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Cytotoxic phenylpropanoid glycosides from *Fagopyrum tataricum* (L.) Gaertn

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ABSTRACT

Fagopyrum tataricum (L.) Gaertn (tartary buckwheat) is an ancient dicotyledonous crop belonging to Polygonaceae family. Besides its benefits for human consumption, tartary buckwheat is also an important folk medicine in China for its antioxidant, antitumour, hypotensive, hypoglycaemic and hypolipidaemic activities. Phytochemical investigation of the ethyl acetate fraction of tartary buckwheat roots led to the isolation of seven new phenylpropanoid glycosides, tatarisides A–G (**1**–**7**), together with a known phenylpropanoid glycoside, diboside A (**8**). Their structures were elucidated by means of spectroscopic methods. All compounds (**1**–**8**) were evaluated for their cytotoxic activity against four human cancer cell lines (A-549, HCT116, ZR-75-30 and HL-60). Tatariside C (**3**) was the most active compound with IC_{50} values of 6.44–7.49 μg/ml against the four tested cell lines.

1. Introduction

The genus *Fagopyrum*, a member of family Polygonaceae, currently comprises 15 species, which are mainly distributed in the North Temperate Zone. A total of eight species, including some common crops and medicinal plants, occur in China, such as tartary buckwheat (*Fagopyrum tataricum* (L.) Gaertn), buckwheat (*Fagopyrum esculentum* Moench.), *Fagopyrum dibotrys* (D. Don) Hara., etc. (Editor committee of Quan Guo Zhong Cao Yao Hui Bian, 1976). The former two species are the main buckwheats, consumed all around the world as a potential "functional food" material (Inglett, Chen, Berhow, & Lee, 2011; Kim et al., 2008; Ruan, Chen, Shao, Wu, & Han, 2011), particularly with respect to their seeds and seed sprouts due to the abundance of phenolic compounds, high quality proteins and a well balanced amount of essential amino acids and minerals (Javornik, Eggum, & Kreft, 1981; Kim, Kim, & Park, 2004; Wijngaard & Arendt, 2006).

Besides its benefits for human as a valuable crop, tartary buckwheat is also important as a pharmaceutical plant, used for antioxidant, antitumour, hypotensive, hypoglycaemic and hypol ipidaemic purposes (Guo, Zhu, Zhang, & Yao, 2007; Liu, Chen, Yang, & Chiang, 2008; Ren et al., 2001; Tomotake et al., 2006; Yao et al., 2008). Phytochemical investigations of this species mainly focused on the seeds and revealed the presence of abundant flavonoids and phenolics (Fabjan et al., 2003; Němcová, Zima, Barek, & Janovská, 2011). Tartary buckwheat seeds have been reported to contain more than 50 times higher phenolics content than that of common buckwheat (Fabjan et al., 2003; Kim et al., 2008), consistent with its significant bioactivity of antioxidant and anti-inflammation (Hu et al., 2009; Liu et al., 2008). In addition, the root is also an important medicinal part of tartary buckwheat, which was traditionally used to treat some stubborn and chronic diseases, such as cancers, rheumatic disorders and general debility in folk medicine in Shanxi, China (Guo, 2003; Guo, Bu, Wang, & Lv, 2006). Tartary buckwheat root is also called "Qiao ye qi", indicating that it might have similar pharmacological effects as "San qi" (*Panax notoginseng* roots) (Guo, 2003). However, to the best of our knowledge, the roots of tartary buckwheat have so far been chemically and pharmacologically unknown, thus being casted away after seeds harvest year by year, with high biomass, which is a waste of potential medicinal resource. Our study was therefore aimed to investigate the secondary metabolites from tartary buckwheat roots and evaluate the antitumour activity of isolated compounds, thus providing scientific basis for making full use of *F. esculentum* (tartary buckwheat). As a result, seven new phenylpropanoid glycosides (Fig. 1), tatarisides A–G (**1**–**7**) were isolated and identified from tartary buckwheat roots, together with a known phenylpropanoid glycoside, diboside A (8). The isolation, structure, elucidation and evaluation for cytotoxic activity of these compounds are described herein.

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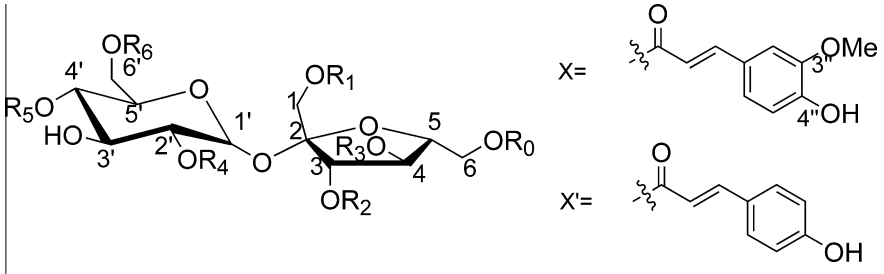

	R_0	R_1	R_2	R_3	R_4	R_5	R_6
1	X'	$COCH_3$	X'	H	$COCH_3$	H	$COCH_3$
2	X'	$COCH_3$	X'	H	$COCH_3$	H	X
3	X'	$COCH_3$	X'	H	$COCH_3$	$COCH_3$	X
4	X	H	X'	H	$COCH_3$	H	X'
5	X'	$COCH_3$	X'	H	$COCH_3$	H	H
6	X	X'	X	H	H	H	X'
7	X'	X'	X	H	H	H	H
8	X	X'	X'	H	H	H	X'

Fig. 1. Phenylpropanoid glycosides (**1**–**8**) isolated from tartary buckwheat roots.

2. Materials and methods

2.1. General

Optical rotations were acquired with a Perkin-Elmer 341 polarimeter. IR spectra were recorded on a Bruker Vector 22 spectrometer with KBr pellets. UV spectra were run on a Varian Cary Eclipse 300 spectrophotometer. NMR spectra were recorded on a Bruker Avance 600, or Avance 400 NMR spectrometer, with TMS as an internal standard. HRESIMS were measured using a Q-TOF micro mass spectrometer (Waters, USA). Materials for column chromatography were silica gel (100–200 mesh; Huiyou Silical Gel Development Co. Ltd., Yantai, China), silica gel H (10–40 μm; Yantai), Sephadex LH-20 (40–70 μm; Amersham Pharmacia Biotech AB, Uppsala, Sweden), and YMC-GEL ODS-A (50 μm; YMC, Milford, MA). HSGF254 silica gel TLC plates (Yantai) were used for analytical TLC.

2.2. Plant material

The roots of tartary buckwheat were collected from JianDe, Zhejiang Province, China in August 2010 and were identified by Prof. Lu-Ping Qin, Department of Pharmacology, Second Military Medical University. A voucher specimen (#20100816) was deposited in the Department of Pharmacology, Second Military Medical University, Shanghai, PR China.

2.3. Extraction and isolation

The roots and roughly powdered material (4.0 kg) was extracted three times with 80% (v/v) ethanol (32 l × 3), under reflux for 2 h each time. After removal of the solvent by evaporation, the extracts were suspended in water and partitioned with petroleum ether (PE), CH_2Cl_2, EtOAc and *n*-BuOH, successively. The EtOAc extract (22.0 g) was subjected to silica gel column chromatography, eluted with CH_2Cl_2–MeOH gradient (50:1, 30:1, 15:1, 5:1, 3:1; each 4 l, v/v) to give three fractions (I–III). Fraction I was repeatedly subjected to silica gel column chromatography (CC) with CH_2Cl_2–MeOH gradient (20:1, 10:1; each 2 l, v/v) to afford two fractions (I_1, I_2). Fraction I_1 was submitted to Sephadex LH-20 (MeOH:H_2O, 8:2; 500 ml, v/v) to give compounds **1** (13.8 mg) and **2** (86 mg). Fraction I_2 was subjected to Sephadex LH-20 (MeOH:H_2O, 8:2; 500 ml, v/v), to yield compound **3** (29 mg). Fraction II was subjected to silica gel column chromatography (CC), with CH_2Cl_2–MeOH gradient (20:1; 2 l, v/v) and Sephadex LH-20 (MeOH:H_2O, 8:2; 500 ml, v/v), to give compounds **4** (28 mg) and **5** (20 mg). Fraction III was subjected to silica gel column chromatography (CC) with CH_2Cl_2–MeOH gradient (15:1, 5:1; each 2 l, v/v), to give two fractions (III_1, III_2). Fractions III_1 was purified with Sephadex LH-20 (MeOH:H_2O, 8:2; 500 ml, v/v), to afford compound **6** (608 mg). Fraction III_2 was subjected to Sephadex LH-20 (MeOH:-H_2O, 8:2; 500 ml, v/v), to yield compounds **7** (186 mg) and **8** (130 mg).

Tatariside A (**1**)*:* yellowish amorphous powder; $[\alpha]_D^{20} + 46.0^\circ$ (c 0.12, MeOH); UV (MeOH) λ_{max} 288, 314 nm; IR (KBr) υ_{max} 3446, 1717, 1604, 1514, 1383, 1167; ^{1}H NMR and ^{13}C NMR spectra (Tables 1 and 2); HRESI-MS *m*/*z* 778.2567 $[M+NH_4]^+$ (calcd 778.2553, $C_{36}H_{40}O_{18}$).

Tatariside B (**2**): yellowish glass; $[\alpha]_D^{20} + 37.5^\circ$ (*c* 0.12, MeOH); UV (MeOH) λ_{max} 289, 314 nm; IR (KBr) υ_{max} 3425, 1685, 1584, 1514, 1383, 1167; ^{1}H NMR and ^{13}C NMR spectra (Tables 1 and 2); HRESI-MS *m*/*z* 912.2931 $[M+NH_4]^+$ (calcd 912.2920, $C_{44}H_{46}O_{20}$).

Tatariside C (**3**): yellowish amorphous powder; $[\alpha]_D^{20} + 41.2^\circ$ (*c* 0.12, MeOH); UV (MeOH) λ_{max} 290, 316 nm; IR (KBr) υ_{max} 3445, 1716, 1632, 1604, 1514, 1383, 1168; ^{1}H NMR and ^{13}C NMR spectra (Tables 1 and 2); HRESI-MS *m*/*z* 954.3035 $[M+NH_4]^+$ (calcd 954.3027, $C_{46}H_{48}O_{21}$).

Tatariside D (***4***)*:* yellowish amorphous powder; $[\alpha]_D^{20} + 5.6^\circ$ (*c* 0.12, MeOH); UV (MeOH) λ_{max} 290, 315 nm; IR (KBr) υ_{max} 3408,