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Two new C-glucoside oxanthrones from *Rumex gmelini*

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Abstract

Two new C-glucoside oxanthrones, 6-methoxyl-10-hydroxyaloin A (**1**) and 6-methoxyl-10-hydroxyaloin B (**2**), were isolated from the roots of *Rumex gmelini* Turcz. Their structures were elucidated on the basis of spectroscopic techniques and chemical means.

Keywords: *Rumex gmelini* Turcz.; C-glucoside oxanthrones; 6-Methoxyl-10-hydroxyaloin A; 6-Methoxyl-10-hydroxyaloin B

Rumex gmelini Turcz. (Family Polygonaceae) has been widely used as a folk medicine for centuries in china. Previously, we reported the isolation and identification of anthraquinones [1–3] and stilbenoids [4], which show interesting biological activities such as antifungal, antitumor, antivirus and antioxidation. During our search for biological active substances from *R. gmelini* Turcz., two new C-glucoside oxanthrones, named 6-methoxyl-10-hydroxyaloin A (**1**) and 6-methoxyl-10-hydroxyaloin B (**2**) were isolated. Structures of the compounds were established through detailed analysis of their spectroscopic data and chemical evidence. Here, we report the isolation and structure elucidation of two new C-glucoside oxanthrones, 6-methoxyl-10-hydroxyaloin A and 6-methoxyl-10-hydroxyaloin B [5].

The air-dried roots of *R. gmelini* Turcz. (5 kg) were extracted with 75% EtOH, and concentrated at 60 °C in a vacuum evaporator to afford residue (1 kg). The residue was subjected to AB-8 porous polymer resin and eluted with H_2O, 30%, 60% and 90% EtOH successively. The fraction eluted with 30% EtOH (300 g) was chromatographed on repeated silica gel column to afford a glucosyoxanthrone-riched portion, this portion was separated by preparative HPLC to afford compounds **1** and **2**.

Compound **1** was obtained as yellowish crystals, mp 138–140 °C and gave positive result to Molish test. Its molecular formula was determined as $C_{22}H_{24}O_{11}$ by HR-FAB-MS ($[M+H]^+$ *m/z* 465.1398, calcd. 465.1397), ^{13}C NMR and MS data. UV (CH_3OH) λ_{max} (nm) (log ε): 211(3.87), 256(0.83), 275(0.88) and 368(1.55). CD (CH_3OH,

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Table 1
NMR spectral data of **1** (^{1}H, 500 MHz; ^{13}C, 125 MHz; in CD_3OD, δ ppm).

No.	δ_H (J, Hz)	δ_C (J, Hz)	No.	δ_H (J, Hz)	δ_C (J, Hz)
1		162.7	12	3.91 (s, 3H)	56.3
2	6.92 (br. s, 1H)	115.2	1a		116.1
3		151.8	4a		148.7
4	7.46 (br. s, 1H)	116.1	5a		148.7
5	6.98 (d, 1H, 1.0 Hz)	107.8	8a		111.7
6		167.1	1′	3.26(d, 1H, 8.5 Hz)	85.5
7	6.47 (d, 1H, 1.0 Hz)	101.3	2′	3.06 (t, 1H, 8.5 Hz, 8.5 Hz, 5.5 Hz)	72.8
8		165.9	3′	3.26 (t, 1H, 8.5 Hz, 8.5 Hz, 5.0 Hz)	79.6
9		192.9	4′	2.86(t, 1H, 8.5 Hz, 8.5 Hz, 5.0 Hz)	71.7
10		76.9	5′	2.93 (m, 1H)	81.6
11	4.66 (dd, 2H, 15.0 Hz, 14.5 Hz)	64.7	6′	3.38(dd, 1H, 6.0 Hz, 5.5 Hz), 3.57(d, 1H, 5.5 Hz)	63.3

c = 0.652 mg/mL): 260(+2.790), 297(+1.601) and 328(−4.450). Glucose was detected after the acid hydrolysis and compared with standard sugar on TLC. Extensive analysis of the ^{1}H NMR data of **1** (7.46, br. s, 1H; 6.98, d, 1H, J = 1.0 Hz; 6.92, br. s, 1H; 6.47, d, 1H, J = 1.0 Hz; 4.66, dd, 2H, J = 15.0 Hz, 14.5 Hz; 3.91, s, 3H) indicated that **1** possessed 1,3-disubstituted A-ring, 6,8-disubstituted B-ring, a hydroxymethyl group and a methoxy group (Table 1). This assumption was subsequently confirmed by its ^{13}C NMR spectral data. Analysis of HMBC spectra enabled deducting the structure. In HMBC spectrum of **1**, ^{1}H–^{13}C long range correlation signals were found between H-2, H-4 and C-11; H-12 and C-6; H-1′ and C-4a, C-5a, C-10. Comparison of ^{13}C NMR data of **1** with that of the known 10-hydroxyaloin A [5], both compounds showed very similar ^{13}C NMR data, but **1** has a group of methoxyl signal. C-6 of **1** is down-shifted for 30.7 ppm and C-5, C-7 of **1** is up-shifted for 11.1 ppm, 17.0 ppm respectively, indicating that the methoxyl group was connected to C-6. **1** showed a CD curve with a positive Cotton effect at $[\theta]_{297}$ and negative Cotton effect at $[\theta]_{328}$ indicated **1** was 10S type. Therefore, compound **1** was identified as (10S) 6-methoxyl-10-hydroxylaloeemodin-9-anthrone-10-C-β-D-glucopyranoside. It is a new compound, named as 6-methoxyl-10-hydroxyaloin A (Table 1, Fig. 1).

Compound **2** was obtained as yellowish needles, mp 138–140 °C and gave positive result to Molish test. Its molecular formula $C_{22}H_{24}O_{11}$ was deduced from HR-FAB-MS ($[M+H]^+$ m/z 465.1396, calcd. 465.1397). UV (CH_3OH) λ_{max} (nm) (log ε): 211(3.87), 256(0.83), 275(0.88) and 368(1.55). CD (CH_3OH, c = 0.484 mg/mL): 260(−7.312), 297(−6.090) and 328(+8.598). Glucose was detected after the acid hydrolysis and compared with standard sugar on TLC. **1** and **2** had the similar NMR and MS data, but they showed a different CD curve. **2** showed a CD curve with a negative Cotton effect at $[\theta]_{297}$ and positive Cotton effect at $[\theta]_{328}$. Comparison of ^{13}C NMR data of **2** with that of the known 10-hydroxyaloin B [5], both compounds showed very similar ^{13}C NMR data, but **2** has a group of methoxyl signal. C-6 of **2** is down-shifted for 30.5 ppm and C-5, C-7 of **2** is up-shifted for 11.4 ppm, 16.7 ppm respectively, indicating that the methoxyl group was connected to C-6. The orientation of the glucose group at C-10 in

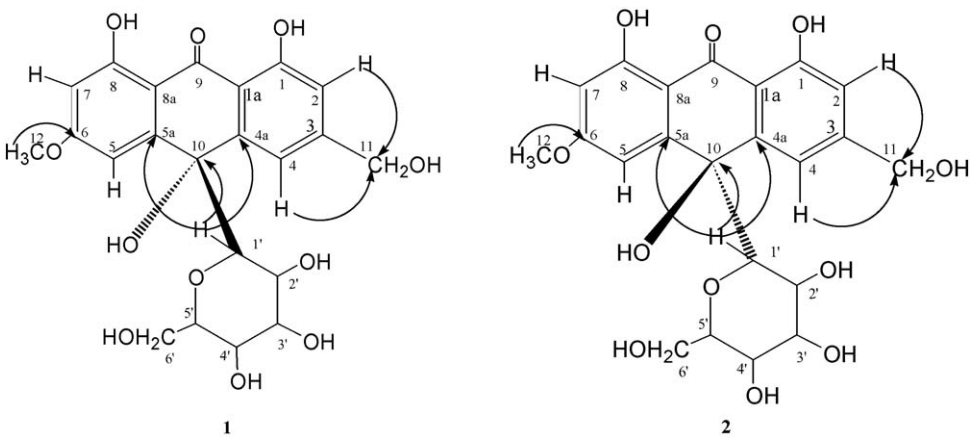

Fig. 1. Structures and key HMBC correlations of compounds **1** and **2**.

Table 2
NMR spectral data of **2** (^{1}H, 500 MHz; ^{13}C, 125 MHz; in CD_3OD, δ ppm).

No.	δ_H (J, Hz)	δ_C (J, Hz)	No.	δ_H (J, Hz)	δ_C (J, Hz)
1		163.1	12	3.90 (3H, s)	56.2
2	6.93 (br. s, 1H)	115.4	1a		116.4
3		151.1	4a		146.6
4	7. 36 (br. s, 1H)	117.0	5a		150.8
5	7.07 (d, 1H, 1.0 Hz)	106.7	8a		111.3
6		167.7	1′	3.30 (d, 1H, 8.5 Hz)	85.8
7	6.45 (d, 1H, 7.5 Hz)	101.3	2′	2.95 (t, 1H, 8.5 Hz, 8.5 Hz, 5.5 Hz)	72.9
8		165.5	3′	3.24 (t, 1H, 8.5 Hz, 8.5 Hz, 5.0 Hz)	79.6
9		192.9	4′	2.83 (t, 1H, 8.5 Hz, 8.5 Hz, 5.0 Hz)	71.7
10		76. 7	5′	3.00 (m, 1H)	81.8
11	4.69(dd, 2H, 5.0 Hz, 14.5 Hz)	64.7	6′	3.39 (dd, 1H, 6.0 Hz, 5.5 Hz) 3.61 (m, 1H)	63.4

2 was confirmed by the identity of the CD spectrum with that reported for the same compound 10-hydroxyaloin B [6]. Therefore, compound **2** was identified as (10R) 6-methoxyl-10-hydroxyl-aloe-emodin-9-anthrone-10-C-β-D-glucoside. It is a new compound, named as 6-methoxyl-10-hydroxyaloin B (Table 2, Fig. 1).

Acknowledgment

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