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Chemical constituents from the aerial parts of *Meconopsis horridula* (Papaveraceae)

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ABSTRACT

Chemical investigation of the aerial parts of *Meconopsis horridula* led to the isolation and structural identification of nine flavonoids, two alkaloids and five terpenoids. Their structures were determined by comparison of ^{1}H and ^{13}C NMR data with those reported in literature. The discovery of alkaloid cavidilinine (**11**) and two pentacyclic triterpenoids (**15** and **16**) from *M. horridula* provides evidence to support the view that Fumarioideae and Papaveroideae should be combined into a single family Papaveraceae.

1. Subject and source

Species of *Meconopsis* are known as “Himalayan poppy” and “the Daughter of the Sun” because of their showy blooms. In Tibet, “the White Tara” generally refers to the flowers of *Meconopsis*, which are called as “Utpala immortal grass” (Sun, 2008).

Meconopsis (Papaveraceae) consists of 54 species all over the world, and 53 species are distributed in the Sino-Himalayan region. Of these 43 species occur in China, mainly distributed in Southwestern regions, particularly in the Qinghai-Tibet plateau (Zhang and Grey-Wilson, 2008a). *Meconopsis horridula* Hook. f. & Thomson is an annual species usually growing on grassy slopes, screes, rock ledges, or stabilized moraines at an altitude of 3600–5400 m, which is close to the limit for vegetation (Zhang and Grey-Wilson, 2008b). The whole plant is traditionally used as a Tibetan medicine for the treatment of headache and fractures (Northwest Institute of Plateau Biology, Chinese Academy of Sciences, 1991).

The aerial parts of *M. horridula* were collected in August, 2012, in Lebu-Gou of Cona County at Shannan district of Tibet Autonomous Region of China. The plant was identified by Prof. Chunsheng Liu (School of Chinese Materia Medica, Beijing University of Chinese Medicine, BUCM). A voucher specimen (No. MH201208) is deposited in the Modern Research Center for Traditional Chinese Medicine, BUCM.

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2. Previous work

Previous phytochemical investigations on the genus of *Meconopsis* revealed the presence of flavonoids, alkaloids, and triterpenoids (Wu et al., 2011). Chemical research on *M. horridula* led to the isolation of fifteen flavonoids, including apigenin, luteolin, hydnocarpin, kaempferide, luteolin 7-*O*-*β*-D-glucopyranoside, quercetin and its glycoside, kaempferol and its glycosides, tricin and its glycoside, and a cyanidin glycoside (Ma et al., 2009; Takeda et al., 1996; Wu et al., 2012), alkaloids including protopine, 8, 9-dihydroprooxocryptochine, (−)-reframoline, (−)-amurensinine (Wu et al., 2009), cinnamamide, *N*-*p*-hydroxyl-*trans*-coumaroyltyramine (Wu et al., 2012), and *β*-sitosterol (Ma et al., 2009).

3. Present study

As a part of systematic studies to clarify the chemical constituents of the genus *Meconopsis*, a phytochemical investigation on the aerial parts of *M. horridula* was undertaken, which led to the isolation and structural identification of nine flavonoids, two alkaloids and five terpenoids. By spectroscopic analysis and comparison of the ^{1}H and ^{13}C NMR data with those reported in the literature, their structures were determined as luteolin (**1**), tricin (**2**), tricin 7-*O*-*β*-D-glucopyranoside (**3**), kaempferol (**4**), quercetin (**5**), kaempferol 3-*O*-*β*-D-glucopyranoside (**6**), quercetin 3-*O*-*β*-D-glucopyranoside (**7**), kaempferol 3-*O*-*β*-D-glucopyranosyl-(1-2)-*β*-D-glucopyranoside (**8**), kaempferol 3-*O*-*β*-D-xylopyranosyl-(1-2)-*β*-D-glucopyranoside (**9**), norsanguinarine (**10**), cavidilinine (**11**), 5, 15-*O*-diacetyl-3-*O*-phenyl-6(17)-epoxylathyrol (**12**), 5-hydroxygeranyllinalol (**13**), cycloart-23-ene-3*β*, 25-diol (**14**), 3*α*-hydroxyolean-12-en-30-oic acid (**15**), and 3*β*-hydroxyolean-12-en-30-oic acid (**16**) (Fig. 1). Among them, compounds **9** and **11**–**16** were isolated from the genus for the first time, and **7** and **10** were isolated from the species for the first time. We describe herein the isolation of these compounds and their chemotaxonomic significances.

The dried aerial parts (ca. 25 kg) of *M. horridula* were exhaustively extracted with 95% EtOH twice (200 L × 2, 2 h each time), and the solvent was combined and evaporated under reduced pressure. The residue was partitioned in H_2O and extracted with petroleum ether (PE), ethyl acetate (EtOAc), and *n*-butanol to provide the extracts. The *n*-BuOH extract (215 g) was subjected to column chromatography (CC) over silica gel eluted with a gradient of $CHCl_3$/MeOH (C-M, 50:1 → 0:1, v/v) to yield Frs. Ba–Bh. Fr. Bc was further separated on silica gel CC (PE/EtOAc, 3:1) and Sephadex LH-20 CC (C-M, 1:1) to get **2** (100 mg), **10** (3 mg), and **11** (5 mg). Fr. Bd was chromatographed on silica gel CC ($CHCl_3$/EtOAc, 1:1) and Sephadex LH-20 CC (C-M, 1:1) to yield **1** (3 mg). Fr. Be was further purified by silica gel CC (EtOAc/MeOH/H_2O, 50:10:1) and ODS CC (MeOH/H_2O, 1:1) to get **3** (2 mg) and **6** (2 g). Fr. Bf was separated on silica gel CC (EtOAc/MeOH/H_2O, 60:10:1) and ODS CC (MeOH/H_2O, 7:3) to yield **7** (3 mg), **8** (100 mg), and **9** (8 mg). The EtOAc extract (120 g) was subjected to silica gel CC eluted with a gradient of $CHCl_3$/MeOH (100:1 →0:1) to yield Frs. Ea–Ej. Fr. Ef was separated on silica gel CC ($CHCl_3$/EtOAc, 2:1) and Sephadex LH-20 CC (MeOH) to yield **4** (5 mg). Fr. Eg was purified by Sephadex LH-20 CC (C-M, 1:1) to get **5** (100 mg). The PE extract (650 g) was subjected to silica gel CC eluted with PE/EtOAc (6:1) to yield 19 fractions (Frs. Pa–Ps). Fr. Pg was further chromatographed on

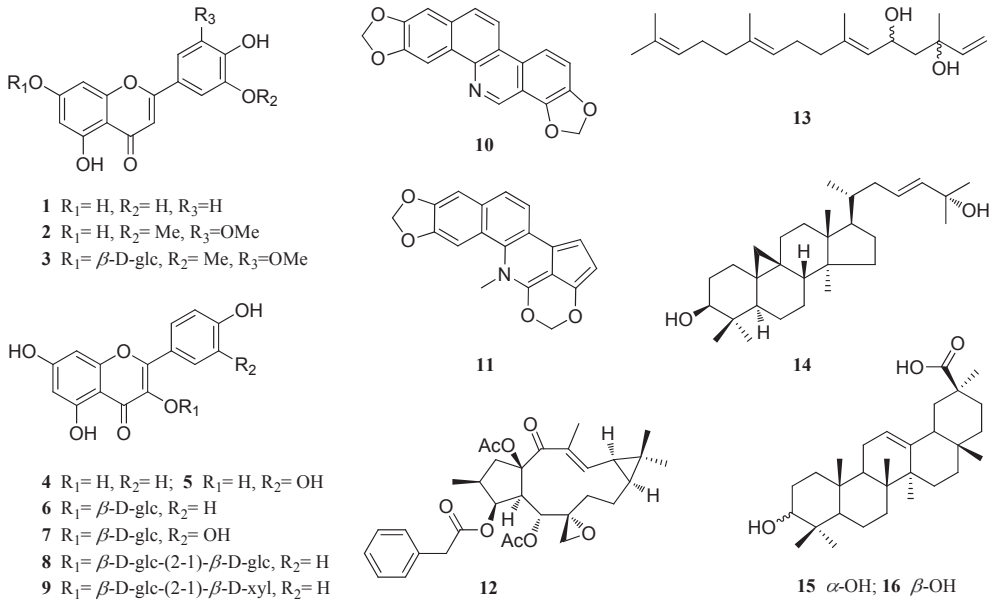

Fig. 1. Chemical structures of compounds **1**–**16** from *Meconopsis horridula*.