SHORT REPORT

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Rec. Nat. Prod. 11:1 (2017) 74-76

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A New Sugar Ester from the Roots of *Acanthus ilicifolius*

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(Received April 09, 2016; Revised June 05, 2016; Accepted June 11, 2016)

Abstract: A new compound, 1,2-di-(syringoyl)-*β*-D-glucopyranose, together with erigeside C, were isolated from the roots of *Acanthus ilicifolius*. The structure of the new compound was elucidated by extensive spectroscopic methods, including 1D, 2D NMR and HRESIMS spectroscopic data. The cytotoxic activities of these compounds were evaluated against HepG2, A-549, and HeLa cells *in vitro*. However, none of them showed cytotoxic activities.

Keywords: *Acanthus ilicifolius*; 1,2-di-(syringoyl)-*β*-D-glucopyranose; cytotoxic activities.

1. Plant Source

In the ongoing search of phytochemical studies of mangrove plants distributed in Hainan Island, China, the chemical constituents of the roots of *Acanthus ilicifolius* were investigated. Herein, we report on the structural elucidation of a new syringate glucoside of 1,2-di-(syringoyl)-*β*-*D*-glucopyranose (**1**) (Figure 1).

The roots of *A. ilicifolius* were collected from Wenchang County, Hainan Province of People's Republic of China in July 2014. The sample was identified by Prof. Niankai Zeng and a voucher specimen (No. A1201407) has been deposited in the Herbarium of School of Pharmaceutical Science, Hainan Medical University.

2. Previous Studies

A. ilicifolius is a spiny herb distributed in the coastal line of subtropical and tropical region in the world. This plant has been used as folk medicine to cure tumor and hepatitis [1]. Alkaloids, lignans and flavonoids with various effects, cytotoxic, anti-inflammatory, have been isolated from *A. ilicifolius* [2]. Previously, we reported four new 2-benzoxazolinone-type alkaloids with cytotoxic activities from this plant [3]. As a continuous work, a new sugar ester is obtained and structurally characterized in present study.

3. Present Study

The dried roots of *A. ilicifolius* (2.0 kg) were cut into pieces and extracted with 95% EtOH (3 × 8.0 L) at 70°C for 2 h x 2 times. The ethanol extract was concentrated under reduced pressure at room temperature. After evaporation of the solvent, the residue was suspended in water and extracted with

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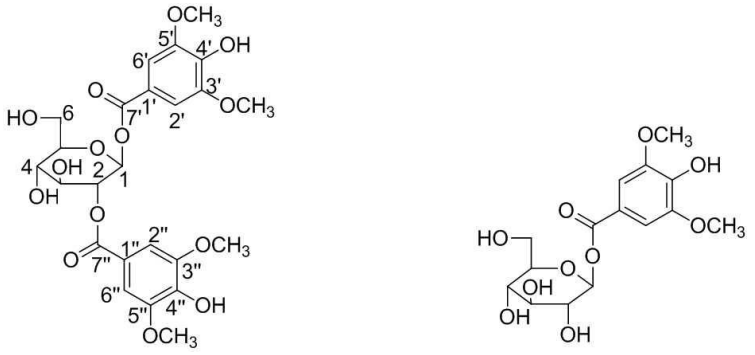
The article was published by Academy of Chemistry of Globe Publications
www.acgpubs.org/RNP © Published 09/21/2016 EISSN: 1307-6167

petroleum ether, and n-BuOH, successively. The *n*-BuOH part (20 g) was subject to silica gel column chromatography (200-300 mesh), using chloroform-acetone gradient elution (9:1, 4:1, 2:1) to afford six fractions (Fr. A-F). Fr. C (2.1 g) was fractioned by Sephadex LH-20 using MeOH as eluent, to give six fractions (subfracs.1-6). Subfracs. 2 was further purified by semi-preparative HPLC (45% MeOH in H_2O, 2.0 mL/min) to afford **1** (tR 17.6 min, 4.5 mg). Subfracs. 4 was further purified by semi-preparative HPLC (40% MeOH in H_2O, 2.0 mL/min) to afford **2** (tR 20.6 min, 6.5 mg).

1,2-di-(syringoyl)-β-D-glucopyranose (1): White amorphous powder, $[\alpha]_D^{25}$ = -22.6 (*c* = 0.1, MeOH); UV ($CHCl_3$): λ_{max} (log ε): 336 (1.22), 287 (1.52), 250 (1.36); IR ν_{max} ($CHCl_3$): = 3450, 1742, 1640, 1608, 1516, 1071 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ (ppm)= 7.24 (2H, s, H-2', 6'), 7.22 (2H, s, H-2", H-6"), 5.89 (1H, d, *J* = 8.4 Hz, H-1), 5.20 (1H, dd, *J* = 10.8, 8.4 Hz, H-2), 3.89 (1H, dd, *J* = 12.0, 1.2 Hz, H-6a), 3.84 (1H, t, *J* = 8.4 Hz, H-3), 3.75 (1H, dd, *J* = 12.0, 4.8 Hz, H-6b), 3.56 (2H, m, H-4, 5), 3.82 (6H, s, 3', 5'-OMe), 3.80 (6H, s, 3", 5"-OMe); ^{13}C NMR (150 MHz, CD_3OD): δ (ppm) = 57.0 ($-OCH_3$, 3', 5', 3", 5"-OMe), 94.8 (CH, C-1), 75.1 (CH, C-2), 79.4 (CH, C-5), 71.6 (CH, C-4), 75.8 (CH, C-3), 62.4 (CH_2, C-6), 121.2 (C, C-1'), 108.6 (CH, C-2'), 149.1 (C, C-3'), 142.7 (C, C-4'), 149.1 (C, C-5'), 108.6 (CH, C-6'), 120.2 (C, C-1"), 108.5 (CH, C-2"), 149.1 (C, C-3"'), 142.4 (C, C-4"), 149.1 (CH, C-5"), 108.5 (CH, C-6"), 166.7 (C-7'), 166.5 (C-7"). HRESIMS: *m/z* 563.1368 ($[M+Na]^+$, calcd. $C_{24}H_{28}NaO_{14}$ for 563.1377).

Cytotoxicity bioassays: The following human cancer cell lines were used: HepG2, A-549, and HeLa. The cytotoxicity assay was performed using the MTT method in 96-well microplates. Half maximal inhibitory (IC_{50}) values were calculated by the previous method [6].

The air-dried and powdered roots of *A. ilicifolius* were extracted with 95% ethanol under reflux. Following, the ethanol extract was filtered and concentrated under reduced pressure to yield a crude extract, which was suspended in distilled water and then successively partitioned with petroleum ether, and n-BuOH. Phytochemical investigation on *n*-BuOH fraction has resulted in the isolation of 1,2-di-(syringoyl)-*β*-D-glucopyranose as shown in Figure 1.



1 **2**

Figure 1. Structures of **1** and **2** isolated from *A. ilicifolius.*

Compound **1** was isolated as white amorphous powder, for which the UV spectrum showed absorption peaks at 336, 287, and 250 nm. Its molecular formula was determined as $C_{24}H_{28}O_{14}$ by HRESIMS analysis at *m/z* 563.1368. The IR spectrum of **1** showed absorption bands for hydroxyl (3450 cm^{-1}), carbonyl (1742 cm^{-1}), and aromatic (1608, 1516 cm^{-1}) moieties . The ^1H NMR spectrum of **1** showed four aromatic protons [δ = 7.24 (2H, s, H-2', 6'), 7.22 (2H, s, H-2", H-6")]. The ^1H NMR data also showed the existence of four methoxy groups at δ_H 3.82 (6H, s), 3.80 (6H, s). These NMR signals suggested the presence of two syringoyl groups in **1** [4]. This was confirmed by its ^{13}C NMR spectra data at δ_C 57.0 (3', 5', 3", 5"-OMe), 121.2 (C-1'), 108.6 (C-2'), 149.1 (C-3'), 142.7 (C-4'), 149.1 (C-5'), 108.6 (C-6'), 120.2 (C-1"), 108.5 (C-2"), 149.1 (C-3"'), 142.4 (C-4"), 149.1 (C-5"), 108.5 (C-6"). The remaining resonances were attributable to a glucosyl moiety [δ = 5.89 (d, *J* = 8.4 Hz, H-1), 5.20 (dd, *J* = 10.8, 8.4 Hz, H-2), 3.89 (dd, *J* = 12.0, 1.2 Hz, H-6a), 3.84 (t, *J* = 8.4 Hz, H-3), 3.75 (dd, *J*

= 12.0, 4.8 Hz, H-6b), 3.56 (m, H-4, 5), 94.8 (C-1), 75.1 (C-2), 79.4 (C-5), 71.6 (C-4), 75.8 (C-3), 62.4 (C-6)]. These data summarized above suggested that **1** was a syringate-glucoside derivative [5]. HMBC correlation between H-1 (δ_H 5.89) and C-7' (δ_C 166.7) and correlation between H-2 (δ_H 5.20) and C-7″ (δ_C166.5) established the connections between the two syringoyl groups and the glucosyl moiety. From a biosynthetic point of view, the configuration of the glucose was tentatively determined to be D since many compounds containing D-glucose have been isolated from this plant previously. Therefore, the structure of **1** was established as shown in Figure 1.

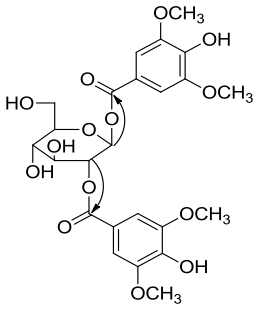


Figure 2. Key HMBC ( ) correlations of **1**.

The known compound was identified as erigeside C [7]. The two isolated compounds were tested for the cytotoxic activities against HepG2, A-549, and HeLa cancer cell lines. The IC_{50} values of all compounds were greater than than 100 μM. These results showed that the two compounds displayed no cytotoxic activities.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of Hainan Province (No.20158362).

Supporting Information

Supporting Information accompanies this paper on http://www.acgpubs.org/RNP

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