

A New Bianthraquinone Glycoside from *Eremurus chinensis*

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Abstract: A new bianthraquinone glycoside, 8-O- β -D-glucopyranosyl-2,7'-bi(1,8-dihydroxy-3-methyl-9,10-anthraquinonyl) **1** was isolated from *Eremurus chinensis* Fedtch. Its structure was established by spectroscopic techniques including 2D-NMR and chemical methods.

Keywords: *Eremurus chinensis*, Liliaceae, bianthraquinone glycoside.

Eremurus chinensis Fedtch has a wide distribution in the western part of China; it has been used in Chinese folk medicine for the treatment of rheumatism and physical weakness¹. Only few reports describe polysaccharides²⁻⁵ rather than other chemical constituents from the genus *Eremurus*. We report here the isolation and structural elucidation of a new bianthraquinone glycoside, 8-O- β -D-glucopyranosyl-2,7'-bi(1,8-dihydroxy-3-methyl-9,10-anthraquinon-yl) **1** from *E. chinensis*.

The EtOAc soluble fraction obtained from an ethanolic extract of the air-dried and ground whole plants of *E. chinensis* was repeatedly subjected to column chromatography over silica gel to afford compound **1**, yellow powder (MeOH), mp 190 °C (decomp.), $[\alpha]_D^{22}$ -33.0 (*c* 0.54, MeOH). The IR spectrum showed absorption bands for chelated hydroxyl groups (3475, 3424, and 3325 cm^{-1}) and bands for conjugated carbonyl groups (1712, 1663 and 1621 cm^{-1}). Its molecular formula $\text{C}_{36}\text{H}_{28}\text{O}_{13}$ was determined by the positive ion HRFABMS m/z 669.16105 (calcd for $\text{C}_{36}\text{H}_{29}\text{O}_{13}$ 669.1599) and NMR data. The ¹H, ¹³C NMR and DEPT data revealed a glycoside structure for **1**. The signals at δ 5.16 (1H, d, J=7.5Hz) and 100.6 (CH) were assignable to C-1" of the glycone moiety, and a β configuration at the anomeric carbon was suggested. Signals at δ_{H} 3.05-3.82 (6H, m) and δ_{C} 77.3, 76.5, 73.2, 69.5 and 60.6 were in good agreement with those of D-glucopyranosyl moiety. The presence of D-glucopyranosyl was further confirmed by acidic hydrolysis of **1** followed by comparison with an authentic sample on TLC.

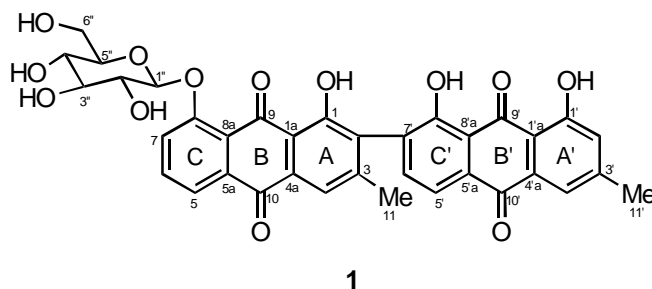


Table 1. ^{13}C NMR of compound **1** (100.62 MHz, DMSO-d_6 , δ , ppm, TMS).

C	δ	DEPT	C	δ	DEPT
1	159.4	C	1'	161.6	C
1a	114.7	C	1'a	113.8	C
2	131.0	C	2'	124.1	CH
3	146.1	C	3'	149.3	C
4	119.5	CH	4'	120.6	CH
4a	131.5	C	4'a	133.0	C
5	122.5	CH	5'	118.9	CH
5a	134.7	C	5'a	133.3	C
6	136.0	CH	6'	138.6	CH
7	120.6	CH	7'	131.2	C
8	158.3	C	8'	158.9	C
8a	120.7	C	8'a	116.0	C
9	187.7	C	9'	191.8	C
10	181.8	C	10'	181.2	C
11	20.4	CH ₃	11'	21.6	CH ₃
1''	100.6	CH	4''	69.5	CH
2''	73.2	CH	5''	76.5	CH
3''	77.3	CH	6''	60.6	CH ₂

^a Assignments were based on HMQC, HMBC.

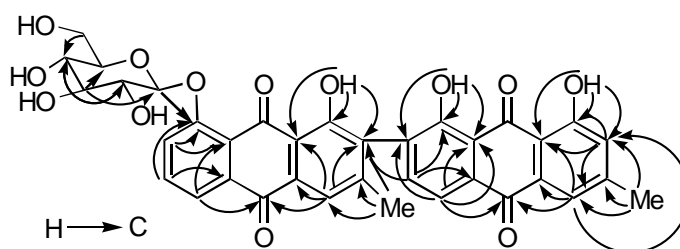
Beside the signals for the glycone moiety, the ^1H NMR spectral data revealed signals for two methyl groups at δ 2.45 and 2.23 (each 3H, s), three *peri* hydroxyl protons at δ 13.25, 12.33 and 11.77 (each 1H, s), as well as eight aromatic protons. The ^{13}C NMR spectrum (**Table 1**) showed 15 pairs of carbon signals and the DEPT spectrum demonstrated the presence of a pair of methyls, 4 pairs of sp^2 hybrid methines and 10 pairs of sp^2 hybrid quaternary carbons in which there were 2 pairs of carbonyl carbons. These spectral data suggested a bianthraquinone aglycone for **1** with one methyl

and two *peri* hydroxyl groups in each monomer.

In the aromatic region of the ^1H NMR spectrum signals for an isolated aromatic proton at δ 7.67 (1H, s, H-4) and two *meta* coupled protons at δ 7.56 (1H, brs, H-4') and 7.21 (1H, brs, H-2') indicated the *ortho* trisubstituted mode of ring A and the *meta* disubstituted mode for A' respectively, while signals for three adjacent aromatic protons with ABC pattern at δ 7.90 (1H, d, $J=7.4\text{Hz}$ H-7), 7.87 (1H, t, $J=7.4\text{ Hz}$, H-6), 7.71 (1H, d, $J=7.4\text{ Hz}$, H-5) and two isolated *ortho* coupled protons at δ 7.83, 7.75 (each 1H, d, $J=7.6\text{ Hz}$) ascribed to H-5', 6' respectively, revealed that ring C possesses a *peri* substituent at C-5 or C-8 and ring C' has two *ortho* substituents at C-5' and C-6' or C-7' and C-8'.

The structure **1** was finally established by detailed analysis of HMQC and HMBC spectra. The HMBC spectrum (**Figure 1**) revealed the key connectivity between the two monomers by C-2 and C-7' through three- and two-bond correlations with H-6'. The location of the D-glucopyranosyl was revealed by the correlation from the anomeric proton to C-8, and the positions for the two methyl groups were determined by the correlations from the methyl proton at δ 2.23 to C-2, C-3 and C-4 and from the other methyl proton at δ 2.45 to C-2', C-3' and C-4' in the HMBC spectrum. Therefore, the structure of **1** was assigned to be 8-O- β -D-glucopyranosyl-2,7'-bi(1,8-dihydroxy-3-methyl-9,10-anthraquinonyl).

Figure 1. HMBC correlations of **1**



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