Chemical Constituents from *Thalictrum ramosum*

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Abstract

*Thalictrum ramosum* is a plant from *Thalictrum genus*, and is also one substitute of Coptidis Rhizoma in Chinese folk medicine. Phytochemical investigation on the EtOH extract of *T. ramosum* led to the isolation of 9 compounds. Their structures were elucidated as berberine (1), columbamine (2), thalidastine (3), magnoflorine (4), 1-(4-hydroxy-3-methoxy)-phenyl-2-[4-(1,2,3-trihydroxy-propyl)-2-methoxy]-phenoxy-1,3-propandiol (5), citrose B (6), glochidionioside A (7), apigenin 6,8-di-C-β-D-xylopyranoside (8) and hydrangeofolin I (9) through 1D and 2D NMR, MS experiments and comparison with literature data. All compounds are isolated from this plant for the first time.

Keywords: Alkaloid; Flavone C-glycoside; Lignan; Megastigmpane glucoside; *Thalictrum ramosum*

Introduction

*Thalictrum* often refers to the plants form *Thalictrum genus* which has been used in Tibetan medicine and Mongolian medicine in China for thousands of years. It was found that 29 plants from *Thalictrum* genus were used as folk medicine in China and 14 of them were used as the succedaneum of Coptidis Rhizoma (Huanglian in Chinese) [1]. The *Thalictrum* herbs were also called ‘mawei huanglian’ or ‘mawei lian’ (mawei in Chinese means horsetail) because they have a horse-tail-like appearance and anti-inflammation and antibacterial functions resembling to Coptidis Rhizoma. Modern pharmacological investigations revealed that the important associations of *Thalictrum* with the bioactivities of antitumor, anti-inflammation, antivirus, and effects on the cardio-vascular, autoimmune and central nervous system, etc [2-3]. Some secondary metabolites including alkaloids, triterpenes, flavonoids, steroids and organic acids have been reported from plants of *Thalictrum* genus [3-7].

*T. ramosum*, is one of the substitutes of Coptidis Rhizoma. Recently, we reported some cycloartane triterpene saponins from the plants in *Thalictrum* genus including this herb [1-3]. Further phytochemical investigations on the n-BuOH-soluble fraction of the EtOH extract of *T. ramosum* has led to the purification of 9 compounds and their structures were elucidated as: berberine (1), columbamine (2), thalidastine (3), magnoflorine (4), 1-(4-hydroxy-3-methoxy)-phenyl-2-[4-(1,2,3-trihydroxy-propyl)-2-methoxy]-phenoxy-1,3-propandiol (5), citrose B (6), glochidionioside A (7), apigenin 6,8-di-C-β-D-xylopyranoside (8) and hydrangeofolin I (9) by means of UV, IR, MS, NMR, HMBC, H15Q, 1H-1H COSY, ROESY, etc.

Experimental

General experimental procedures

HR-ESI-MS measurements were carried out on an Agilent series 1200SL HPLC (Agilent Technologies, USA). NMR spectra were recorded on Bruker Avance-300, 400, 500 and 600 spectrometers. Prep-HPLC purification was carried out on a Cosmosil 5C18-AR-II column (250 mm × 20 mm i.d., 5 mm, Cosmosil, Japan) on a Shimadzu LC-20AP Series prep-HPLC apparatus (Shimadzu, Japan). Column chromatography was performed on ODS (Alltech, USA), silica gel (200 - 300 mesh, Qingdao Marine Chemical Group Co., Qingdao, China), Macroporous resin (D101, Haiguang Chemical Group Co., Tianjin, China), Sephadex LH-20(Pharmacia, USA). The solvents of analytical grade, used for extraction, gel chromatography and macroporous resin column chromatography, were supplied by Kaitong Chemical Co. Ltd. (Tianjin, China). Solvents applied for preparative column and HPLC analysis were of HPLC grade and purchased from Merck (Darmstadt, Germany). Distilled water was purified with a Millipore Milli Q-Plus system (Millipore, Milford, MA, USA).

Plant material

The rhizomes of *T. ramosum* Boivin were collected from Emei, Sichuan Province, China in 2012, and authenticated by Dr. Chun-Feng Qiao. A voucher specimen was deposited in Institute of Traditional Chinese Medicine, Guangdong Food and Drug Vocational College.

Isolation and purification

Dried plants of *T. ramosum* were powdered and extracted with 95% ethanol (3 × 20L) under reflux. The ethanol extract was suspended in water and then successively extracted with petroleum ether, EtOAc and n-BuOH.

The n-BuOH solution was concentrated and gives a residue (344 g), which was separated by a silica gel column using CHCl3-MeOH
Chemical study on Thalictrum ramosum led to the isolation of nine compounds including four alkaloids, one lignan, two megastigmane glycosides, one flavone C-glycoside and a benzylated disaccharide. And their structures were characterized as follows.

**Compound 1 yellow crystals:** C\textsubscript{20}H\textsubscript{18}NO\textsubscript{4}. ESI-MS m/z 342 [M+H]-. 1\textsuperscript{H} NMR (CD\textsubscript{3}OD, 500 MHz) δ: 6.04 (1H, d, J = 1.8 Hz, H-2), 7.02 (1H, d, J = 1.7 Hz, H-2′), 6.90 (1H, d, J = 8.2 Hz, H-5′), 6.85 (1H, dd, J = 8.2, 1.6 Hz, H-6′), 6.84 (1H, dd, J = 8.2, 1.6 Hz, H-6), 6.74 (1H, d, J = 8.1 Hz, H-5), 4.84 (1H, d, J = 5.8 Hz, H-7), 4.56 (1H, d, J = 6.0 Hz, H-7′), 4.36 (1H, dt, J = 5.7, 3.8 Hz, H-8), 3.87 (1H, dd, J = 12.0, 3.7 Hz, H-9a), 3.83 (3H, s, 3′-OMe), 3.80 (1H, dd, J = 12.0, 3.7 Hz, H-9b), 3.67 (1H, dt, J = 5.9, 4.1 Hz, H-9′b), 3.50 (1H, dd, J = 11.2, 4.0 Hz, H-9′a), 3.38 (1H, dd, J = 11.2, 4.1 Hz, H-9b); 1\textsuperscript{3}C NMR (CD\textsubscript{3}OD, 100 MHz) δ: 151.7 (C-3′), 148.7 (C-3), 148.6 (C′-4′), 147.0 (C-4), 137.1 (C′-1′), 134.2 (C-1), 121.0 (C-6′), 120.5 (C-6), 118.7 (C-5′), 115.6 (C-5), 112.3 (C-2′), 111.8 (C-2), 86.2 (C-7′), 77.4 (C-8′), 75.1 (C-7′), 74.7 (C-1′), 64.2 (C-9′), 62.2 (C-9), 56.5 (3′-OCH\textsubscript{3}), 56.3 (3-OCH\textsubscript{3}). These data were consistent those in the literature [11]. Therefore, compound 5 was elucidated as 1-(4-hydroxy-3-methoxy)-phenyl-2-[4-(1,2,3-trihydroxy-propyl)-2-methoxy]-phenoxycyclic-1,3-propanold.
Thalictrum showed different morphological features from Coptidis Rhizoma, many Thalictrum plants have a very close name to Coptidis Rhizoma (horsetail-Coptidis-Rhizoma) and were used as the succedaneum of Coptidis Rhizoma for the treatment of inflammation and infectious diseases for thousands years in China. As is known, bioactivities and functions of herbal medicine are closely related with its chemical composition. The phytochemical investigation in current study and reported literatures showed that the plants of those two genera (Thalictrum and Coptis) contain some same constituents such as berberine-type alkaloid [16-18]. Berberine-type alkaloids showed potent anti-inflammatory and antibacterial activities [19-23]. Compounds berberine (1), columbamine (2) and magnoflorine (3) has also been reported from Coptidis Rhizoma before [10]. Those compounds occurrence in both genera led them to have some same functions and explained why those Thalictrum plants were used as the substitute of Coptidis Rhizoma for the treatment of inflammatory and infectious diseases. Furthermore, together with Thalictrum genus, Coptis genus, the source of Coptidis Rhizoma, also belongs to the subfamily Thalictrideae. Researches on the chemical composition and pharmacological activities should be beneficial for the further development and application of T. ramosum and other plants of Thalictrum genus.

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References


