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Polymethoxylated flavonoids from *Citrus reticulata* Blanco

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ABSTRACT

A new glycoside of polymethoxylated flavonol, citrusunshitin A (**1**), together with five known analogues (**2**–**6**) were isolated from peels of *Citrus reticulata* Blanco. The structure of **1** was elucidated by NMR and MS data, and further confirmed by single-crystal X-ray diffraction. Compounds **1**–**5** were isolated from *C. reticulata* Blanco. for the first time, and **1**–**6** were considered as the chemotaxonomic markers for the species *C. reticulata* Blanco.

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1. Subject and source

The dried citrus peel, namely Pericarpium Citri Reticultae, is used as a traditional medicine for the treatment of stomachic, diaphoresis, and expectorans in China and Japan. According to Chinese Pharmacopoeia, it could be obtained from various species of the genus *Citrus* such as *C. reticulata* '*Chachi*', *C. reticulata* '*Unshiu*', and *C. reticulata* '*Dahongpao*' (Chinese Pharmacopoeia Commission, 2015). *C. reticulata* '*Unshiu*', also known as *Citrus reticulata* Blanco, is widely distributed in south area of the Yangtze River in China (Flora of China Editorial Committee (1997)).

The pericarps of *Citrus unshiu* were collected in Guilin, Guangxi Zhuang Autonomous Region of China in August 2013, and were identified by one of the authors (Prof. L. Jiang). A voucher specimen (chenpi-2013-08-03) was deposited at School of Pharmaceutical Sciences, Sun Yat-sen University.

2. Previous work

Apart from essential oils, the major chemical constituents of the pericarps of *C. unshiu*, some types of limonoids, flavonoids (Kuroyanagi et al., 2008), and alkaloids (Dragull et al., 2008) were also isolated from this plant. These flavonoids, especially the polymethoxylated flavones, displayed various biological activities such as anticarcinogenic (Walle, 2007), anti-inflammatory (Lin et al., 2003; Li et al., 2007), and antioxidative (Miyake, 2006) properties.

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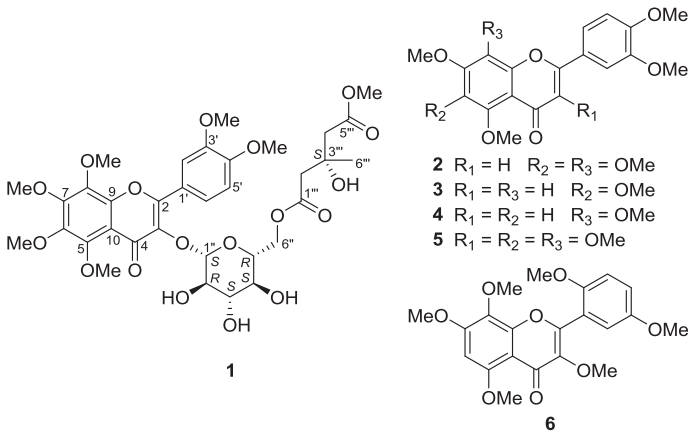

Fig. 1. Chemical structures of **1**–**6**.

3. Present study

3.1. Extraction and isolation

The dried and powdered peels of *C. unshiu* (8 kg) were extracted with 80% CH_3OH (30 L, three times) under room temperature by using ultrasound vibration. After filtration, the organic solvent was removed from the combined extracts under vacuum to afford a total crude extract (2 kg). The residue was dissolved in H_2O and then extracted successively with petroleum ether (PE), EtOAc, and *n*-BuOH. The EtOAc extract (55 g) was subjected to MCI gel column chromatography (CC) eluted with MeOH/H_2O gradient system (0:100 → 100:0) to afford Fr. A–E. Fr. B (3.9 g) was further separated by silica gel CC eluting with CH_2Cl_2/MeOH (100:0 → 0:100) to obtain five sub-fractions (Fr. B1–B5). Fr. B3 was loaded onto a Sephadex LH-20 column eluted with CH_2Cl_2/MeOH (1:1) and reversed-phase C_{18} (RP-C_{18}) CC (MeOH/H_2O, 7:3 → 10:0) to yield compound **1** (17 mg). Fraction E (3.2 g) was subjected to a silica gel CC eluted with CH_2Cl_2/MeOH (100:0 → 0:100), followed by a Sephadex LH-20 column (MeOH), and then purified by preparative HPLC to afford compounds **2** (39 mg), **3** (5 mg), **4** (21 mg), **5** (37 mg), and **6** (4 mg). The chemical structures of **1**–**6** are shown in Fig. 1.

3.2. Structure elucidation

Citrusunshitin A (**1**) was obtained as a yellow crystal. Its molecular formula was determined to be $C_{34}H_{42}O_{18}$ by the HRESIMS ion at *m/z* 739.2415 $[M + H]^+$ (calcd 739.2444). The IR spectrum of **1** indicated that the presence of hydroxyl (3407 cm^{-1}), carbonyl (1735 cm^{-1}), and aromatic (1599, 1516, and 1483 cm^{-1}) groups. The 1D NMR data of **1** (Table 1)

Table 1
^1H NMR (600 MHz) and ^{13}C NMR (150 MHz) data of compound **1** in $CDCl_3$ (δ in ppm).

No.	δ_H (*J* in Hz)	δ_C, type	No.	δ_H (*J* in Hz)	δ_C, type
2		155.4, C	Glc-3″	3.67, overlapped	77.2, CH
3		137.3, C	Glc-4″	3.52, m	69.7, CH
4		174.2, C	Glc-5″	3.42, m	74.3, CH
5		148.2, C	Glc-6″	4.27, dd (12.0, 5.2) 4.11, overlapped	63.6, CH_2
6		144.3, C	1‴		171.7, C
7		152.1, C	2‴	2.54, d (15.1) 2.47, d (15.1)	44.7, CH_2
8		137.9, C	3‴		69.8C,
9		146.9, C	4‴	2.57, d (15.3) 2.47, d (15.3)	44.9, CH_2
10		114.3, C	5‴		172.3, C
1′		122.6, C	6‴	1.24, s	27.3, CH_3
2′	7.94, d (2.0)	112.5, CH	5-OMe	3.935, s	62.5, CH_3
3′		148.4, C	6-OMe	3.92, s	61.9, CH_3
4′		151.7, C	7-OMe	4.10, s	61.8, CH_3
5′	6.95, d (8.7)	110.7, CH	8-OMe	3.99, s	62.2, CH_3
6′	7.87, dd (8.7, 2.0)	122.7, CH	3′-OMe	3.940, s	56.0, CH_3
Glc-1″	4.97, d (7.2)	104.9, CH	4′-OMe	3.937, s	56.0, CH_3
Glc-2″	3.67, overlapped	74.4, CH	5‴-OMe	3.64, s	51.9, CH_3

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