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Chemical constituents from the immature buds of *Cinnamomum cassia* (Lauraceae)

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ABSTRACT

Phytochemical investigations on the immature buds of *Cinnamomum cassia* (cassia buds) led to the isolation of fifteen compounds, including two phenylmethanol glycosides (**1** and **2**), two phenylethyl glycosides (**3–5**), two butanol glycosides (**6** and **7**), a megastigmane sesquiterpenoid (**8**), a pair of isomeric monoterpenoids (**9**) and their glycosides (**10**), a monoterpenoid glycoside (**11**), a geraniol type monoterpenoid (**12**), two phenolic glycosides (**13** and **14**), and cinnamic acid (**15**). Their structures were identified by spectroscopic analyses and comparison with literature data. Compounds **1**, **2**, and **4–13** were isolated from *Cinnamomum cassia* for the first time, and compounds **1**, **2**, **4–7**, and **9–11** were reported in the Lauraceae family for the first time. The chemotaxonomic significance of these compounds was discussed.

1. Subject and source

The genus *Cinnamomum* (Lauraceae) includes approximately 250 species and is mainly distributed in tropical and subtropical Asia, Australia, and the Pacific islands (Li et al., 2008). *Cinnamomum cassia* Presl. is an evergreen tree. Its immature buds were not only used as a spice, but also as a traditional Chinese and Uighur medicine (Editorial Committee of Chinese Materia Medica, 1999). The dried immature buds of *C. cassia* were purchased from Yulin Medical Market, Guangxi Province of China, in June 2015, and authenticated by Prof. C.G. Zhang at the School of Pharmacy, Tongji Medical College, Huazhong University of Science and Technology. The voucher specimen (No. 20150601) was deposited in the Hubei Key Laboratory of Natural Medicinal Chemistry and Resource Evaluation, School of Pharmacy, Tongji Medical College, Huazhong University of Science and Technology.

2. Previous work

Previous phytochemical investigations of *C. cassia* mainly focused on its barks and leaves, and resulted in the isolation of sesquiterpenoids (Yan et al., 2015), diterpenoids (Yagi et al., 1980; Nohara et al., 1980, 1981, 1982; Kashiwada et al., 1981; Ngoc et al., 2009a; Zeng et al., 2014; He et al., 2016a; Zhou et al., 2017), phenylpropanoids (Tanaka et al., 1989; Ngoc et al., 2009b, 2012), phenolic glycosides (Shiraga et al., 1988; Liao et al., 2009; Ngoc et al., 2012; Luo et al., 2013), cinnamic aldehyde derivatives (Kwon et al., 1996; Liu et al., 2009), procyanidines (Killday et al., 2011; Morimoto et al., 1986), polysaccharides (Kanari et al., 1989), butyrolactones (Kim et al., 2017; He et al., 2016b), and coumarins (Huong et al., 2000; Ngoc et al., 2014). The chemical constituents of the essential oils of *C. cassia* were reported to be phenylpropanoids, monoterpenoids, and sesquiterpenoids (Heide, 1972; Choi et al., 2001; Chang et al., 2013; Li et al., 2013; Huang et al., 2014). However, phytochemical studies on the buds of *C. cassia* are rare, and only one paper reports the presence of sesquiterpenoids and their antimicrobial activities (Guoruoluo et al., 2017).

3. Present work

3.1. Extraction and isolation

The dried immature buds of *C. cassia* (5.0 kg) were powered and extracted with 95% EtOH three times at 45 °C. After filtration and

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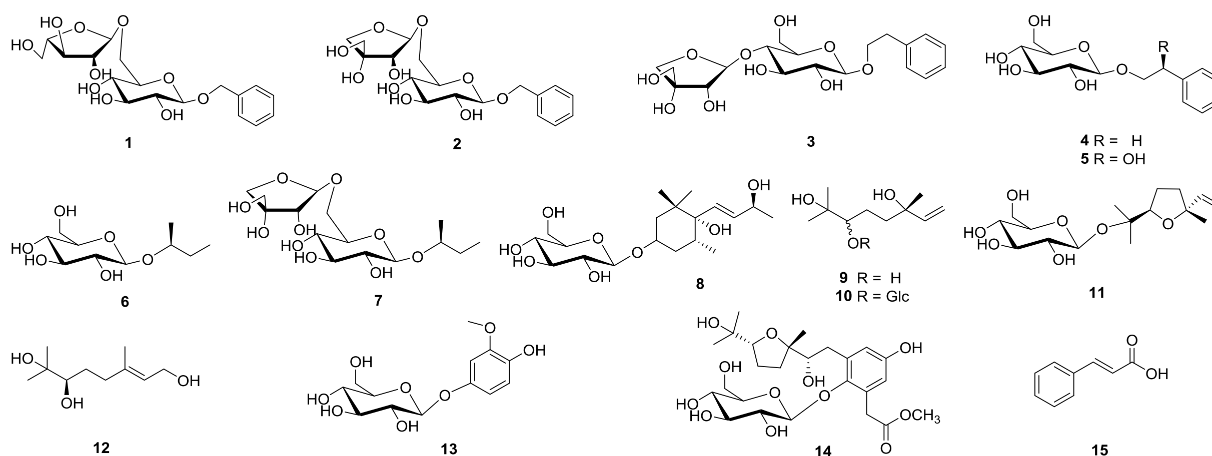

Fig. 1. Structures of compounds **1–15**.

combination, the solvent was removed in vacuum, and the residue was extracted with petroleum ether, EtOAc, and MeOH, excessively. The MeOH extract (100.0 g) was fractionated using silica gel CC eluting with $CHCl_3$/MeOH (15:1 to 2:1, v/v) to give nine fractions (A–I). Fraction B (1.0 g) was subjected to an RP–C_{18} gel eluted with MeOH–H_2O (0:100 to 30:70, v/v) to afford six subfractions (B_1–B_6). Subfraction B_2 was further separated on silica gel column using a solvent petroleum ether/acetone (4:1, v/v), purified with Sephadex LH–20 CC (MeOH) and semi-preparative HPLC on RP–C_{18} (50% MeOH in H_2O, flow rate 1.5 mL/min, wavelength 205 nm) to afford compound **9** (2.2 mg, retention time 15 min). Fraction C (6.0 g) was subjected to an RP–C_{18} gel with MeOH–H_2O (0:100 to 30:70, v/v) to give nine subfractions (C_1–C_9). Subfraction C_2 chromatographed on a silica gel column eluted with $CHCl_3$/MeOH (10:1, v/v), and purified by semi-preparative HPLC on RP–C_{18} (32% MeOH in H_2O, flow rate 1.5 mL/min, wavelength 205 nm) to yield compound **6** (31.0 mg, retention time 23 min). Subfraction C_4 was subjected by RP–C_{18} gel eluted with MeOH–H_2O (0:100 to 30:70, v/v) to afford compound **14** (49.0 mg). Further separation of the remains of the subfraction C_4 by Sephadex LH–20 CC (MeOH) and on silica gel column eluted with $CHCl_3$/MeOH (40:1, v/v), and final purification by semi-preparative HPLC on RP–C_{18} (32% MeOH in H_2O, flow rate 1.5 mL/min, wavelength 205 nm) yielded compound **4** (62.5 mg, retention time 64 min). Subfraction C_5 was separated by Sephadex LH–20 CC (MeOH) to give compound **11** (10.0 mg). Fraction D (4.0 g) was subjected to an RP–C_{18} gel with MeOH–H_2O (0:100 to 30:70, v/v) to give nine subfraction (D_1–D_9). Subfraction D_2 was subjected to a Sephadex LH–20 column eluted with MeOH, chromatographed on a silica gel column eluted with $CHCl_3$/MeOH (20:1, v/v), and purified by semi-preparative HPLC on RP-C_{18} (17% MeOH in H_2O, flow rate 1.5 mL/min, wavelength 205 nm) to obtain compound **13** (3.4 mg, retention time 18 min). Fraction E (12.0 g) was separated by an RP–C_{18} gel with MeOH–H_2O (0:100 to 30:70, v/v) to give 15 subfraction (E_1–E_{15}). Subfraction E_{10} was subjected to Sephadex LH–20 CC (MeOH), then applied to silica gel column eluted with $CHCl_3$/MeOH (25:1, v/v), and compound **5** (11.0 mg, retention time 70 min) was isolated by semi-preparative HPLC on RP-C_{18} (18% MeOH in H_2O, flow rate 1.5 mL/min, wavelength 205 nm). Subfraction E_{12} was subjected to Sephadex LH–20 CC (MeOH) to afford compound **10** (40.0 mg) and further separated by silica gel column eluted with $CHCl_3$/MeOH (24:1, v/v), purified by semi-preparative HPLC on XB-phenyl (23% MeOH in H_2O, flow rate 1.5 mL/min, wavelength 205 nm) to obtain compounds **1** (3.0 mg, retention time 81 min) and **2** (3.0 mg, retention time 101 min). Subfraction E_{14} was separated with Sephadex LH–20 CC (MeOH) and silica gel column eluted with $CHCl_3$/MeOH (15:1, v/v) to give compound **3** (40.3 mg). Fraction F (25.0 g) was subjected to an RP–C_{18} gel with MeOH–H_2O (0:100 to 30:70, v/v) to give seven subfraction (F_1–F_7). Subfraction F_3 was separated with Sephadex LH–20 CC (MeOH) and silica gel column eluted with $CHCl_3$/MeOH (20:1, v/v) to give compound **7** (10.2 mg). Subfraction F_4 was subjected to an phenyl gel with MeOH–H_2O (0:100 to 30:70, v/v), further separated with silica gel column eluted with $CHCl_3$/MeOH (15:1, v/v) and Sephadex LH–20 CC (MeOH) to obtain compound **8** (10.4 mg). Subfraction F_5 was subjected with Sephadex LH–20 CC (MeOH) and silica gel column eluted with $CHCl_3$/MeOH (40:1, v/v), purified by semi-preparative HPLC on XB-phenyl (23% MeOH in H_2O, flow rate 1.5 mL/min, wavelength 205 nm) to obtain compound **12** (1.1 mg, retention time 42 min). The part of EtOAc (90.0 g) was fractionated using silica gel CC eluting with $CHCl_3$/MeOH (50:1 to 5:1, v/v), and further subjected by RP–C_{18} gel with MeOH–H_2O (0:100 to 50:50, v/v) to obtain compound **15** (1.1 g) by crystallization. The chemical structures of compounds **1–15** were shown in Fig. 1.

3.2. *Structure determination*

Compounds **1–15** were identified as phenylmethanol O-*α*-L-arabinofuranosyl (1 → 6)-*β*-D-glucopyranoside (**1**) (Baltenweck-Guyot et al., 2000) phenylmethanol O-*α*-L-arabinopyranosyl (1 → 6)-*β*-D-glucopyranoside (**2**) (Cui et al., 1993), icariside DC (**3**) (Ngoc et al., 2009b), 2-phenylethyl-O-*β*-D-glucopyranoside (**4**) (Melnikov et al., 1975), 2-O-*β*-D-glucosyl-(1*S*)-phenylethylene glycol (**5**) (Ooi et al., 1985), (2*S*)-butan-2-O-*β*-D-glucopyranoside (**6**) (Cable and Nocke, 1975), (2*S*)-2-butan-2-O-*β*-D-apiofuranosyl (1 → 6)-glucopyranoside (**7**) (Prawat et al., 1995), (3*S*,5R,6*S*,9*S*)-3,6,9-trihydroxymegastigman-7-ene 3-O-*β*-D-glucopyranoside (**8**) (Yu et al., 2002), 3,7-dimethyl-1-octene-3,6,7-triol (**9**) (Manns, 1995), 3,7-dimethyl-oct-1-en-3,6,7-triol-6-O-*β*-D-glucopyranoside (**10**) (Manns, 1995), *trans*-linalool-3,6-oxide-*β*-D-glucopyranoside (**11**) (Li et al., 2012), (6R)-geraniol-6,7-diol (**12**) (Zhang et al., 1991), isotachioside (**13**) (Zhong et al., 1999), cinnacasside F (**14**) (Zeng et al., 2017), and cinnamic acid (**15**), respectively, by MS, 1D and 2D NMR spectroscopic data analysis and comparison with those reported in the literature.

4. Chemotaxonomic significance

A total 15 compounds were isolated from the immature fruits of *C. cassia*, including two phenylmethanol glycosides (**1** and **2**), two phenylethyl glycosides (**3–5**), two butanol glycosides (**6** and **7**), a megastigmane sesquiterpenoid (**8**), a pair of isomeric monoterpenoids (**9**) and their glycosides (**10**), a monoterpenoid glycoside (**11**), a geraniol type monoterpenoid (**12**), two phenolic glycosides (**13** and **14**), and a cinnamic acid (**15**).

Phenylmethyl glycosides are common ingredients in the fruits or flowers of plants. However, compounds **1** and **2** have not been reported from any species of the genus *Cinnamomum* and the family Lauraceae.

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