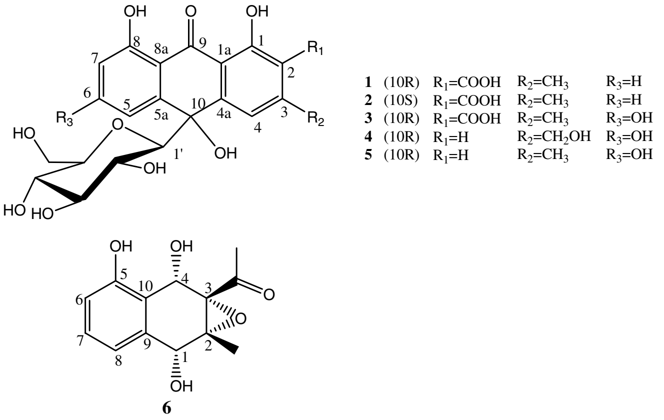
Table 1
^1H NMR spectroscopic data for compounds **1**–**5** in D_2O[a]

	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**.

ranges 270–380 nm, indicating the opposite configuration of C-10 for these oxanthrones. Thus rumejaposide A (**1**) showed a positive Cotton effect and rumejaposide B (**2**) a negative one. These results were the same as those reported for aloin A and aloin B (Manitto et al., 1990; Rauwald and Lohse, 1992). Therefore, rumejaposide A (**1**) has the 10*S* configuration while rumejaposide B (**2**) is the 10*R* diastereoisomer. Consequently, compounds **1** and **2** were identified as (10*S*)10-*C*-β-glucopyranosyl-1,8,10-trihydroxy-2-carboxyl-3-methyl-9(10*H*)-anthracenone and (10*R*)10-*C*-β-glucopyranosyl-1,8,10-trihydroxy-2-carboxyl-3-methyl-9-(10*H*)-anthracenone, namely rumejaposide A and B, respectively (Figs. 1 and 2).

Based on the HRESIMS analyses, $[M+H]^+$ 479.1193, 451.1218 and 435.1271, the molecular formulas of $C_{22}H_{22}O_{12}$ (**3**), $C_{21}H_{22}O_{11}$ (**4**) and $C_{21}H_{22}O_{10}$ (**5**) were deduced, respectively. Compounds **3–5** were also elucidated as oxanthrone *C*-glycosides by comparing their UV, IR and NMR spectra with those of compounds **1** and **2**. The absence of a H-6 signal and a downfield shift of C-6 (δ 167.2) in the NMR spectra of **3** indicated that a hydroxyl group was attached to the C-6 carbon atom. The C-2 of compounds **4** and **5** were methine (δ 116.3 for **4** and δ 118.5 for **5**) instead of quaternary carbons in compounds **1–3**. The presence of proton signals at δ 6.89 (1H, *s*) for **4** and δ 6.66 (1H, *s*) for **5** also supported this. Moreover, the methyl group of compounds **1–3** and **5** were replaced by an oxymethylene (δ 65.1) moiety in compound **4**. The assignment of ^{1}H and ^{13}C NMR chemical shifts of compounds **3–5** was obtained by analyzing the COSY, HMQC and HMBC spectroscopic data (Tables 1 and 2). Compounds **3–5** showed negative Cotton effects (Fig. 4) similar to mayoside (10*R*) and opposite to saroside (10*S*), which indicated the 10*R* configuration of rumejaposides C–E (Hernandez-Medel et al., 1999). Therefore, compounds **3–5** were determined to be (10*R*)10-*C*-β-glucopyranosyl-1,6,8,10-tetrahydroxy-2-carboxyl-3-methyl-9(10*H*)-anthracenone (**3**), (10*R*)10-*C*-β-glucopyranosyl-1,6,8,10-tetrahydroxy-3-hydroxymethyl-9(10*H*)- anthracenone (**4**) and (10*R*)10-*C*-β-glucopyranosyl-1,6,8,10-tetrahydroxy-3-methyl-9(10*H*)-anthracenone (**5**), namely rumejaposide C–E, respectively.



1	(10R)	R_1=COOH	R_2=CH_3	R_3=H
2	(10S)	R_1=COOH	R_2=CH_3	R_3=H
3	(10R)	R_1=COOH	R_2=CH_3	R_3=OH
4	(10R)	R_1=H	R_2=CH_2OH	R_3=OH
5	(10R)	R_1=H	R_2=CH_3	R_3=OH

6

Fig. 1. The structures of compounds **1–6**.

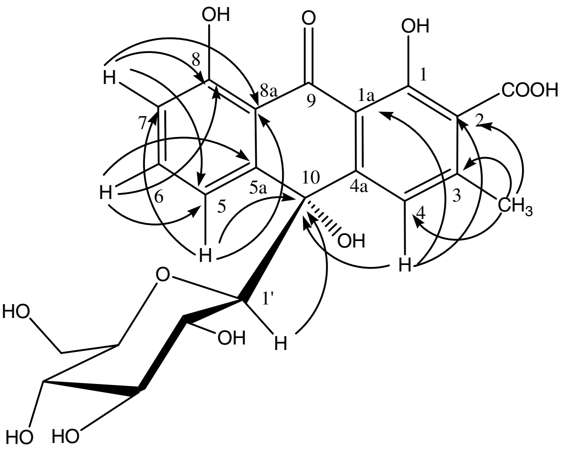


Fig. 2. Key HMBC correlations of compound **1**.

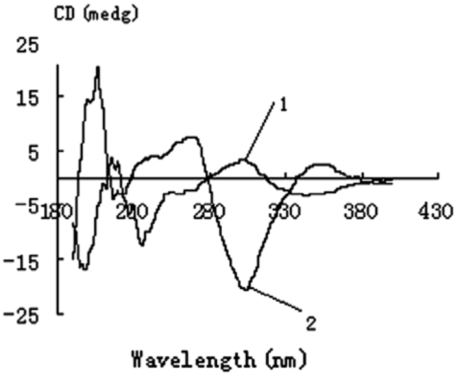


Fig. 3. CD spectra of compounds **1** and **2**.

Compound **6** was obtained as white amorphous powder. Its IR spectrum suggested the presence of hydroxyl (3463 cm^{-1}), carbonyl (1718 cm^{-1}), double bonds (1587 cm^{-1}) and epoxide (1257, 993 and 800 cm^{-1}) functional groups. The molecular formula, $C_{13}H_{14}O_5$, was determined by analyses of the HREIMS spectrum ($[M]^+$ *m/z* 250.0841), ^{1}H and ^{13}C NMR and DEPT spectroscopic data. The ^{13}C NMR spectrum showed one carbonyl (δ 209.0), six sp^2 carbon signals (δ 157.9, 138.3, 130.4,

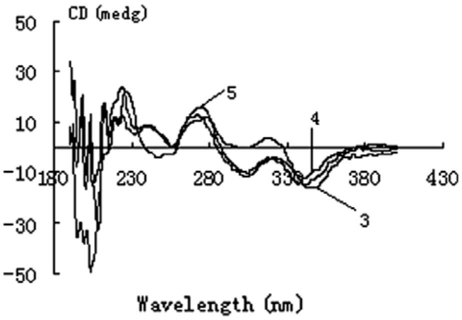


Fig. 4. CD spectra of compounds **3–5**.

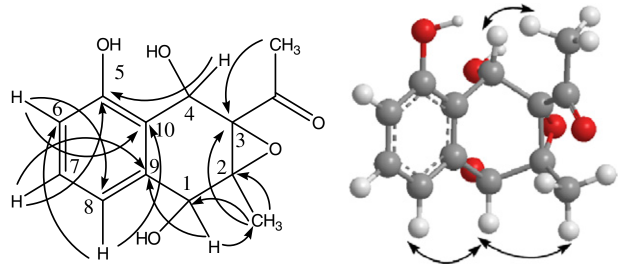


Fig. 5. Key HMBC (→), ROESY (↔) correlations of compound **6**.

120.7, 119.6, 116.4), among which were three methines, one quarternary carbon bearing an oxygen and six sp^3 carbon signals (δ 73.1, 70.7, 68.6, 66.1, 29.6, 16.4), of which two methyls, two oxymethines and two quarternary carbons bearing oxygen were confirmed by their chemical shifts and a DEPT experiment. In the ^{1}H NMR spectrum of compound **6**, the signals due to three olefins (δ 7.23, 7.14, 6.76), two methyls (δ 2.41, 1.52) and two oxymethines (δ 5.62, 4.67) protons were observed. The above results indicated that compound **6** was a naphthoquinol derivative, whose epoxide ring was inferred by chemical shifts (δ 73.1, 66.1) and seven degrees of unsaturation. The detailed analyses of the 2D NMR (^{1}H–^{1}H COSY, HMQC, HMBC) spectra provided the chemical structure of compound **6** (Figs. 1 and 5). In the ROESY spectrum, H-1 had correlations with H-8 and 2-CH_3, and H-4 had cross peaks with $COCH_3$, which meant that two hydroxyl groups and one epoxy group were on the same side (Fig. 5). Therefore, compound **6** was identified as 3-acetyl-2-methyl-1,4,5-trihydroxy-2,3-epoxynaphthoquinol.

Known compounds **7**–**14** were identified by NMR and MS analyses and comparison with reference data as following: 2,6-dihydroxy benzoic acid (**7**) (Scott, 1972), 4-hydroxy benzoic acid (**8**) (Wang et al., 1999), epicatechin (**9**) (Foo et al., 1997), 4-hydroxy-3-methoxy benzoic acid (**10**) (Yamanak et al., 1995), 2,6-dimethoxy-4-hydroxyl benzoic acid (**11**) (Adam, 1999), rutin (**12**) (Nawwar et al., 1984), emodin (**13**) (Gill et al., 1988) and 2-acetyl-1,8-dihydroxy-3-methyl-6-methoxynaphthalene (**14**) (Nishina et al., 1993), respectively.

3. Concluding remarks

As species of Rumex are very similar in their morphology, it is often difficult to distinguish one from another. However, the diverse distribution of anthraquinone derivatives among the species (Midiwo and Rukunga, 1985; Demirezer, 1994) affords an opportunity to authenticate the morphologically similar species according to the different types or contents of anthraquinone derivatives contained in the species. A total of five new oxanthrone *C*-glycosides and a known anthraquinone, emodin, was identified in this study from the roots of *R. japonicus*. This provides valuable information to distinguish *R. japonicus* from morphologically similar species.

4. Experimental

4.1. General experimental procedures

ORD spectra were obtained on Perkin–Elmer 341 polarimeter, whereas CD spectra were acquired using a JASCO J-810 spectrometer. UV spectra were recorded on Shimadzu UV-2450 spectrophotometer, whereas IR spectra were obtained on a Perkin–Elmer 577 spectrometer. ESI and EI mass spectra were recorded on a Quattro mass spectrometer and a Finnigan/Mat 95 spectrometer, respectively. NMR spectra were acquired in D_2O and CD_3OD using a Varian mercury NMR spectrometer operating at 300 and 400 MHz. CC was carried out on Sephadex LH-20 (20–80 μm, Pharmacia Fine Chemical Co. Ltd.), TSK gel Toyopearl HW-40F (30–60 μm, Toso Co., Ltd.), MCI gel CHP-20P (75–150 μm, Mitsubishi Chemical Industries Co., Ltd.), and Cosmosil 75 C_{18}-OPN (40–105 μm, Nacalai Tesque Inc.). TLC was performed on $HSGF_{254}$ silica gel plates (Yantai, China).

4.2. Plant material

The roots of *R. japonicus* Houtt. were collected at Jiangsu, China, in autumn 2003, and identified by Prof. Heming Yang. A voucher specimen (No. RJ001) is deposited at the Shanghai Institute of Materia Medica, Chinese Academy of Sciences, China.

4.3. Extraction and isolation

Air-dried, powdered roots (5 kg) were extracted with aqueous acetone (70:30 v/v, 15 L) at r.t. (25 °C) for 24 h each and for 4 times. After concentration in vacuo to remove the acetone, the suspension was subjected to centrifugation to remove any insoluble residues. The resulting aqueous solution was next submitted to Sephadex LH-20 gel CC and eluted with H_2O–MeOH (1:0, 1:4, 6:4, 4:6, v/v). The aqueous fraction was discarded and the other three fractions (H_2O–MeOH, 1:4, 6:4, 4:6, v/v eluate) were submitted to CC using MCI gel CHP-20P, Cosmosil75 C_{18}-OPN and Toyopearl HW-40F, repeatedly, to give six new compounds. Fraction II (H_2O–MeOH, 1:4, v/v eluate) gave compound 1 (25 mg), 2 (15 mg), 3 (10 mg), 7 (8 mg), 8 (20 mg), and 9 (30 mg). Fraction III (H_2O–MeOH, 6:4, v/v eluate) afforded compound 4 (30 mg), 6 (8 mg), 10 (20 mg), and 11 (20 mg). Fraction IV (H_2O–MeOH, 4:6, v/v eluate) provided compound 5 (15 mg), 12 (15 mg), 13 (15 mg), and 14 (40 mg).

4.4. Rumejaposide A (*1*)

Yellow amorphous powder; $[\alpha]_D^{20}$ +4.6 (H_2O; c 0.35). CD $\Delta\varepsilon_{235}$ −12.46, $\Delta\varepsilon_{302}$ +3.31, $\Delta\varepsilon_{344}$ −3.35 (H_2O; c 1.02). UV $\lambda_{max}^{H_2O}$ nm (log ε): 270 (3.82), 307 (3.87), 364 (3.98). IR_{max}^{KBr} cm^{-1}: 3396, 2927, 1710, 1616, 1450, 1282, 1085. For ^{1}H and ^{13}C NMR spectroscopic data, see Tables 1 and 2. ESIMS positive ion m/z: 485 $[M+Na]^+$, ESIMS negative ion m/z: 461 $[M-H]^-$. HRESIMS m/z: 485.1047 $[M+Na]^+$ (calc. for $C_{22}H_{22}O_{11}Na$, 485.1060).

4.5. *Rumejaposide B (**2**)*

Yellow amorphous powder; $[\alpha]_D^{20}$ −54 (H_2O; c 0.30). CD $\Delta\varepsilon_{256}$ +7.62, $\Delta\varepsilon_{304}$ −20.74, $\Delta\varepsilon_{356}$ +2.57 (H_2O; c 1.01). UV $\lambda_{max}^{H_2O}$ nm (log ε): 270 (3.84), 307 (3.91), 364 (4.01). IR_{max}^{KBr} cm^{-1}: 3419, 2923, 1606, 1450, 1282, 1081. For ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2. ESIMS positive ion m/z:485 $[M+Na]^+$, ESIMS negative ion m/z: 461 $[M-H]^-$. HRESIMS m/z: 463.1242 $[M+H]^+$ (calc. for $C_{22}H_{23}O_{11}$, 463.1240).

4.6. *Rumejaposide C (**3**)*

Yellow amorphous powder; $[\alpha]_D^{20}$ −25 (H_2O; c 0.22). CD $\Delta\varepsilon_{277}$ +11.79, $\Delta\varepsilon_{344}$ −16.48 (H_2O; c 1.06). UV $\lambda_{max}^{H_2O}$ nm (log ε): 278 (4.00), 368 (4.23). IR_{max}^{KBr} cm^{-1}: 3407, 2925, 1610, 1456, 1382, 1267, 1083. For ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2. ESIMS positive ion m/z:501 $[M+Na]^+$, ESIMS negative ion m/z:477 $[M-H]^-$. HRESIMS m/z:479.1193 $[M+H]^+$ (calc. for $C_{22}H_{23}O_{12}$, 479.1190).

4.7. *Rumejaposide D (**4**)*

Yellow amorphous powder; $[\alpha]_D^{20}$ −53 (CH_3OH; c 0.23). CD $\Delta\varepsilon_{272}$ +12.92, $\Delta\varepsilon_{340}$ −12.23 (CH_3OH; c 1.33). UV $\lambda_{max}^{H_2\ O}$ nm (log ε): 256 (3.72), 274 (3.77), 365 (4.03). IR_{max}^{KBr} cm^{-1}: 3388, 2923, 1619, 1481, 1375, 1269, 1083. For ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2. ESIMS positive ion m/z:473 $[M+Na]^+$, ESIMS negative ion m/z: 449 $[M-H]^-$. HRESIMS m/z: 451.1218 $[M+H]^+$ (calc. for $C_{21}H_{23}O_{11}$, 451.1240).

4.8. *Rumejaposide E (**5**)*

Yellow amorphous powder; $[\alpha]_D^{20}$ −28 (MeOH; c 0.13). CD $\Delta\varepsilon_{275}$ +16.12, $\Delta\varepsilon_{340}$ −14.80 (H_2O; c 1.19). UV$\lambda_{max}^{H_2\ O}$ nm (log varepsilon): 254 (3.93), 275 (4.01), 364 (4.28). IR_{max}^{KBr} cm^{-1}: 3419, 2921, 1618, 1481, 1378, 1267, 1166, 1085. For ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2. ESIMS positive ion m/z: 457 $[M+Na]^+$, ESIMS negative ion m/z: 433 $[M-H]^-$. HRESIMS m/z: 435.1271 $[M+H]^+$ (calc. for $C_{21}H_{23}O_{10}$, 435.1291).

4.9. *3-Acetyl-2-methyl-1,4,5-trihydroxy-2,3-epoxynaphthoquinol (**6**)*

White amorphous powder; $[\alpha]_D^{20}$ +44 (MeOH; c 0.18). UV$\lambda_{max}^{H_2O}$ nm (log ε): 276 (3.38). IR_{max}^{KBr} cm^{-1}: 3463, 3261, 1718, 1461, 1257, 993, 800, 578. For ^1H and ^{13}C NMR spectroscopic data, see Table 3. EIMS 70 eV, m/z (rel. int.): 250 (37), 232 (14), 203 (47), 161 (100). HREIMS m/z: 250.0841 $[M]^+$ (calc. for $C_{13}H_{14}O_5$, 250.0841).

Table 3
^1H and ^{13}C NMR spectroscopic data for compound **6** (400 MHz in CD_3OD)

	δ_H	δ_C
1	4.67 (1H, *s*)	70.7
2		66.1
3		73.1
4	5.62 (1H, *s*)	68.6
5		157.9
6	6.76 (1H, *d*, 7.5)	116.4
7	7.23 (1H, *dd*, 8.2, 7.4)	130.4
8	7.14(1H, *d*, 7.6)	119.6
9		138.3
10		120.7
2-CH_3	1.52 (3H, *s*)	16.4
AcO		209.0
Me-Ac	2.41 (3H, *s*)	29.6

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References

Adam, K.P., 1999. Phenolic constituents of the fern *Phegopteris connectilis*. Phytochemistry 52, 929–934.

Demirezer, L.O., 1994. Quantitative determination of some Rumex species with regards of anthraquinone derivatives. Pharmazie 49, 936–937.

Erturk, S., Ozbas, M., Imre, S., 2001. Anthraquinone pigments from *Rumex cristatus*. Acta Pharmaceutica Turcica 43, 21–22.

Foo, L.Y., McNabb, W.C., Waghorn, G., Ulyatt, M.J., 1997. Proanthocyanidins from *Lotus pedunculatus*. Phytochemistry 45, 1689–1696.

Gill, M., Gimenez, A., McKenve, R.W., 1988. Pigments of fungi, Part 8. Bianthraquinones from *Dermocybe austroveneta*. J. Nat. Prod. 51, 1251–1256.

Harding, W.W., Henry, G.E., Lewis, P.A., Jacobs, H., McLean, Reynolds, W.F., 1999. Alvaradoins A–D. Anthracenone *C*-arabinosides from *Alvaradoa jamaicensis*. J. Nat. Prod. 62, 98–101.

Hernandez-Medel, M.D.R., Ramirez-Corzas, C.O., Rivera-Dominguez, M.N., Ramirez-Mendez, J., Santillan, R., Rojas-Lima, S., 1999. Diastereomeric *C*-glycosyloxanthrones from *Picramnia antidesma*. Phytochemistry 50, 1379–1383.

Manitto, P., Monti, D., Speranza, G., 1990. Studies on Aloe. Part 6. Conformation and absolute configuration of aloins A and B and related 10-*C*-glucosyl-9-anthrones. J. Chem. Soc., Perkin Trans. I, 1297–1299.

Masood, M., Minocha, P.K., Rathore, Y.K.S., Tiwari, K.P., 1982. 10-*C*-glucopyranosyl-1,8- dihydroxy-3-methylanthraquinone from *Rumex vesicarius* Linn. Proc. Natl. Acad. Sci., India, Sect. A 52, 123–125.

Midiwo, J.O., Rukunga, G.M., 1985. Distribution of anthraquinone pigments in Rumex species of Kenya. Phytochemistry 24, 1390–1391.

Muller, B.M., Kraus, J., Fraz, G., 1989. Chemical structure and biological activity of water-soluble polysaccharides from *Cassia angustifolia* leaves. Planta Med. 55, 536.

Nawwar, M.A.M., Ishak, M.S., Michael, H.N., Buddrust, J., 1984. Leaf flavonoids of *Ziziphus spina-christi*. Phytochemistry 23, 2110–2111.

Nishina, A., Kubota, K., Osawa, T., 1993. Antimicrobial components, trachrysone and 2-methoxystypandrone, in *Rumex japonicus* Houtt. J. Agric. Food Chem. 41, 1772–1775.

Rauwald, H.W., Lohse, K., 1992. Structure revision of 4-Hydroxyaloin: 10-Hydroxyaloins A and B as main in vitro-oxidation products of the diastereomeric aloins. Planta Med. 58, 259–262.

Scott, K.N., 1972. Carbon-13 nuclear magnetic resonance of biologically important aromatic acids. I. Chemical shifts of benzoic acid and derivatives. J. Am. Chem. Soc. 94, 8564–8568.

Wang, M.F., Shao, Y., Li, J.G., Zhu, N.Q., Rangarajan, M., LaVoie, E.J., Ho, C.T., 1999. Antioxidative phenolic glycosides from sage (*Salvia officinalis*). J. Nat. Prod. 62, 454–456.

Xiao, K., Xuan, L.J., Xu, Y.M., Bai, D.L., 2000. Stilbene glycoside sulfates from *Polygonum cuspidatum*. J. Nat. Prod. 63, 1373–1376.

Xiao, K., Xuan, L.J., Xu, Y.M., Bai, D.L., Zhong, D.X., Wu, H.M., Wang, Z.H., Zhang, N.X., 2002. Dimeric stilbene glycosides from *Polygonum cuspidatum*. Eur. J. Org. Chem. 2002, 564–568.

Xiao, K., Xuan, L.J., Xu, Y.M., Bai, D.L., 2003a. Studies on chemical constituents possessing DNA cleavage activity. Chin. Traditional Herbal Drugs 34, 203–206.

Xiao, K., Xuan, L.J., Xu, Y.M., Bai, D.L., 2003b. Studies on water-soluble constituents in rhizome of *Polygonum cuspidatum*. Chin. Traditional Herbal Drugs 34, 496–498.

Xu, M.S., Wang, Z.Y., Kang, Y.H., 2004. Recent advance on the chemistry and bioactivity of genus Rumex. Chin. Arch. Traditional Chin. Med. 22, 417–420.

Yamanak, M., Shimomura, K., Sasaki, K., Yoshihira, K., Ishimaru, K., 1995. Glucosylation of phenolics by hairy root cultures of *Lobelia sessilifolia*. Phytochemistry 40, 1149–1150.

Yuan, Y., Chen, W.S., Yang, G.J., Li, L., Zhang, H.M., 2000. Anthraquinones of patience dock (*Rumex patientia*). Chin. Traditional Herbal Drugs 31, 330–332.

Zaghloul, M.G., El-Fattah, H.A., 1999. Anthraquinones and flavonoids from *Rumex tingitanus* growing in Libya. Zagazig J. Pharmaceut. Sci. 8, 54–58.