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Flavonoids and polyacetylenes from the aerial parts of *Bidens tripartita*

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ABSTRACT

Fourteen flavonoids (**1**–**14**) and two polyacetylenes (**15** and **16**) were isolated from the aerial parts of *Bidens tripartita*. Thirteen compounds (**1**–**7**, **9**, **11**, **12**, and **14**–**16**) were isolated from this species for the first time, of which a flavonoid (**11**) was obtained for the first time from the genus *Bidens*. The chemotaxonomic significance of these compounds was summarized.

1. Subject and source

The genus *Bidens* (Asteraceae) includes about 230 species worldwide and occurs mainly in the tropical and temperate zones. There are 9 species and 2 varieties grown in China that are distributed in all parts of the country (Wu, 1996). Some species have been used as folk medicine, such as *Bidens tripartita*, *Bidens pilosa*, *Bidens frondosa*, and so on (Song, 1999). *B. tripartita* was collected in July 2007 from Wanxian mountain, Hui county of Henan province, China, and identified by Prof. Cheng-Ming Dong (School of Pharmacy, Henan University of Traditional Chinese Medicine). A voucher specimen (BT200707) has been deposited at the Herbarium, School of Pharmacy, Xinxiang Medical University.

2. Previous work

Previous phytochemical studies on *B. tripartita* have resulted in the isolation and identification of flavonoids (Serbin et al., 1972a,b, 1975a,b) and coumarins (Serbin et al., 1972c).

3. Present study

The dried, powdered aerial parts of *B. tripartita* (7.5 kg) were extracted with 90% ethanol three times (3 × 80 L) at room temperature. The solvent was removed under reduced pressure to give a residue (850 g), which was suspended in H_2O and successively partitioned with petroleum ether, EtOAc, and *n*-BuOH, respectively. The EtOAc extract (90 g) was subjected to column chromatography (CC) on silica gel eluted with a gradient of petroleum ether–EtOAc (1:0, 10:1, 5:1, 2:1, 1:1, 1:2) to give fractions A–H. Fraction C was chromatographed over silica gel (petroleum ether–EtOAc, 50:1 → 5:1) and purified by CC on Sephadex LH-20 (MeOH) to afford compounds **1** (32 mg), **2** (12 mg), **9** (8.5 mg), **11** (9.2 mg), **12** (11 mg), and **13** (24 mg).

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Fraction D was isolated by CC on silica gel eluted with a gradient of petroleum ether–EtOAc (30:1 → 1:1) to yield compounds **4** (27 mg), **8** (7.8 mg), **14** (13 mg), **15** (9.0 mg), and **16** (10 mg). Fraction E was separated by CC on silica gel eluted with a gradient of CH_2Cl_2–Me_2CO (20:1 → 1:1) to afford compounds **3** (6.8 mg), **6** (8.4 mg), and **7** (11 mg). Fraction F was subjected to CC on Sephadex LH-20 eluted with MeOH to yield compounds **5** (5.9 mg) and **10** (9.5 mg).

The structures of the isolated compounds were elucidated on the basis of their spectroscopic data (IR, MS, 1D and 2D NMR, and ORD), and by comparison of their spectroscopic data with those reported in the literature. Their structures were identified as butein (**1**) (Tian et al., 2011), 3,2′,4′-trihydroxy-4-methoxychalcone (**2**) (Tian et al., 2011), 4′-*O*-β-D-glucopyranosyl-2′,3-dihydroxy-4-methoxychalcone (**3**) (Calanasan and Macleod, 1998), okanin (**4**) (Hoffman and Hölzl, 1989), okanin 4′-*O*-β-D-glucopyranoside (**5**) (Hoffman and Hölzl, 1988a), okanin 4′-*O*-(6″-*O*-acetyl-β-D-glucopyranoside) (**6**) (Hoffman and Hölzl, 1988b), bidenoside G (**7**) (Li et al., 2005), luteolin (**8**) (Tian et al., 2011), diosmetin (**9**) (Xie et al., 2009), luteoside (**10**) (Abdel-Gawad and El-Zait, 1981), axillarin (**11**) (Ai-Yahya et al., 1988), quercetagetin 3,6,3′-trimethyl ether (**12**) (Exner et al., 1981), sulfuretin (**13**) (Julian and Crawford, 1972), 6,7,3′,4′-tetrahydroxyaurone (**14**) (Venkateswarlu et al., 2004), 2-β-D-glycopyrasyloxy-1-hydroxytrideca-3,5,7,9,11-pentayne (**15**) (Rücker et al., 1992), and 3(*R*),8(*E*)-8-decene-4,6-diyne-3,10-dihydroxy-1-*O*-β-D-glucopyranoside (**16**) (Wang et al., 2001) (Fig. 1).

4. Chemotaxonomic significance

The genus *Bidens* (Asteraceae) is an important flavonoid and polyacetylene-bearing plant genus (Karikome et al., 1992; Li et al., 2003; Mccormick et al., 1984; Redl et al., 1993; Rybalchenko et al., 2010; Tommasi and Pizza, 1997; Tommasi et al., 1998; Wang et al., 2001, 2010). Therefore, the two kinds of compounds are commonly considered as chemotaxonomic markers for the genus *Bidens*.

The present paper reports the isolation of fourteen flavonoids (**1**–**14**) and two polyacetylenes (**15** and **16**) from *B. tripartita*. Among them, compound **11** was isolated for the first time from the genus *Bidens*. In addition, compounds **1**–**7**, **9**, **12**, and **14**–**16** were obtained from this species for the first time. Okanin (**4**) and okanin 4′-*O*-β-D-glucopyranoside (**5**) are two flavonoids which have once been isolated from other species of *Bidens* (Huang et al., 2006; Karikome et al., 1992; Sashida et al., 1991). Furthermore, both of them have been found in species of *Coreopsis* (Zhang et al., 2006). Previous phytochemical investigations indicated that there is a close genetic relationship between the genus *Bidens* with the genus *Coreopsis* because they are rich in polyacetylenes (Zhou and Duan, 2005). From our research and literature reported, it is indicated that not only polyacetylenes but also flavonoids possibly have chemotaxonomic value for both genera.

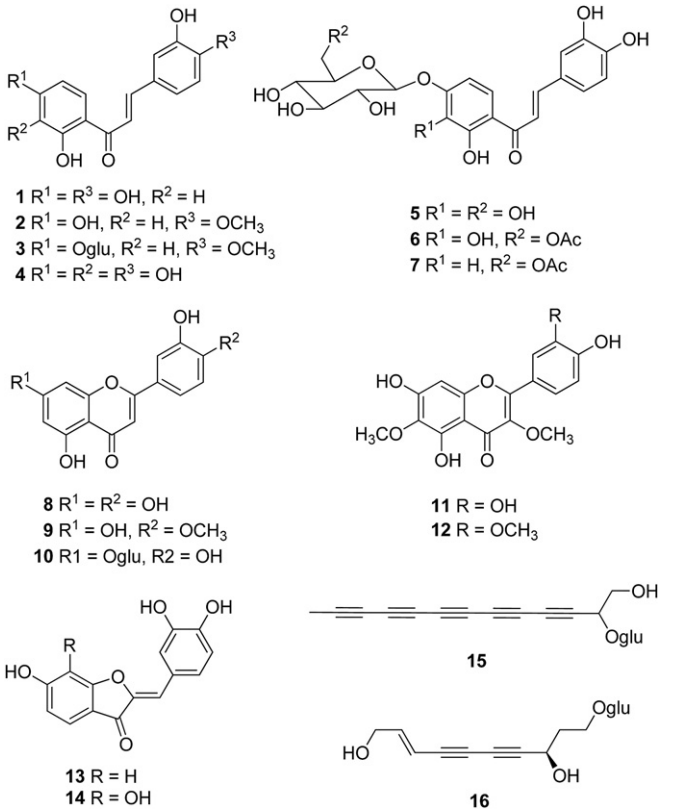

Fig. 1. Chemical structures of the isolated compounds from *Bidens tripartita*.

4′-*O*-β-D-Glucopyranosyl-2′,3-dihydroxy-4-methoxy-chalcone (**3**) has once been reported from the genus *Megalodonata* of family Asteraceae (Roberts, 1980) apart from the genus *Bidens* (Tian et al., 2011). Meanwhile, 6,7,3′,4′-Tetrahydroxyaurone (**14**) and compound **15**, a polyacetylene, have been isolated not only from the genus *Bidens* (Huang et al., 2006; Zhao et al., 2004) but also from the genera *Lasthenia* and *Microglossa* of family Asteraceae, respectively (Bohm et al., 1974; Rücker et al., 1992). These studies suggest that the genus *Bidens* possibly has also a closer chemotaxonomic relationship with other genera in the Asteraceae. On the other hand, to the best of our knowledge, okanin 4′-*O*-(6″-*O*-acetyl-β-D-glucopyranoside) (**6**), bidenoside G (**7**), and compound **16**, a polyacetylene, have only been isolated from this genus to date (Karikome et al., 1992; Li et al., 2005; Tommasi and Pizza, 1997; Wang et al., 2001). Therefore, these compounds may be chemotaxonomically useful to distinguish *Bidens* from other genera in the Asteraceae.

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