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Four new glycosides from the stems of *Dendrobium fimbriatum* Hook

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ABSTRACT

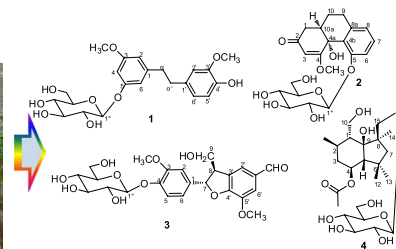
Four new glucosides, named as gigantol-5-*O*- β -D-glucopyranoside (**1**), 9,10-dihydro-aphyllone A-5-*O*- β -D-glucopyranoside (**2**), ficusal-4-*O*- β -D-glucopyranoside (**3**), botrydiol-15-*O*- β -D-glucopyranoside (**4**), together with eight known compounds (**5–12**) were isolated from the *n*-BuOH extract of the stems of *Dendrobium fimbriatum* Hook. Their structures were elucidated by the analyses of spectroscopic data.

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1. Introduction

The stems of some species of 'Shi-hu' (Orchidaceae) have been used as tradition folk medicines owing to their nourishing the stomach, promoting secretion of saliva and reducing fever for the Chinese since thousands of years ago. *Dendrobium* genus led to the isolation of alkaloids, sesquiterpenoids, phenanthrenes, bibenzyls, flavonoids, fluorenones and their related glycosides (Ye et al. 2003; Xu et al. 2013; Sun et al. 2014; Zhao et al. 2016). The stems of *Dendrobium fimbriatum* Hook is one of the famous herbal medicine as well as a high-quality healthy food. It is widely distributed in the southwest of PR China and some other Asian countries, such as Burma, Vietnam, Thailand, Nepal and India (Ji 1999; Xiao et al. 2008). In our previous phytochemical studies on the EtOAc extract of its stem, we reported the

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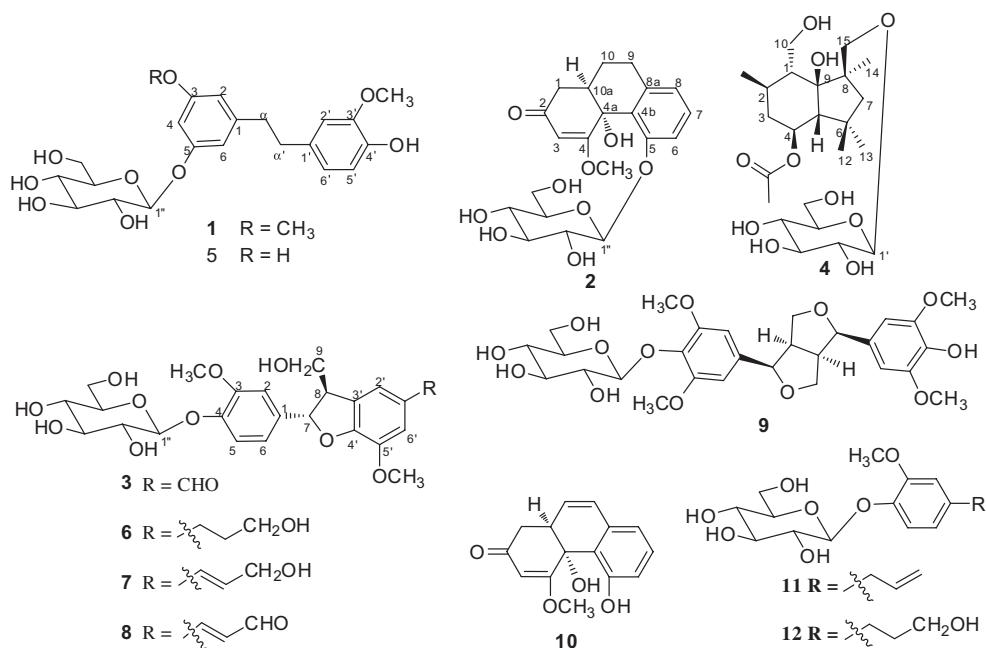


Figure 1. Structures of compounds 1–12 from *D. fimbriatum* Hook.

bibenzyl dimers with a linkage of a methylene moiety, phenanthrenes, bibenzyls and so on (Xu et al. 2014). In our continuous investigation on the *n*-BuOH extract of this plant, four new glucosides (**1–4**), together with eight known compounds (Figure 1), trisin-5-*O*- β -D-glucopyranoside (**5**) (Biondi et al. 2005), ceurusin-4-*O*- β -D-glucopyranoside (**6**) (Huo et al. 2009; Ouyang et al. 2011), dehydrodiconiferyl alcohol-4-*O*- β -D-glucopyranoside (**7**) (Tan et al. 2005), balanophonin-4-*O*- β -D-glucopyranoside (**8**) (Warashina et al. 2005; Yuen et al. 1998), syringaresinol-4-*O*- β -D-glucopyranoside (**9**) (Wang & Yu 1998; Chen et al. 2012), aphenyllone A (**10**) (Yang et al. 2015), eugenol-4-*O*- β -D-glucopyranoside (**11**) (Li et al. 2003), dihydroconiferin (**12**) (Mazur et al. 2007), were isolated and identified. Herein, the isolated process and the structure elucidation of the new compounds are reported.

2. Results and discussion

Gigantol-5-*O*- β -D-glucopyranoside (**1**) was obtained as a white amorphous powder, and its HRESIMS gave a pseudomolecular ion at m/z 459.1640 [$M + Na$]⁺, corresponding to the molecular formula C₂₂H₂₈O₉Na (calc. 459.1626), with 9° of unsaturation. The ¹H NMR spectrum of **1** exhibited signals of two groups of aromatic protons, one was 1,3,4-trisubstituted aromatic ring [δ_H 6.67 (1H, d, $J = 7.8$ Hz), 6.67 (1H, dd, $J = 1.8$ Hz), 6.57 (1H, dd, $J = 7.8, 1.8$ Hz)], the other one was 1,3,5-trisubstituted aromatic ring [δ_H 6.50, 6.48, 6.38 (1H each, br s)], two characteristic methylene protons at δ_H 2.74 and 2.78 (2H each, m) (Hu et al. 2008; Dong et al. 2012), as well as a set of characteristic protons attached to oxygen-bearing carbons at δ_H 4.77 (d, $J = 7.8$ Hz, H-1''), 3.42 (d, $J = 7.2$ Hz, H-2''), 3.44 (d, $J = 7.8$ Hz, H-3''), 3.36 (d, $J = 8.4$ Hz, H-4''), 3.40 (m, H-5''), 3.86 (dd, $J = 12.0, 1.8$ Hz, H-6''a), 3.67 (dd, $J = 12.0, 5.4$ Hz, H-6''b) ascribable to a β -glucose moiety. The ¹³C NMR and DEPT spectra (Table S1) revealed 22 carbon resonances,

including three methylenes [two aliphatic carbons at δ_c 39.7 (t), 38.5 (t) and one oxygenated], five oxygenated methines, 12 aromatic carbons, two methoxy carbons. Among of them, 14 carbon signals were attributed to a bibenzyl and six to a glucopyranosyl moiety [δ_c 102.5 (d, C-1''), 75.0 (d, C-1''), 78.0 (d, C-1''), 71.5 (d, C-1''), 78.2 (d, C-1''), 62.6 (t, C-1'')] (Biondi et al. 2005; Dong et al. 2012). The expected key correlations: from H-2 (δ 6.38) to C-a, C-3, C-4 and C-6, from H-6 (δ_H 6.48) to C-a, C-2, C-4 and C-5, from H-6' (δ_H 6.57) to C-2', C-4' and C-a', from H-a' (δ_H 2.74) to C-2', C-6' and C-a were observed in the HMBC spectrum (Figure S1). The above data demonstrated **1** is a glycoside derivate of gigantol. The glucopyranosyl attached to C-5 could be determined by the long-range correlation in the HMBC spectrum from H-1'' (δ_H 4.77) to C-5 (δ_c 160.2). Thus, the structure of **1** was identified as 3,3'-dimethoxy-4'-hydroxyl-bibenzyl-5-O- β -D-glucopyranoside, named as gigantol-5-O- β -D-glucopyranoside.

9,10-dihydro-aphyllone A-5-O- β -D-glucopyranoside (**2**) was obtained as a white amorphous power, its molecular formula was assigned as C₂₁H₂₆O₉ from HRESIMS (m/z 423.1663 [M + H]⁺). The ¹H NMR spectrum (Table S2) revealed a 1,2,3-trisubstituted aromatic ring [δ_H 7.26 (d, J = 7.8 Hz), 7.18 (t, J = 7.8 Hz), 6.86 (dd, J = 7.8, 0.6 Hz)], an olefin proton [δ_H 5.27 (s)] and an anomeric proton [δ_H 4.95 (d, J = 7.8 Hz)] signals. The ¹³C NMR and DEPT spectra (Table S2) exhibited 21 carbon resonances, including four methylenes, 10 methines, six quaternary carbons (one carbonyl) and one oxygenated methyl. By comparison of the NMR spectroscopic data with those of aphyllone A (Yang et al. 2015), they were very similar except that a $\Delta^{9,10}$ double bond in aphyllone A was replaced by two H-atoms, as well as the presence of a glucose moiety in **2**. The HMBC correlations (Figure S1) from H-3 (δ_H 5.27, s) to C-1, C-2, C-4 and C-4a established the spin systems for the molecular fragments of an α , β -unsaturated ketone group (C-2-C-3-C-4). Additionally, correlations from H-1 [δ_H 3.14 (1H, dd, J = 17.4, 5.4 Hz), 2.18 (1H, dd, 17.4, 3.0 Hz)] to C-1a, C-10 and C-2, from H-9 to C-1a, C-5a, C-8 and C-8a, from H-10 to C-1, C-1a, C-4a and C-8a were observed. The location of the methoxy group at C-4 was determined by HMBC correlations from H-OCH₃ (δ_H 3.66, s) to C-4 in the HMBC spectrum and H-OCH₃ ↔ H-3 in the ROESY spectrum. The long-range correlation in the HMBC spectrum from H-1' (δ_H 4.95, J = 7.8 Hz) to C-5 (δ_c 159.4) indicated the glucopyranosyl attached to C-5 via a β -linkage. Based on the above evidences, the planar structure of **2** was elucidated. From a biosynthetic point of view and the CD curve of **2** showed a negative Cotton effect around 202 nm and a positive value around 248, the configuration of compound **2** was established to be identical with aphyllone A (Yang et al. 2015). Thus, compound **2** was identified as 9,10-dihydro-aphyllone A-5-O- β -D-glucopyranoside.

Ficusal-4-O- β -D-glucopyranoside (**3**) was obtained as a white amorphous power, its molecular formula was determined as C₂₄H₂₈O₁₁ by HRESIMS (m/z 515.1533 [M + Na]⁺, calc. for 515.1524). In the ¹H NMR spectrum, the signals were assigned to an ABX system protons [δ_H 7.03 (d, 1.8), 7.15 (d, 8.4), 6.93 (dd, 8.4, 1.8)], a pair of phenyl protons with broad meta-couple [δ_H 7.51 and 7.47], an aromatic aldehyde proton [δ_H 9.79 (s)] and an anomeric proton [δ_H 4.90 (d, J = 7.2 Hz)]. The ¹³C NMR spectrum displayed 12 signals indicative of two aromatic rings in the molecular. The ¹H and ¹³C NMR (Table S3) exhibited signals at δ_H 5.71 (d, J = 6.6 Hz, H-7) and 3.85 (2H, dd, J = 13.8, 5.4 Hz, H-9), 3.59 (1H, m, H-8) and δ_c 90.2 (C-7), 54.7 (C-8) and 64.6 (C-9), which were similar to a dehydrodiconiferyl alcohol-type lignan (Li & Kuo 2000). The spectroscopic data of **3** were similar to those of balanophonin 4-O- β -D-glucopyranoside (**8**) (Warashina 2005) except that an aldehyde group replaced a propenal group. The stereochemistry between aryl and hydroxymethyl group was suggested to be trans, by the absence of the nuclear ROSEY correlation between H-7 and H-8, which was also supported by the

coupling constant of H-7 ($J = 6.6$ Hz), along with the ROESY correlation between H-7 and H-9 (Liu et al. 2011). The assignment listed was also supported by HSQC and HMBC experiments (Figure S1, Table S3). Thus, compound **3** was identified as ficalin-4- O - β -D-glucopyranoside.

Botrydiol-15- O - β -D-glucopyranoside (**4**) was obtained as a white amorphous powder which had a molecular formula of $C_{23}H_{40}O_{10}$ in HR-ESIMS (m/z 499.2524 $[M + Na]^+$, calcd. for 499.2514). The 1H NMR spectrum of compound **4** revealed three singlet methyl signals [2.00 (3H, s, CH₃CO), 1.23 (3H, s, H-12), 1.16 (3H, s, H-14), 1.03 (3H, s, H-13)] and a double methyl [0.98 (3H, d, 6.0, H-11)] signals, two oxygenated-methylene groups [3.91 (1H, dd, 12.0, 3.0), 3.83 (1H, br d, 12.0) and 4.07, 3.70 (1H each, 9.6)] signals. The ^{13}C NMR and DEPT spectra (Table S4) exhibited 23 carbon signals, containing four methyl, four methylenes (two oxygenated), four methines (two oxygenated), three quaternary carbons (one oxygenated), an acetyl group as well as a hexose unit signals at δ_c 104.9 (d), 75.1 (d), 78.3 (d), 71.7 (d), 78.1 (d) and 62.8 (t), implying that **4** is a sesquiterpenoid glucoside with a botryane skeleton. The NMR data of aglycone were similar to those of botrydiol (Reino et al. 2003; Xu et al. 2014). An anomeric proton resonance at δ_H 4.28 (1H, d, $J = 8.4$ Hz) in the 1H NMR spectrum indicated β -glycosidic linkage. The glucose moiety was attached to C-15 (Figure S1) supported by the correlation from H-1' to C-15 in the HMBC spectrum and the signal C-15 was downfield by 8.8 ppm in the ^{13}C NMR spectrum. Thus, the structure of **4** was elucidated as botrydiol-15- O - β -D-glucopyranoside.

3. Conclusions

Further chemical investigation of the stems of *D. fimbriatum* resulted in isolation of four new glucosides (**1–4**) and eight known compounds (**5–12**). Isolation of botrydiol-15- O - β -D-glucopyranoside (**4**) was the first evidence of sesquiterpene glucoside from *D. fimbriatum*. 9,10-dihydro-aphyllone A-4- O - β -D-glucopyranoside (**2**) and the existence of phenanthrene derivatives in *Dendrobium* species (Yang et al. 2015) was further confirmed by the aphyllone A (10) elucidation.

Supplementary material

Experimental section, HRESIMS, 1D and 2D NMR spectra of compounds **1–4**, CD spectrum of compound **2** are available as Supporting material.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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