Phytochemistry Letters 21 (2017) 256–259

Contents lists available at ScienceDirect

Phytochemistry Letters

journal homepage: www.elsevier.com/locate/phytol

A new semiterpenoid glycoside and a new benzofuran derivative glycoside from the roots of *Heracleum dissectum*☆

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ARTICLE INFO

Keywords:
Heracleum dissectum
Ethnic herb
Semiterpenoid glycosid
Benzofuran derivative glycoside
Anti-inflammation

ABSTRACT

A new semiterpenoid glycoside, 3-methylbutan-1, 3-diol-1-*O*-*β*-D-glucopyranoside (**1**) and a new benzofuran derivative glycoside, 6-carboxylethyl-benzofuran-5-*O*-*β*-D-xylopyranosyl-(1 → 2)-*β*-D-glucopyranoside (**2**), together with seven known compounds (**3-9**) were isolated from the roots of *Heracleum dissectum* Ledeb. Their structures were elucidated on the basis of physicochemical properties and the detailed interpretation of various spectroscopic data. All the isolated compounds were screened for anti-inflammatory activity *in vitro*. And the result showed that compound **2** exhibited significantly inhibitory activity on nitric oxide production in RAW264.7 cells, which IC_{50} value was equivalent to that of the positive control indomethacin.

1. Introduction

Heracleum dissectum Ledeb. is a perennial herb of Apiaceae family, mainly distributed in the northeastern region of China and Far East areas of Russia. The aerial parts of the plant are used as the delicious vegetable and folk remedy for treatment of hypertension and diabetes by local Oroqen people. Meanwhile, the roots are used as Chinese folk medicine for dispelling wind and eliminating dampness, curing rheumatoid diseases, waist or knee pain, headache, etc. However, up to now, the reports on the chemical constituents of this plant are few, mainly focused on the essential oil components from the aerial parts (Montanarella et al., 1986; Papageorgiou et al., 1985) and several simple coumarins from the roots of this plant (Belenovskaya et al., 1977). In addition, the pharmacological activities of this plant *in vitro* or *in vivo* have not been conducted so far.

In our previous study, we isolated and characterized two new compounds from the roots (Gao et al., 2014) and proved the antidiabetic effects of the aerial parts of *H. dissectum* in animals (Zhang et al., 2017). As a part of our continuous program towards the complete elucidation of chemical constituents of this ethnic herb, a new semiterpenoid glycoside, 3-methylbutan-1,3-diol-1-*O*-*β*-D-glucopyranoside (**1**) and a new benzofuran derivative glycoside, 6-carboxylethyl-benzofuran-5-*O*-*β*-D-xylopyranosyl-(1 → 2)-*β*-D-glucopyranoside (**2**) (Fig. 1), together with seven known compounds were isolated from the roots of *H. dissectum* in this present study. Herein, we report the isolation and structural characterization of two new compounds. Furthermore, the inhibitory activity of all isolates on nitric oxide (NO) production in RAW264.7 cells were also described in this paper.

2. Results and discussion

Compound **1** was obtained as yellow oil. The molecular formula of $C_{11}H_{22}O_7$, was indicated by HR-ESI MS at *m/z* [289.1257 $[M+Na]^+$ (calcd. for 289.1258 $[M+Na]^+$) combined with the NMR data. In the ^1H NMR spectrum, protons at δ_H 1.26 (6H, s) indicated that two methyl groups attached to a quaternary carbon. The protons of a methylene at δ_H 1.86 (2H, t, J = 6.8 Hz) should link to another methylene, which was consolidated in ^1H–^1H COSY of compound **1**. In the ^{13}C NMR and DEPT spectra, eleven carbons including two methyl carbons, one methylene carbon, two oxymethylene carbons, one oxygenated quaternary carbon, and five oxymethine carbons were observed. There was an anomeric proton observed at δ_H 4.31 (1H, d, J = 7.6 Hz) in the ^1H NMR spectrum of **1** suggesting the occurrence of a sugar unit in the molecule. Acid hydrolysis of compound **1** followed by GC analysis showed the sugar was D-glucose. And the coupling constant of the anomeric protons of the glucose (J = 7.6 Hz) indicated the configuration of glucose was *β*-orientation. Apart from six carbons of glucose unit, another five

☆ This work was supported by Natural Science Foundation of China under Grant 81673564; Natural Science Foundation of Shaanxi Province under Grant 2015JM8413; and the start scientific research fund for returned overseas students of Ministry of Education of China under Grant [2012] No. 940.

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http://dx.doi.org/10.1016/j.phytol.2017.06.009
Received 30 March 2017; Received in revised form 31 May 2017; Accepted 16 June 2017

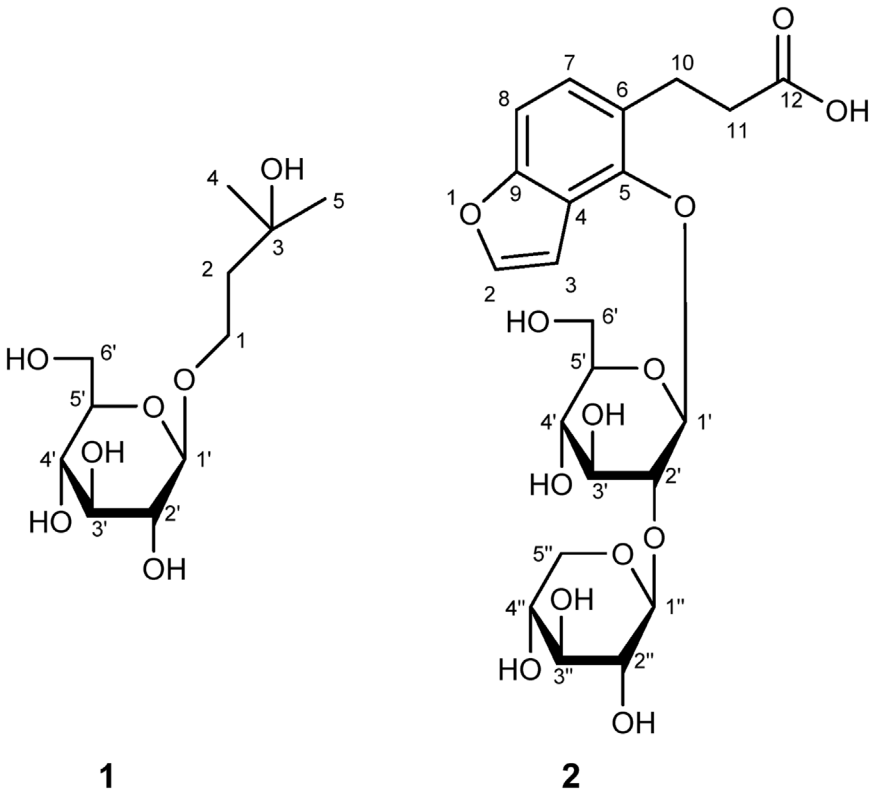

Fig. 1. The chemical structures of compounds **1** and **2** from the roots of *H. dissectum*.

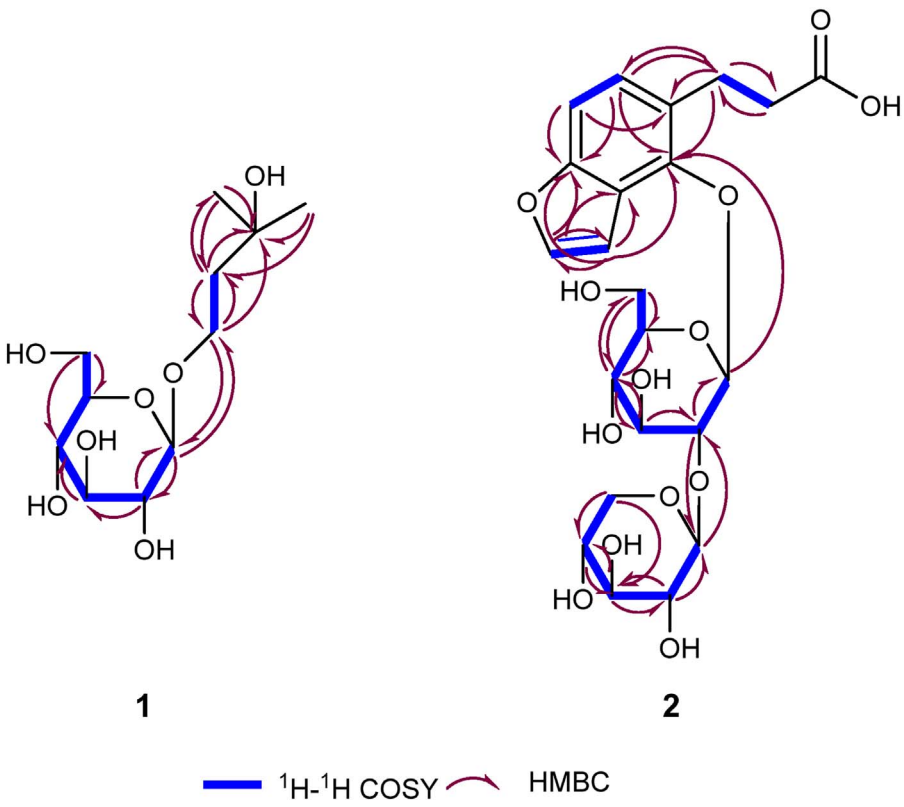

Fig. 2. Main ^{1}H-^{1}H COSY (blue thick lines) and HMBC (arrows) correlations in the spectra of compounds **1** and **2**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

carbons were assigned to two methylenes linked each other and a moiety of two methyl carbons attached to an oxygenated quaternary carbon. In HMBC spectrum, two methylene protons at δ_H 1.86 (2H, t, J = 6.8 Hz), 3.73 (1H, m) and 4.10 (1H, m) correlated with the quaternary carbon at δ_C 70.9 revealed that the aglycone of compound **1** was 3-methylbutane-1, 3-diol. The linkage position of glucose unit was determined by HMBC spectrum of **1**, in which protons at δ_H 3.73 (1H, m, H-1) and 4.10 (1H, m, H-1) correlated with the anomeric carbon at δ_C 104.0 (C-1′) and the anomeric proton of glucose at δ_H 4.31 (1H, d, J = 7.6 Hz, H-1′) correlated with the methylene carbon at δ_C 67.7(C-1) (Fig. 2). Therefore, compound **1** was identified as 3-methylbutan-1, 3-diol-1-*O*-*β*-D-glucopyranoside. Although the structure was simple, it was