Biochemical Systematics and Ecology 70 (2017) 95–98

Contents lists available at ScienceDirect

Biochemical Systematics and Ecology

journal homepage: www.elsevier.com/locate/biochemsyseco

Chemical constituents from the leaves of *Cinnamomum parthenoxylon* (Jack) Meisn. (Lauraceae)

Xuan Wei [a], Guo-Hui Li [b], Xiao-Ling Wang [c], Ji-Xiang He [a], Xiao-Ning Wang [d], Dong-Mei Ren [d], Hong-Xiang Lou [d], Tao Shen [d, *]

[a] School of Pharmaceutical Sciences, Shandong University of Traditional Chinese Medicine, Jinan, PR China
[b] Department of Pharmacy, Jinan Maternity and Child Care Hospital, Jinan, PR China
[c] The Second Hospital of Shandong University, Jinan, PR China
[d] Key Lab of Chemical Biology (MOE), School of Pharmaceutical Sciences, Shandong University, Jinan, PR China

ARTICLE INFO

Article history:
Received 25 August 2016
Received in revised form 1 November 2016
Accepted 5 November 2016

Keywords:
Cinnamomum parthenoxylon
Lauraceae
Chemical constituents
Flavonoids

ABSTRACT

Phytochemical investigation of the ethanolic extract from the leaves of *Cinnamomum parthenoxylon* (Jack) Meisn. led to the isolation of (3*R*, 4*R*, 3′*R*, 4′*R*)-6,6′-dimethoxy-3, 4, 3′, 4′-tetrahydro-2H, 2′H-[3, 3′]bichromenyl-4, 4′-diol (**1**), 4-hydroxybenzaldehyde (**2**), 1,2,4-trihydroxybenzene (**3**), kaempferol-3-*O*-α-L-rhamnoside (**4**), herbacetin (**5**), quercetin-3-*O*-α-L-rhamnoside (**6**), daucosterol (**7**), and β-sitosterol (**8**). The structures were established by extensive analysis of their MS and NMR spectroscopic data and comparison with literature data. In the present research, all of the isolated compounds **1**–**8** are reported for the first time in the species *C. parthenoxylon*. Compounds **1**–**6** were firstly isolated from genus *Cinnamomum*. Compounds **1**, **3**, **5** and **6** have not been reported from any species in Lauraceae family. The chemotaxonomic significance of the isolated compounds is discussed.

1. Subject and source

The genus *Cinnamomum* belongs to the Lauraceae family which includes approximately 250 species and is mainly distributed in tropical and subtropical Asia, Australia and the Pacific islands (Li et al., 2008). Some plants of this genus [e.g. *C. verum* J. Presl, *C. cassia* (L.) J. Presl, *C. loureiroi* Nees, and *C. burmannii* (Nees & T. Nees) Blume] are used as spice, fragrances, and traditional medicines (Wang et al., 2013). The species *Cinnamomum parthenoxylon* (Jack) Meisn. [synonym *Cinnamomum porrectum* (Roxb.) Kosterm.] is evergreen tree and widely occurs in Southern China up to altitudes of 1500 m (Li et al., 2008). The leaves of *C. parthenoxylon* used in the present research were collected from Xishuangbanna, Yunnan Province, P. R. China, in September 2011, and authenticated by Prof. Lan Xiang, a pharmaceutical botanist and pharmacognosist in Department of Pharmacognosy, School of Pharmaceutical Sciences, Shandong University, P. R. China. The plant was identified by comparison of their characteristics in plant morphology and taxonomy with that described in Flora of China (Li et al., 2008). A voucher specimen (XSBN2011-ZK-12) has been deposited at the Laboratory of Pharmacognosy, School of Pharmaceutical Sciences, Shandong University.

* Corresponding author. School of Pharmaceutical Sciences, Shandong University, 44 West Wenhua Road, Jinan 250012, PR China..
E-mail address: shentao@sdu.edu.cn (T. Shen).

http://dx.doi.org/10.1016/j.bse.2016.11.004
0305-1978/

2. Previous work

Phytochemical investigations of the plants from genus *Cinnamomum* led to the isolation of diverse types of chemical ingredients, including monoterpenoids (Fuchino et al., 2015), sesquiterpenoids (Shu et al., 2013; Yan et al., 2015), diterpenoids (He et al., 2016; Ngoc et al., 2009; Zeng et al., 2014b), phenylpropanoids (Wei et al., 2013), alkaloids (Kao et al., 2015; Li et al., 2012; Masnon et al., 2014), phenolic glycosides (Zeng et al., 2014a), coumarins (Ngoc et al., 2014), flavonoids (Lin and Chang, 2012; Prasad et al., 2009), steroids (Wei et al., 2013), proanthocyanidins (Killday et al., 2011), amides (Hong et al., 2011), butanolides (Lin et al., 2011), benzenoids (Lin et al., 2011), dibenzocycloheptanoids (Lin and Lee, 2012), and lignans (Chen et al., 2010; Cuong et al., 2001; Hsieh et al., 2006). The essential oils from plenty of *Cinnamomum* species have been extracted and analyzed using gas chromatography (GC)-based techniques (Hammid et al., 2016; Jiang et al., 2016; Li et al., 2014; Patel et al., 2007). Phenylpropanoids, monoterpenoids, and sesquiterpenoids have been found to be the dominant constituents of the essential oils. However, few researches have been carried out on the phytochemical aspects of *C. parthenoxylon*. To our knowledge, only one paper concerning the phytochemical investigations of *C. parthenoxylon* woods have been published and reported the isolation of lignans (dehydroxycubebin, hinokinin, and cubebin) and phenylpropanoids (3-(3,4-methylenedioxyphenyl)-1,2-propanediol, and safrole) (Adfa et al., 2016).

3. Present study

Dried and powdered leaves (250 g) of *C. parthenoxylon* were extracted with 95% EtOH (2L X 3) for 2 h each time. The solvent was removed in vacuo by rotary evaporators to give the EtOH extract (26.78 g). The extract was dissolved in 0.8 L H_2O and partitioned successively with 0.8 L petroleum ether, EtOAc and n-butanol (0.8 L X 4 for each). The EtOAc extract (4.37 g) was fractionated by silica gel column chromatography using a gradient of CH_2Cl_2–MeOH (from 150:1 to 70:30) to afford fifteen fractions (Frs. E1-E15). Fraction E5 was separated by column chromatography on Sephadex LH-20 with the eluent CH_2Cl_2–MeOH (1:1, v/v) to give seven subfractions (Frs. E5A-E5G). **1** (1.5 mg) was purified from subfraction E5C by semi-preparative HPLC on RP-18 column eluted with a gradient of MeCN–H_2O (30:70 to 38:62). Subfraction E5G was purified by semi-preparative HPLC on RP-18 column eluted with a gradient of MeOH–H_2O (65:30 to 80:20) to afford **2** (0.6 mg). Fraction E8 was fractionated by a Sephadex LH-20 column chromatography eluted with (CH_2Cl_2–MeOH = 1:1, v/v) give nine subfractions (Frs. E8A-E8I). Semi-preparative RP-18 HPLC column chromatography with a gradient of MeCN–H_2O (20:80 to 40:60) was used to purified subfraction E8I to give **3** (0.8 mg). Fraction E10 was separated by a Sephadex LH-20 column chromatography (CH_2Cl_2–MeOH = 1:1, v/v) to give three subfractions (E10A-E10C), and then **7** (1.5 mg) was precipitated from subfraction E10C. Fraction E11 was chromatographed on a Sephadex LH-20 eluted with CH_2Cl_2–MeOH (1:1, v/v) to afford eight subfractions (E11A-E11H). **4** (1.5 mg) was purified from subfraction E11H by semi-preparative RP-18 HPLC chromatography with a gradient of MeOH–H_2O (60:40 to 90:10). A Sephadex LH-20 column chromatography was used to separate fraction E12 (CH_2Cl_2–MeOH = 1:1, v/v) to get five subfractions (Frs.E12A-E12E). Subfraction E12I was subjected to a semi-preparative RP-18 HPLC column with a gradient of MeOH–H_2O (60:40 to 80:20) to afford **5** (1.1 mg). **6** (2.3 mg) was isolated from fraction E13 by a semi-preparative RP-18 HPLC column chromatography with a gradient of MeOH–H_2O (60:40 to 80:20). The petroleum ether extract (5.5 g) was separated on a silica gel column using a gradient of petroleum ether-EtOAc (100:0 to 60:40) to get fourteen fractions (Frs. P1–P14). Fraction P6 was chromatographed on a Sephadex LH-20 column (CH_2Cl_2–MeOH = 1:1, v/v) to afford **8** (12.6 mg).

The structures of the isolated compounds were established by MS and NMR experiments, and by comparison with data from the literature. These compounds were determined to be (3*R*, 4*R*, 3′*R*, 4′*R*)-6, 6′-dimethoxy-3, 4, 3′, 4′-tetrahydro-2H, 2′H-[3, 3′]bichromenyl-4, 4′-diol (**1**) (Sielinou et al., 2012), 4-hydroxybenzaldehyde (**2**) (Lin et al., 2011), 1,2,4-trihydroxybenzene (**3**) (Zhang et al., 2014), kaempferol-3-*O*-α-L-rhamnoside (**4**) (Hong et al., 2013), herbacetin (**5**) (Braunberger et al., 2013; El-Sayed et al., 1999), quercetin-3-*O*-α-L-rhamnoside (**6**) (Das et al., 2016), daucosterol (**7**) (Chen et al., 2006), and β-sitosterol (**8**) (Li et al., 2015).

4. Chemotaxonomic significance

In our present research, eight compounds including one chromene dimer (**1**), two benzenoids (**2**–**3**), three flavonoids (**4**–**6**), and two steroids (**7**–**8**) have been isolated from the EtOH extract of the leaves of *C. parthenoxylon* (Fig. 1). Notably, this is the first report of compounds **1**–**8** from the species *C. parthenoxylon*, compounds **1**–**6** from the genus *Cinnamomum*, and compounds **1**, **3**, **5** and **6** from the family Lauraceae. Adfa et al. (2016) have previously investigated the woods of *C. parthenoxylon* and reported the isolation of lignans and phenylpropanoids which have not been found in *C. parthenoxylon* leaves in our present research. Therefore, the chemical constituents in the leaves and the woods of *C. parthenoxylon* differ. These results suggested that the occurrence of lignans and phenylpropanoids in woods is chemical evidence for distinguishing plant parts, and implied that a systematic study on leaves and woods of *C. parthenoxylon* is required.

Benzenoids are the common characteristic chemical constituents within the genus *Cinnamomum*. Previous phytochemical investigation on the genus *Cinnamomum* led to the isolation of plenty of benzenoids, for instance, syringic acid and methyl-eugenol isolated from *C. tenuifolium* (Makino) Sugim. (Cheng et al., 2011), cinnamic acid and eugenol isolated from *C. macrostemon* Hayata (Li et al., 2015), vanillic acid isolated from *C. cassia* (Yuan et al., 1982), benzoic acid, 4-hydroxybenzoic acid and 3,4-dihidroxybenzoic acid detected from *C. verum* (Mateos-Martín et al., 2012), and *p*-hydroxybenzaldehyde isolated