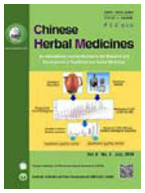

Available online at SciVarse ScienceDirect

Chinese Herbal Medicines (CHM)

ISSN 1674-6384

Journal homepage: www.tiprpress.com E-mail: chm@tiprpress.com

Letter

Chemical Constituents from *Pericarpium Citri Reticulatae*

Man-qin Fu, Geng-sheng Xiao, Ji-jun Wu, Yu-long Chen, Bo Zou, Ke-jing An, Yu-juan Xu*

Key Laboratory of Functional Foods, Ministry of Agriculture, Guangdong Key Laboratory of Agricultural Products Processing, Sericultural & Agric-Food Research Institute Guangdong Academy of Agricultural Sciences, Guangzhou 510610, China

ARTICLE INFO

Article history

Received: August 12, 2016

Revised: September 17, 2016

Accepted: October 10, 2016

Available online:

December 29, 2016

DOI:

10.1016/S1674-6384(17)60081-9

ABSTRACT

Objective To study the chemical constituents from *Pericarpium Citri Reticulatae* (*Citrus reticulata*). **Methods** The chemical constituents were isolated and purified by silica gel column, Sephadex LH-20, and ODS column chromatography. The structures were identified by spectral data. **Results** Nineteen compounds were isolated and identified as 4′,5,6,7-tetramethoxyflavone (**1**), 3,3′,4′,5,6,7,8-heptmethoxyflavone (**2**), sinensetin (**3**), 5-*O*-demethylnobiletin (**4**), tangeretin (**5**), nobiletin (**6**), apigenin (**7**), 5-*O*-desmethyltangeretin (**8**), 5,7-dihydroxy-3,3′,4′,6-tetramethoxyflavone (**9**), pachypodol (**10**), 4′,5,6,7-tetramethoxyflavanone (**11**), 3′,4′,5,7,8-pentamethoxyflavanone (**12**), agestricin C (**13**), scoparone (**14**), isoscopoletin (**15**), hesperidin (**16**), didymin (**17**), methylhesperidine (**18**), and naringin (**19**). **Conclusion** Compounds **9**-**15** are obtained from this plant for the first time.

Key words

agestricin C; *Citrus reticulata*; isoscopoletin; *Pericarpium Citri Reticulatae*; scoparone

© 2017 published by TIPR Press. All rights reserved.

1. Introduction

Pericarpium Citri Reticulatea (PCR, *Chenpi* in Chinese), the matured and dried tangerine pericarp, is one of the most famous Chinese herbal medicine officially listed in *Chinese Pharmacopoeia* 2015 and has been widely used for the treatment of indigestion and some inflammatory syndromes such as bronchitis and asthma (Liu et al, 2013). In addition, it is also often used as health-care food in the folk tradition of southern China with the effectiveness of soothing asthma, stimulating appetite, and enhancing immune system functions (Xu et al, 2014). And it is usually added to foods as a condiment or sometimes used to regulate the taste of Chinese medicines because of its smell, flavor, and curative effects (Xia et al, 2006). Among the main *Chenpi* cultivars, the dried ripe pericarp of *C. reticulate* (*Guangchenpi* in Chinese), grown in Xinhui district of Guangdong province in China, is regarded as the source of genuine PCR due to its excellent quality (Sun et al, 2010).

Phytochemical and pharmacological studies demonstrated that the major components in PCR were dietary flavonoids, which were generally categorized into two groups such as flavanone glycosides (mainly including hesperidin, etc.) and polymethoxylated flavones (PMFs, mainly including nobiletin, tangeretin, etc.) (Ho and Kuo, 2014). Hesperidin is a chemical reference substance singly used for quality control of PCR in *Chinese Pharmacopoeia* 2015 because of its extremely high concentration (no less than 3%) and wealth of various pharmacological activities such as anticancer (Devi et al, 2015), antioxidation (Pari et al, 2015), and anti-inflammation

*Correspondence author: Xu YJ E-mail: xyj6510@126.com Tel: +86-20-3721 9162 Fax: +86-20-8723 6354

Funds: Project of Guangdong Natural Science Foundation (No. 2015A030310284, No. 2015A030312001); Project of Chinese Public Welfare Industry Special (Agriculture) Research (No. 201503142-03); Project of Agricultural Research in Guangdong Province (No. 2015A020209065).

(Chang et al, 2015). PMFs generally presented as minor components in the aqueous extract of citrus plants though they were more active than the flavonoid glycosides (Xu et al, 2014). And they were found to possess antioxidant (Xi et al, 2014), anticancer (Kim et al, 2010; Sergeev et al, 2006), antiviral (Xu et al, 2014), antiangiogenesis (Saito et al, 2015), antimicrobial (Wu et al, 2014), and anti-inflammatory (Green et al, 2013) activities. However, up to date the investigation is not enough to elucidate the clinical use of this plant. Our further systematic study on this species resulted in the identification of 19 known compounds. These compounds were identified as 4′,5,6,7-tetramethoxyflavone (**1**), 3,3′,4′,5,6,7,8-heptmethoxyflavone (**2**), sinensetin (**3**), 5-*O*-demethylnobiletin (**4**), tangeretin (**5**), nobiletin (**6**), apigenin (**7**), 5-*O*-desmethyltangeretin (**8**), 5,7-dihydroxy-3,3′,4′,6-tetramethoxyflavone (**9**), pachypodol (**10**), 4′,5,6,7-tetramethoxyflavanone (**11**), 3′,4′,5,7,8-pentamethoxyflavanone (**12**), agestricin C (**13**), scoparone (**14**) isoscopoletin (**15**), hesperidin (**16**), didymin (**17**), methylhesperidine (**18**), and naringin (**19**). Herein, we demonstrated the isolation and structural elucidation of the isolated compounds, and compounds **9**−**15** were reported for the first time in this plant.

2. Materials and methods

2.1 Apparatus

TLC was performed on silica gel GF_{254} plates (Qingdao Marine Chemical Ltd., China). TLC coloring agent is 5% sulphuric acid in ethanol. For column chromatography, silica gel (100−300 mesh, Qingdao Marine Chemical Ltd., China), polyamide (60−100 mesh), Develosil ODS (75 μm, Nomura Chemical Co. Ltd., Japan), and Sephadex LH-20 (Pharmacia) were used. ESIMS were collected on an MDS SCIEX API 2000 LC/MS/MS Instrument. ^{1}H-NMR (600 MHz) and ^{13}C-NMR (150 MHz) data were recorded on a Bruker DRX−600 Instrument using the residual solvent peak as reference.

2.2 Plant materials

About 50 kg fresh fruits of *Citrus reticulata* Chachi were collected from Xinhui district of Guangdong province in China. Then, the peels were collected and dried in a heat pump dryer (GHRH−20, Guangdong Agri-machinery Research Institute, China) at 45 °C until the moisture ratio was reduced to about 0, which were used for the tested samples. The voucher specimens, identified by Prof. Yu-long Chen, have been deposited at the Laboratory of Guangdong Academy of Agricultural Sciences, China.

2.3 Extraction and isolation

The powdered dry PCR (10 kg) was extracted for three times with 95 % ethanol (3 × 10 L) at room temperature, for 3 d each. After evaporation of the solvent *in vacuo*, the combined crude ethanolic extract (1.5 kg) was suspended in water and partitioned successively with EtOAc (3 L × 3) and *n*-BuOH (3 L×3). The EtOAc-soluble extract (600 g) was subjected to silica gel column chromatography (CC), eluted with $CHCl_3$-MeOH mixtures with increasing polarities (90:10→10:90) to yield eight fractions (Frs. 1−8). Fr. 2 (80.5 g) was further separated by polyamide CC with MeOH-H_2O (70:30→100:0) to afford three sub-fractions (Frs. 2a−2c). Fr. 2a (20.8 g) was subjected to silica gel column eluted with petroleum ether-EtOAc (90:10→60:40) to afford compounds **1** (10 mg), **2** (18 mg), and **5** (280 mg). Fr. 2b (13.4 g) was subjected to recrystallization with MeOH to give compounds **6** (300 mg), **8** (20 mg), and **15** (50 mg). Fr. 2c (5.3 g) was further separated by Sephadex LH-20 CC using MeOH as mobile phase to yield compounds **3** (65 mg) and **16** (800 mg). Fr. 3 (63.8 g) was subjected to silica gel CC, eluted with petroleum ether-acetone (85:15→50:50) to afford four sub-fractions (Frs. 3a−3d). Fr. 3a (10.5 g) was subjected to silica gel CC, eluted with $CHCl_3$-MeOH (80:20→50:50) to yield compound **7** (40 mg). Fr. 3b (12.5 g) was subjected to ODS CC to yield compound **11** (20 mg). Fr. 3c (3.5 g) was separated by ODS CC with 70% MeOH, followed by Sephadex LH-20 CC with MeOH to obtain compounds **9** (50 mg) and **10** (32 mg). Fr. 3d (1.8 g) was subjected to silica gel CC, eluted with $CHCl_3$-MeOH (90:10→50:50) to yield compounds **12** (10 mg) and **13** (30 mg). Fr. 6 (150.8 g) was further separated by silica gel CC eluted with $CHCl_3$-MeOH (80:20→100:0) to afford three sub-fractions (Frs. 6a−6c). Fr. 6a (10.6 g) was subjected to silica gel CC, eluted with $CHCl_3$-MeOH (90:10→60:40) to yield compounds **4** (50 mg) and **14** (50 mg). Fr. 6b (40.5 g) was subjected to recrystallization with MeOH to give compounds **18** (88 mg) and **19** (40 mg). Fr. 6c (22.3 g) was subjected to silica gel CC, eluted with MeOH-H_2O (80:20→100:0) to yield compound **17** (38 mg).

3. Results

Compound **1**: white amorphous powder. ESI-MS *m/z*: 365 $[M + Na]^+$, 381 $[M + K]^+$; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 3.89 (3H, s, OCH_3), 3.96 (3H, s, OCH_3), 3.99 (3H, s, OCH_3), 4.01 (3H, s, OCH_3), 6.44 (1H, s, H-5), 6.61 (1H, s, H-3), 7.02 (2H, d, J = 9.0 Hz, H-3′, 5′), 7.89 (2H, d, J = 9.0 Hz, H-2′, 6′); ^{13}C-NMR (150 MHz, $CDCl_3$) data were given in Table 1. Compound **1** was identified as 4′,5,6,7-tetramethoxyflavone by comparison of the physical, ^{1}H-NMR, and ^{13}C-NMR data with the reported data (Zheng et al, 2013).

Compound **2**: yellow amorphous powder. ESI-MS *m/z*: 433 $[M + H]^+$; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 3.89 (3H, s, OCH_3), 3.95 (6H, s, 2 × OCH_3), 3.98 (3H, s, OCH_3), 4.02 (6H, s, 2 × OCH_3), 4.10 (3H, s, OCH_3), 7.02 (1H, d, J = 8.4 Hz, H-5′), 7.82 (1H, d, J = 1.8 Hz, H-2′), 7.84 (1H, d, J = 8.4, 1.8 Hz, H-6′); Compound **2** was identified as 3,3′,4′,5,6,7,8-heptmethoxyflavone by comparison of the physical, ^{1}H-NMR, and reference standard with the reported data (Zheng et al, 2013).

Compound **3**: yellow amorphous powder. ESI-MS *m/z*: 373 $[M + H]^+$, 395 $[M + Na]^+$, ^{1}H-NMR (600 MHz, $CDCl_3$)

Download English Version:

https://daneshyari.com/en/article/8692379

Download Persian Version:

https://daneshyari.com/article/8692379

Daneshyari.com