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A New Acylated Benzyl Alcohol Glucoside from *Syzygium austroyunnanense*

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Abstract: A new acylated benzyl alcohol glucoside, benzyl alcohol 3',6'-di-*O*-galloyl-β-glucopyranoside (**1**), together with a known analogue, 6'-*O*-galloyl-β-glucopyranoside (**2**) and a cyanogenic glucoside, 6'-*O*-galloylprunasin (**3**) were isolated from the leaves of *Syzygium austroyunnanense*. Their structures were characterized based on the spectroscopic methods and comparison with literature. This is the first phytochemical study on *Syzygium austroyunnanense*.

Keywords: *Syzygium austroyunnanense;* Myrtaceae; acylated glycoside.

1. Introduction

The genus *Syzygium* (Myrtaceae) comprises about 500 species, mostly grown in the tropic regions of the world [1]. Many of them have been used as edible and medicinal plants in Southeast Asian [2]. Previous research has demonstrated that hydrolysable tannins, flavonoids, chromone derivatives, phenylpropanoids, triterpenes, and phloroglucinols derivatives are the main bioactive constituents in this genus [3−9]. *Syzygium austroyunnanense* Chang et Miau, called as "Bajiamiao" in the Dai nationality, is a fruit tree which is native to Xishuang Banna Prefecture Yunnan province and Guangxi province in China [10]. To the best of our knowledge, no phytochemical research of this species have been reported so far. In our efforts to search for bioactive constituents, the leaves of *S. austroyunnanense* were investigated and one new acylated glycoside, benzyl 3',6'-di-*O*-galloyl-*β*-glucopyranoside (**1**), together with two known analogues, benzyl 6'-*O*-galloyl-*β*-glucopyranoside (**2**) and 6'-*O*-galloylprunasin (**3**) were obtained. Here, we present the isolation and characterization of the new compound.

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2. Materials and Methods

UV spectra were acquired in MeOH with a Shimadzu UV-2401PC UV-vis spectrophotometer. IR spectra were measured on a Bruker Tensor 27 FTIR Spectrometer with KBr disks. NMR spectra were recorded on a Bruker Avance III-600 and a Bruker AM-400 instruments with TMS as internal standard. ESI-MS spectra were recorded on a Waters Xevo TQ-S UPLC Triple Quadrupole Mass Spectrometer. Column chromatography was performed using silica gel (Qingdao Marine Chemical Factory, China, 200–300 mesh), Sephadex LH-20 (Pharmacia Biotech Ltd., Sweden). Thin-layer chromatography (TLC) was performed using precoated silica gel GF_{254} plates (Qingdao Marine Chemical Factory). Semipreparative HPLC was performed on a Hitachi Chromaster system (Hitachi, Ltd., Japan) equipped with an YMC-Triart C_{18} column (250 mm × 10 mm i.d., 5 μm, YMC Corporation, Japan), using a flow rate of 3.0 mL/min at a column temperature of 25 °C, and detection was performed with a DAD detector.

2.2. Plant Material

The leaves of *Syzygium austroyunnanense* Chang et Miau were collected in October 2014 from Xishuang Banna Tropical Botanical Garden, Yunnan Province, People's Republic of China, and were authenticated by Mr. Yu Chen at the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Science. Voucher specimens (KIB 20141009) were deposited at Kunming Institute of Botany, Chinese Academy of Science.

2.3. Extraction and Isolation

The air-dried and powdered leaves of *S. austroyunnanense* (2.5 kg) were extracted with CH_3OH (6 L × 3) at room temperature. The extracts were concentrated by rotary evaporator under reduced pressure to remove organic solvent. The extract (530 g) was suspended in H_2O (0.5 L) and then successively partitioned with petroleum ether (4 × 1 L), EtOAc (4 × 1 L), and n-BuOH (4 × 1 L), sequentially. The EtOAc extract (42.0 g) was subjected to silica gel column chromatography (CC) using a gradient system of petroleum ether (PE)-Me_2CO (1:0−0:1) to afford eight fractions (Fr A−H).

Fraction F (3.5 g) was decolorized on a MCI gel (CHP 20P) CC eluted by 92%MeOH-H_2O, and then divided into three subfractions (Fr. F-1−3) by silica gel (200−300 mesh) CC eluting with $CHCl_3$-MeOH (8:1). Subfraction Fr. F-1 was further divided into three subfractions (Fr. F-1-1−3) by silica gel CC eluting with $CHCl_3$-MeOH (14:1). Fr. F-1-1 was separated by Sephadex LH-20 column (MeOH-$CHCl_3$, 1:1), followed by semipreparative HPLC (HITACHI HPLC system; YMC-Triart C_{18} column, 250 × 10 mm; DAD detector, MeOH-H_2O 35:65, 210 nm, 3.0 mL/min) to give compounds **2** (3.5 mg, t_R = 17.5 min) and **3** (21.0 mg, t_R = 12.5 min). Fr. F-2 was further divided into four subfractions (Fr. F-2-1−4) by silica gel CC eluting with $CHCl_3$-MeOH (10:1). Compound **1** (5.0 mg, t_R = 21.0 min) was purified from Fr. F-2-4 by Sephadex LH-20 column (MeOH-$CHCl_3$, 1:1), and semipreparative HPLC (HITACHI HPLC system; YMC-Triart C_{18} column, 250 × 10 mm; DAD detector, MeOH-H_2O 35:65, 210 nm, 3.0 mL/min), sequently.

*Benzyl 3',6'-di-O-galloyl-β-glucopyranoside (**1**)*: Amorphous powder; ^{1}H-NMR (600 MHz, CD_3OD) and ^{13}C-NMR (150 MHz, CD_3OD) spectral data see Table 1; HR-ESI-MS at *m/z* 597.1216 $[M + Na]^+$ (calcd for $C_{27}H_{26}O_{14}$, 597.1215).

Benzyl 6'-*O*-galloyl-*β*-glucopyranoside *(**2**)*: Amorphous powder; ^{1}H-NMR (600 MHz, CD_3OD) and ^{13}C-NMR (150 MHz, CD_3OD) spectral data see Table 1.

6'-*O*-galloylprunasin *(**3**)*: Amorphous powder; ^{1}H-NMR (500 MHz, CD_3OD) δH: 6.70 (1H, s, H-2), 6.87 (1H, d, *J* = 8.5 Hz, H-5), 6.71 (1H, d, *J* = 8.5 Hz, H-6), 3.35 (2H, d, *J* = 8.5 Hz, H-7), 5.97 (1H, m, H-8), 5.10 (1H, m, Ha-9), 5.08 (1H, m, Hb-9), 3.90 (3H, s); ^{13}C-NMR (125MHz, CD3OD) δC: 131.9 (C-

1), 111.1 (C-2), 146.4 (C-3), 144.2 (C-4), 114.2 (C-5), 121.2 (C-6), 39.9 (C-7), 137.8 (C-8), 115.5 (C-9), -OCH_3 (55.9).; ESI-MS at *m/z* 421 $[M - H]^-$.

Table 1. ^{1}H NMR and ^{13}C NMR Data for **1**−**2** in MeOD at 600 MHz and 150 MHz, respectively

NO.	**1** δ_H	**1** δ_C	NO.	**1** δ_H	**1** δ_C	NO.	**2** δ_H	**2** δ_C	NO.	**2** δ_H	**2** δ_C
1		140.1	1''		121.6	1		140.1	1''		121.6
2	7.35 br d (7.3)	129.5	2''	7.12 s	110.4	2	7.26 br d (7.2)	129.5	2''	7.02 s	110.3
3	7.29 t (7.3)	129.5	3''		146.6	3	7.18 t (7.2)	129.6	3''		146.7
4	7.24 t (7.3)	129.0	4''		138.8	4	7.14 t (7.2)	128.9	4''		138.9
5	7.29 t (7.3)	129.5	5''		146.6	5	7.18 t (7.2)	129.6	5''		146.7
6	7.35 br d (7.3)	129.5	6''	7.12 s	110.4	6	7.26 br d (7.2)	129.5	6''	7.02 s	110.3
7a	4.86 d (11.8)	72.1	7''		168. 3	7a	4.74 d (11.8)	71.8	7''		168.5
7b	4.66 d (11.8)		1'''		121.9	7b	4.53 d (11.8)				
1'	4.50 d (7.9)	103.3	2'''	7.13 s	110.5	1'	4.24 d (7.7)	103.2			
2'	3.53 dd (9.5,7.9)	73.8	3'''		146.7	2'	3.27 t (9.0)	75.3			
3'	5.14 t (9.2)	79.1	4'''		139.9	3'	3.32 t (9.2)	78.1			
4'	3.68 m	70.4	5'''		146.7	4'	3.42 m	72.0			
5'	3.68 m	75.7	6'''	7.13 s	110.5	5'	3.54 m	75.7			
6'a	4.58 d (11.6)	64.7	7'''		168.4	6'a	4.45 dd (11.9,1.8)	64.9			
6'b	4.48 m					6'b	4.33 dd (11.9,6.0)				

3. Results and Discussion

Compound **1** was obtained as a lavender amorphous powder. Its molecular formula, $C_{27}H_{26}O_{14}$, was deduced from the HR-ESI-MS (*m/z* 597.1216 $[M + Na]^+$, calcd. 597.1215). Strong UV absorptions at 214 nm and 276 nm implied it had large conjugated systems. Its IR spectrum showed absorption bands for conjugated carbonyl groups at 1700 cm^{-1} and hydroxyl groups at 3397 cm^{-1}. The ^{1}H NMR spectrum

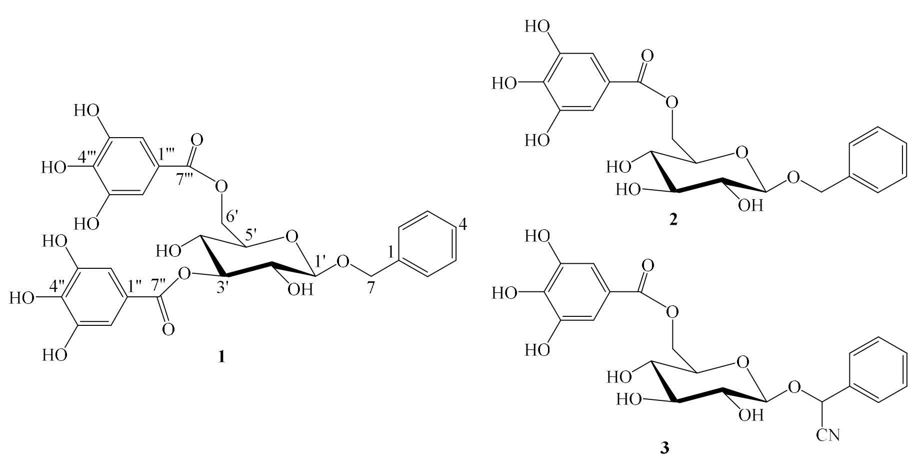
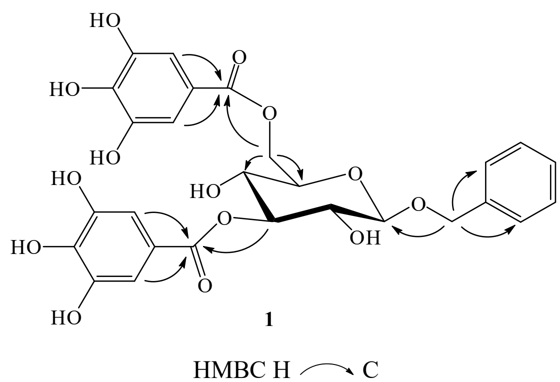


Figure 1. The chemical structures of compounds **1**−**3**

revealed the presence of two galloyl groups (*δ* 7.12, 2H, s; 7.13, 2H, s),a monosubstituted benzene ring (*δ* 7.35, 2H, br d, *J* = 7.3 Hz; 7.29, 2H, t, *J* = 7.3 Hz; 7.24, 1H, t, *J* = 7.3 Hz), and signals diagnostic of a $^4C_1$-glucopyranosyl residue. An anomeric proton signal of the glucose at *δ* 4.50 (d, *J* = 7.9 Hz) indicated a *β*-configuration for the glucosidic bond. These spectral features along with two carboxyl carbon signals at *δ* 168.3 and 168.4 in the ^{13}C NMR spectrum suggested that **1** is a di-*O*-galloyl-*β*-glucopyranoside. Additionally, a methylene group [δ_H 4.86, 4.66 (each d, *J* = 11.8 Hz); δ_C 72.1] was evident. The ^{1}H and ^{13}C NMR spectra of **1** closely resembled those of a known compound **2**, benzyl 6'-*O*-galloyl-*β*-glucopyranoside [11], except that **1** had one more galloyl than **2**. The location of galloyl units at 3'-*O* and 6'-*O* of the glucopyranose moiety was established by the low-field shifts of the H-3' (δ_H 5.14) and H-6' signals (δ_H 4.58, 4.48), which was proved by the correlations of H-3'/C-7'' and H-6'/C-7'''. The location of benzyl was attached to C-1' through O atom, which was confirmed by the cross peaks from H_2-7 to C-1' and from H_2-7 to C-2 and C-6. Thus, compound **1** was assigned as benzyl 3', 6'-di-*O*-galloyl-*β*-glucopyranoside.



1

Figure 2. Key HMBC (H→C) correlations of **1**

The known compounds were determined to be benzyl 6'-*O*-galloyl-*β*-glucopyranoside (**2**) and 6'-*O*-galloylprunasin (**3**) [11] by comparing their spectroscopic data with those in the literature.

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Supporting Information

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