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Chemical constituents from *Piper boehmeriifolium* (Miq.) Wall. ex C. DC

Tie Liu [a], Qian Liang [a, b], Xin-Min Zhang [c], Gen-Qian Li [a], Bo Xu [a], Wen-Hui Xu [a, *]

[a] *Key Laboratory for Forest Resources Conservation and Utilization in the Southwest Mountains of China, Ministry of Education, Southwest Forestry University, Kunming 650224, PR China*
[b] *Department of Medicinal Plant, School of Forestry, Southwest Forestry University, Kunming 650224, PR China*
[c] *Key Laboratory of Forest Disaster Warning and Control of Yunnan Province, Southwest Forestry University, Kunming 650224, PR China*

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ABSTRACT

The chemical investigation of whole plants *Piper boehmeriifolium* (Miq.) Wall. ex C. DC. led to the isolation of 22 compounds, including two lignans (**1**–**2**), sixteen amide alkaloids (**3**–**18**), one diterpene (**19**), two monoterpenes (**20**–**21**), and one phenylpropanoid (**22**). Their structures were elucidated by extensive spectroscopic analyses including NMR, MS, and by comparison with the literature. Compounds **1**–**2**, **6**–**7**, **11**–**12**, **14**, and **17**–**22** were firstly isolated from *P. boehmeriifolium*, while compounds **2**, and **19**–**20** were isolated from *Piper* genus for the first time. The chemotaxonomic significance of these isolated compounds is discussed.

1. Subject and source

The *Piper* genus belongs to the family Piperaceae, with approximately 1000 species widely distributed in the tropical and subtropical regions of the world. There are approximately 33 species grown in China. *Piper boehmeriifolium* (Miq.) Wall. ex C. DC. is an endemic perennial subshrub mainly distributed in Yunnan Province of China, eastern India and northern Vietnam (Gutierrez et al., 2013; Editorial Committee of Chinese flora, 1994). The whole parts of *P. boehmeriifolium* were collected in Lincang, Yunnan Province, China, in August 2014, and identified by Prof. Fan Du (School of Forestry, Southwest Forestry University, Kunming 650224, China). A voucher specimen (No.140817) is deposited in the Key Laboratory for Forest Resources Conservation and Utilization in the Southwest Mountains of China, Southwest Forestry University, Kunming City, Yunnan Province, China.

2. Previous work

Extensive chemical studies on *Piper* genus have resulted in the isolation of a large number of structurally diverse compounds, including amide alkaloids, lignans, neolignans, phenylpropanoids, monoterpenes, sesquiterpenes and steroids etc. Amide alkaloids and lignans are considered as the major characteristic secondary metabolites and taxonomic markers of *Piper* genus (Parmar et al., 1997; Gutierrez et al., 2013; Xu and Li, 2011). However, there are few reports on the phytochemical of *P. boehmeriifolium*. Previous phytochemical studies on *P. boehmeriifolium* led to the isolation of several amide alkaloids (Desai et al., 1989, 1990; Tang et al., 2011). The volatile constituents from *P. boehmeriifolium* have been extracted and analyzed using gas chromatography (GC)-based techniques. Monoterpenoids and sesquiterpenoids have been found to be the dominant constituents of its volatile constituents. (Zong et al., 2013).

3. Present study

Powdered, air-dried whole parts of *P. boehmeriifolium* (11.0 kg) were exhaustively extracted with 95% EtOH (50 L × 3) at room temperature for 72 h. The extraction was evaporated to dryness *in vacuo*. The residue (1.50 kg) was suspended in H_2O and then partitioned with petroleum ether and EtOAc, respectively. The petroleum ether layer was evaporated to dryness and the resultant residue (303.0 g) was subjected to silica gel liquid chromatography using stepwise gradient elution petroleum ether -acetone (200:1 → 3:1, v/v) to afford 12 pooled fractions A-L according to TLC. Fraction H was decolorized on MCI gel eluted with MeOH-H_2O (90:10, v/v), followed by C18 reversed-phase column eluting with

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* Corresponding author.
E-mail address: Wenhuix001@hotmail.com (W.-H. Xu).

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MeOH-H_2O (50:50 → 95:5, v/v) to give **1** (74.0 mg), **4** (11.0 mg), **5** (16.0 mg), **6** (7.8 mg), **7** (10.0 mg), and **17** (14.0 mg). Fraction J was decolorized on MCI gel eluted with MeOH-H_2O (90:10, v/v), then purified on silica gel column eluted with petroleum ether -acetone (14:1 → 2:1, v/v) and C18 reversed-phase column with MeOH-H_2O (50:50 → 95:5, v/v) to afford **2** (6.3 mg), **8** (2.9 mg), **9** (23.0 mg), **10** (12.8 mg), **11** (9.6 mg), **12** (11.0 mg), **14** (5.7 mg) and **18** (10.4 mg). Fraction K was further purified on a C18 reversed-phase column eluted with MeOH-H_2O (70:30 → 95:5, v/v) to yield 9 subfractions (K1-K9). Fraction K2 was subjected to C18 Semi-HPLC (35% MeOH/H_2O, at a flow rate of 4 mL/min) to afford **22** (82.2 mg). Fraction K3 was chromatographed on a semipreparative C18 reversed phase HPLC column, using 47% MeOH/H_2O, at a flow rate of 4 mL/min, to give **3** (11.0 mg). Fraction K5 was further purified on C18 Semi-HPLC (72% MeOH/H_2O, at a flow rate of 4 mL/min) to afford **13** (9.6 mg). Compounds **15** (23.7 mg) and **16** (34.1 mg) were obtained by C18 Semi-HPLC (73% MeOH/H_2O, at a flow rate of 4 mL/min) from fraction K7. The EtOAc layer (146.0 g) was subjected to silica gel column eluted with $CHCl_3$-MeOH (100:1 → 2:1, v/v) to afford 10 pooled fractions 1–10. Fractions 2 was purified on C18 reversed phase column eluted with MeOH-H_2O (50:50 → 95:5, v/v) to give **19** (14.0 mg). Compounds **20** (14.2 mg) was obtained by C18 column eluted with MeOH-H_2O (40:60 → 80:20, v/v). Fractions 6 was decolorized on MCI gel eluted with MeOH-H_2O (80:20, v/v), then by purified by C18 column eluted with MeOH-H_2O (40:60 → 80:20, v/v) to give **21** (12.0 mg).

The structures of the isolated compounds were elucidated on the basis of spectroscopic data (1D and 2D NMR, ESI-MS) and by comparison of these data with literature (Fig. 1). They were identified as (+)-sesamin (**1**), (Rukachaisirikul et al., 2004), (+)-5-methoxysesamin (**2**), (Tan et al., 1998), 3-(4-hydroxy-3,5-dimethoxyphenyl)propanoylpyrrole (**3**) (Tang et al., 2011), 3-(3,4,5-trimethoxyphenyl)propanoylpyrrole (**4**) (Tang et al., 2011), pellitorine (**5**) (da-Cunha and de Oliveira Chaves, 2001), N-isobutyl-2*E*,4*E*-dodecadienamide (**6**) (Stoehr et al., 1999), *N*-Isobutyl-2*E*,4*E*-octadecadienamide (**7**) (Stoehr et al., 1999), pipercallosidine (**8**) (McFerren and Rodriguez, 1998), retrofractamide C (**9**) (Banerji et al., 1985), pipercide (**10**) (Park et al., 2002), guineensine (**11**)

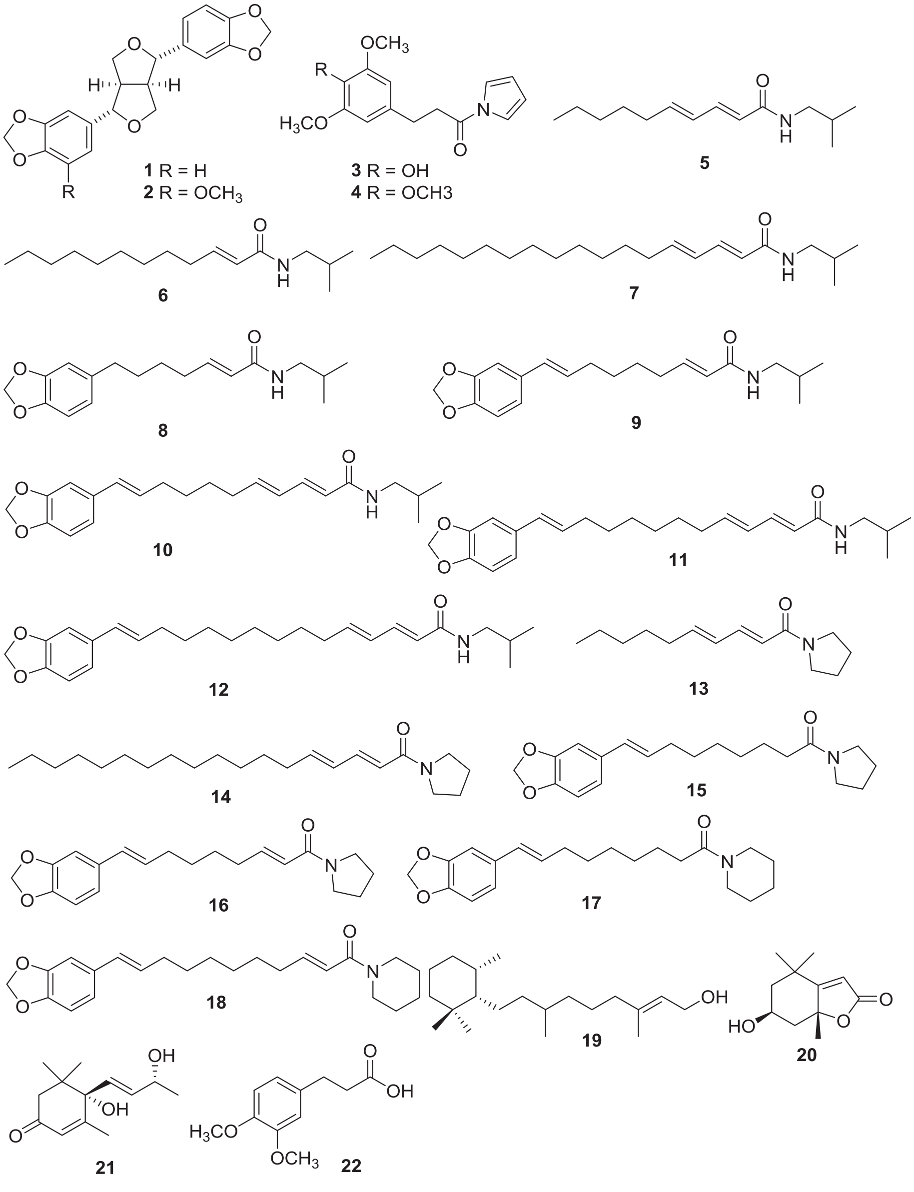

Fig. 1. Structures of compounds **1**–**22**.