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CINNAMIC ACID DERIVATIVES FROM THE ETHYL ACETATE FRACTION OF *Sargentodoxa cuneata*

Jian Tang, Yun Qian, Qian-Qian Li, Xiu-Quan Xu*, and Zhen Ouyang

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Sargentodoxa cuneata Rehd. et Wils. (Sargentodoxaceae, previously attributed to Lardizabalaceae) is used as the traditional Chinese medicine "Hongteng", which promotes blood circulation and has anti-inflammatory, antioxidant, and antibacterial effects; it is used for the treatment of rheumatic arthritis, acute appendicitis, amenorrhea, and painful menstruation [1].

Previous phytochemical studies on this plant described several kinds of constituents, including anthraquinones, sterols, triterpenoids, lignans, flavonoids, and organic acids [1, 2], such as vanillic acid, syringic acid, *p*-hydroxybenzoic acid, and ferulic acid [3]. Some of them and their crude extract exhibited antioxidant effects [4]. The ethyl acetate fraction and total organic acids showed obvious antioxidant activities in DPPH assay, much higher than the *n*-butanol fraction (Table 1).

This paper describes the results of investigation of cinnamic acid derivatives from the ethyl acetate fraction of *S. cuneata* collected in Qin Mountain, Shan′xi province, China in September 2009. The air-dried and powdered stems (6.0 kg) were percolated with 80% alcohol for 24 h × 2. The extract was concentrated to an aqueous residue and then partitioned successively with EtOAc and *n*-BuOH to give two portions. The EtOAc portion (94 g) was subjected to silica gel column chromatography (300–400 mesh, 1.0 kg) using the gradient CH_2Cl_2–CH_3OH (10:0–10:1–5:1–1:1–0:1) as eluent to obtain nine fractions: I_A (9 g), I_B (5 g), II_A (13 g), II_B (10 g), III_A (8 g), III_B (5 g), IV_A (7 g), IV_B (3 g), V (11 g). Fraction I_B (5 g) was subjected to silica gel column chromatography twice, eluting with petroleum: ethyl acetate (4:1–2:1), to yield compound **1** (8 mg). Fraction II_A (13 g) was subjected to silica gel column chromatography to give three subfractions II_{A1}-II_{A3}. Subfraction II_{A1} was purified repeatedly on a silica gel column with gradient petroleum–ethyl acetate (4:1–2:1) to obtain compounds **2** (6 mg) and **3** (9 mg). Subfraction II_{A2} was chromatographed over a silica gel column, eluting with petroleum and ethyl acetate solution (4:1–2:1–1:1), and the portion eluted with 2:1 solvent system was concentrated to 20 mL and kept in an icebox after adding 5 mL of petroleum to yield needle crystal **4** (420 mg). The mother liquor was further purified over a silica gel column to obtain compounds **5** (7 mg), **6** (14 mg), and **7** (11 mg). Analogously, compound **8** (21 mg) was obtained from subfraction II_{A3}. Fraction III_B (5 g) was chromatographed over a silica gel column with an eluent of CH_2Cl_2–CH_3OH (10:1–5:1–2:1) to give subfractions III_{B1}-III_{B2}, and subfraction III_{B2} was purified repeatedly over Toyopearl HW-40C, eluting with 80% methanol, to give a pale yellow compound **9** (13 mg).

On the basis of PMR (600 MHz), ^{13}C NMR (150 MHz), ^{1}H–^{13}C HMBC, and mass spectral analysis, these compounds were determined as protocatechuic acid (**1**) [5], syringic acid (**2**) [6], 4-hydroxyphenylethanol ferulate (**3**) [7], ferulic acid (**4**) [8], ethyl caffeate (**5**) [9], *p*-coumaric acid (**6**) [10], 4-hydroxyphenylpropionic acid (**7**) [10], caffeic acid (**8**) [11], and chlorogenic acid (**9**) [8]. Compounds **5**, **7**, and **8** were isolated from *S. cuneata* for the first time.

The total organic acids were prepared according to the described procedure [12] and were tested for their scavenging effect on the DPPH radical using the reported method [13] with respect to the AcOEt fraction, the *n*-BuOH fraction, the total organic acids and ferulic acid (**4**), caffeic acid (**8**), and chlorogenic acid (**9**). The results (Table 1) showed that the antioxidant activities might be related to organic acids, especial cinnamic acid derivatives.

School of Pharmacy, Jiangsu University, Zhenjiang 212013, P. R. China, fax: +86 0511 85038201, e-mail: jt.u@hotmail.com.
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TABLE 1. DPPH Free Radical Scavenging Activity of Three Fractions and Compounds **4**, **8**, **9**

Sample	Scavenging ratio, $\mu g \cdot mL^{-1}$				IC_{50}, $\mu g \cdot mL^{-1}$
	10	20	50	100	
AcOEt fraction	27.1	54.6	92.04	93.31	17.1
n-BuOH fraction	Not detected	6.1	23.4	51.3	99.7
Organic acids	35.4	64.2	89.7	94.1	13.9
4	18.7	44.6	75.7	91.8	25.6
8*	16.1	67.4	82.4	96.1	6.3
9	37.4	56.4	82.7	94.1	15.5

*Concentrations: 2, 10, 20, and 50 $\mu g \cdot mL^{-1}$, respectively.

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