· Letters ·

A New Phenolic Acid from Rhizomes of *Abacopteris penangiana*

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Abstract: Objective To study the chemical constituents of *Abacopteris penangiana*. **Methods** The compounds were separated and purified by various chromatographic techniques and their structures were elucidated on the basis of physiochemical properties and spectroscopic methods. **Results** Seven compounds were purified and their structures were identified as: (7′*Z*)-3-*O*-(3,4-dihydroxy phenylethenyl)-caffeic acid (**1**), caffeicin B (**2**), matteucinol (**3**), protocatechuic acid (**4**), *p*-methoxybenzoic acid (**5**), β-sitosterol (**6**), and daucosterol (**7**). **Conclusion** Compound **1** is a new phenolic acid compound named abacopteric acid, and the other compounds are isolated from the plant for the first time.

Key words: *Abacopteris penangiana*; abacopteric acid; phenolic acid
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Introduction

Abacopteris penangiana (Hook.) Ching is widely distributed in the south of China. The rhizomes of *A. penangiana* are used for the treatment of pharyngitis, upper respiratory tract infections, and dysentery (Chen, Pu, and Cai, 2004; Jiangsu New Medical College, 1977). Previous phytochemical studies on *A. penangiana* have resulted in the isolation of several flavan-4-ol and flavonol glycosides (Zhao *et al*, 2006, Zhao *et al*, 2008). In the efforts to search for the novel bioactive constituents from natural source, we investigated the chemical constituents of *A. penangiana*. In the present paper, we described the isolation and structure elucidation of one new phenolic acid, as well as six known compounds.

Materials and Methods

Equipments

Melting points were determined on an X4 micro melting point apparatus. UV spectra were measued with a UV—756 MC UV—Visible spectrophotometer. The IR spectra were recorded on a Perkin—Elmer Spectrum One FT-IR spectrometer. Optical rotations were measured with a Perkin—Elmer Model 341 polarimeter. MS spectra were recorded on a Finnigan LCQ—DECA spectrometer and a Mariner spectrometer. NMR spectra were measured on a Bruker AM—400 spectrometer. Silica gel for column chromatography and GF_{254} silica gel for TLC were purchased from Qingdao Marine Chemistry Co. ODS (230–400 mesh) and Sephadex LH-20 (25–100 μm) for column chromatography were produced by Fluka BioChemika.

Plant material

The rhizomes of *Abacopteris penangiana* (Hook.) Ching were collected in Wufeng County, Hubei Province, China, in October 2004 and were authenticated by Prof. RUAN Jin-lan. A specimen (PZX0310) was deposited in the Tongji College of Pharmacy, Huazhong University of Science and Technology.

Extraction and isolation

The air-dried rhizomes (5.0 kg) were ground and extracted with MeOH (5 × 10 L) at room temperature. The MeOH extract was concentrated, suspended in H_2O (3 L) and then extracted with $CHCl_3$ (3 × 3 L), EtOAc (3 × 3 L), and *n*-BuOH (3 × 3 L), sequentially.

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The $CHCl_3$ extract (15 g) was chromatographed on silica gel column (100–200 mesh) eluting with petroleum-acetone (50:1→5:1) to yield **6** (100 mg), **3** (30 mg), **5** (20 mg) and **7** (30 mg). A part of the EtOAc extract (50 g) was chromatographed on silica gel column (200–300 mesh, 800 g) eluting with $CHCl_3$-MeOH (50:1→1:1), then subjected to silica gel, Sephadex LH-20, and ODS column chromatography to obtain **1** (15 mg), **2** (39 mg), and **4** (28 mg).

Results and discussion

Compound **1**: pale white needles, mp 167–170 ℃, found to have the molecular formula $C_{17}H_{14}O_6$ by EI-MS spectrum (*m/z* 314[M]$^+$) and ^{1}H-NMR and ^{13}C-NMR data analysis (Table 1). The UV-Vis spectrum displayed λ_{max} 216 and 274 nm. The IR spectrum indicated the presence of hydroxyl (3282 cm^{-1}) carbonyl (1681 cm^{-1}) and phenyl (1601, 1514, and 1438 cm^{-1}) groups (Fig. 1).

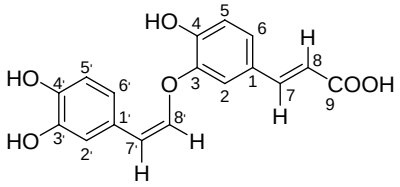

Fig. 1 Chemical structure of compound 1

The ^{1}H-NMR spectrum of compound **1** (Table 1) showed signals characteristic for a pair of the *trans* olefinic proton doublets at δ 7.62 (d, J = 16.0 Hz) and 6.42 (d, J = 16.0 Hz), a pair of the *cis* olefinic proton doublets at δ 5.59 (d, J = 6.7 Hz) and 6.55 (d, J = 6.7 Hz), two sets of signals of AMX type at δ 6.78 (d, J = 7.0 Hz), 7.00 (dd, J = 7.0, 2.0 Hz) and 7.34 (d, J = 2.0 Hz); δ 7.03 (d, J = 8.0 Hz), 7.33 (dd, J = 8.0, 2.0 Hz), and 7.47 (d, J = 2.0 Hz) attributed to two trisubstituted phenyl groups. The ^{13}C-NMR spectrum of compound **1** analyzed with the aid of DEPT and HSQC showed the existence of one conjugated carbonyl carbon (δ 167.8), four phenoxyl carbons (δ 145–151), two aromatic quaternary carbons (δ 127.5 and 126.9), six aromatic methine carbons (δ 115–126), and four olefinic carbons (δ 144.7, 140.7, 111.5, and 116.5). Comparing ^{1}H-NMR and ^{13}C-NMR spectroscopic data of compound **1** with those of caffeicin B (**2**), it was evident that their structures were similar. The EI-MS of compound **1** showed an ion peak at *m/z* 270 ([M-COO]$^+$) which was a -COO fragment less than the molecular ion peak at *m/z* 314[M]$^+$, suggesting that the presence of a carboxyl group. The above spectra data showed the presence of one carboxyl, two double bonds, and two 1,3,4-trisubstituted phenyl rings in compound **1**. To further establish the structure of compound **1**, an HMBC experiment was performed. As observed in the HMBC spectrum, the correlations of C-1′ (127.7) to H-7′ (5.59) and H-8′ (6.55) suggested the *cis* double bond was attached to one trisubstituted phenyl group, which revealed the occurrence of a 3,4-dihydroxy phenyl-ethenyl moiety, and the correlations of C-1 (127.5) to H-7 (7.62) and H-8 (6.42) and C-9 (167.8) to H-7 and H-8 confirmed the presence of a caffeic acid moiety (Fig. 2).

The attachment of the phenylethenyl moiety and the caffeic acid moiety, which were connected through an ether linkage between C-8′ (140.7) and C-3 (146.2), was evidenced from the correlation of the H-8′ with C-3 (146.2) in the HMBC spectrum (Fig. 2). On the basis of these evidences, compound **1** was determined to be (7′*Z*)-3-*O*-(3,4-dihydroxy phenylethenyl)-caffeic acid and named as abacopteric acid.

Table 1 ^{13}C-NMR and ^{1}H-NMR data of compound 1 (in acetone-d_6)

Position	1	
	δ_C	δ_H
1	127.5	7.47 (d, J = 2.0 Hz)
2	117.0	
3	146.2	
4	150.0	
5	117.4	7.03 (d, J = 8.0 Hz)
6	125.6	7.33 (dd, J = 8.0, 2.0 Hz)
7	144.7	7.62 (d, J = 16.0 Hz)
8	116.5	6.42 (d, J = 16.0 Hz)
9	167.8	
1′	127.7	
2′	116.4	7.34 (d, J = 2.0 Hz)
3′	144.8	
4′	145.1	
5′	115.4	6.78 (d, J = 7.0 Hz)
6′	121.6	7.00 (dd, J = 7.0, 2.0 Hz)
7′	111.5	5.59 (d, J = 6.7 Hz)
8′	140.7	6.55 (d, J = 6.7 Hz)

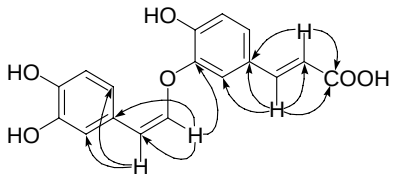

Fig. 2 Key HMBC correlation for compound 1

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Introduction of *Chinese Traditional and Herbal Drugs*

The journal, *Chinese Traditional and Herbal Drugs* (CTHD), published monthly since January 1970 is an academic and technical journal sponsored by Chinese Pharmaceutical Association and Tianjin Institute of Pharmaceutical Research (TIPR). The journal which has a long history of 40-years offers the columns of research papers, brief reports, reviews, dissertation, and special treatises to report the recent achievements of our basic study, production, quality control, and clinic application on traditional Chinese medicine and Chinese materia medica.

The editorial committee consists of over one hundred of specialists with a great academic attainment in pharmaceutical research, education, production, quality control, and clinic application. Among them, one is from Hong Kong and one from abroad. There are seven academicians of Chinese Academy of Sciences and Chinese Academy of Engineering, and about 2/3 Doctor tutors. Prof. TANG Lida, the President of TIPR, is the director committee member and the editor-in-chief of the journal.

The characters of the journal are new (selecting the subject newly and publishing the research achievement with blazing new trials), rapid (editing and publishing in a high speed), and high (the article with the advanced academic level and improved editorial quality). It carries a variety of scientific papers with a great quantity of pharmaceutical information and modern academic level. The articles on the project supported by State Natural Science Foundation, on State Key Task of Science and Technology, and on the items and achievements subsidized by other science foundations on ministries and commissions level are over 50%. At the same time, the articles in the journal have been collected and quoted in the famous publications both domestic and international, such as *Chinese Science Citation Database* (CSCD), *Chinese Pharmaceutical Abstracts* (CPA), *Chemical Abstracts* (CA), MSB-S in USA, Ulrich's Periodicals Directory in USA, International Pharmaceutical Abstracts (IPA), IM/MEDLINE in USA, EMBASE in Holland, and IC in Poland, etc. It has been selected in 1000 periodicals for the highest frequency of CA recent years; It enjoyed the head place of periodicals in Chinese materia medica among the core periodicals on Chinese natural science. It was included for five times continuously in Dominant Catalogue of Chinese Core Journals in 1992, 1996, 2000, 2004, and 2008 year. The statistic data for successive eight years in CSCD indicate that the journal has been arranged in the 15th or above in the arrangement table of Chinese S & T Journal Citation Frequency, and the first in the journals of Chinese materia medica. It was awarded with the first prize for the First Appraisement of Outstanding S & T Journals organized by the Propaganda Ministry of the Central Committee of the Communist Party of China, State Scientific Committee, Government Press Office in 1992 and the second prize for the second in 1996. It entered the ranks of Chinese Journal Position of Double Awards in 2001. It was awarded with the prize in the Second State Journal Award at the very beginning of 2003 and enjoyed one of the ten best journals around eight provinces and cities in North China in 2004. It was awarded with the nomination prize in the Third State Journal Award in 2005. It has the honor of 100 Excellent Academic Periodicals of China for five times since 2005 to 2009. In 2010, the journal was honored as “the Most Effective Journal in the Past 60 Years”.

It has been recognized as the source periodical of CSCD and Comprehensive Evaluation Data of China Academic Periodicals by the Research Center of Estimation and Evaluation on Chinese Science References the Commission of Chinese Academic Periodicals (Disc Issue). And all the papers of the journal are collected in the www.CNKI.com and Chinese Academic Periodicals.

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