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Chemical constituents from the leaves of *Alchornea trewioides* (Ⅲ). Quinic acids

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Abstract: *Alchornea trewioides* is a kind of Traditional Chinese Medicine, which was used to treat prostate gland, shigella, lumbocrural pain, inflammation and other diseases in China, and its chemical constituents and antioxidation activity have been reported. To continue invested the chemical composition and master the material basis of *A. trewioides*, 80% acetone extracts of the fresh leaves of *A. trewioides* was successively separated by Sephadex LH-20, MCI gel CHP 20P, and Toyopearl Butyl-650C column chromatography to yield five quinic acids. Their structures were elucidated spectroscopic analyses as: 3-*O*-caffeoylquinic acid(**1**), 4-*O*-caffeoylquinic acid(**2**), 5-*O*-caffeoylquinic acid(**3**), 4-*O*-galloylquinic acid (**4**), and 5-*O*-galloylquinic acid(**5**). Compounds **1-5** were isolated from the Alchornea for the first time. Oxygen radical absorbance capacity (ORAC) of the all compounds were also compared and compounds **1-5** were observed to show the strongest antioxidation activity.

Key words: *Alchornea trewioides*; chemical constituents; extraction and separation; quinic acid; antioxidation activity
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红背山麻杆叶的化学成分研究(Ⅲ)—奎宁酸类化合物

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摘 要: 红背山麻杆作为一种常用的传统中药材,它常被用来治疗前列腺、腰腿痛、炎症等疾病,它的化学成分及抗氧化活性已有研究报道。为了继续研究红背山麻杆的化学成分,以掌握其物质基础,对新鲜叶子80%丙酮提取物水萃取部位,利用凝胶、MCI及Toyopearl Butyl-650C柱色谱进行分离、纯化得到5个奎宁酸类化合物。根据化合物的波谱数据分析鉴定为3-*O*-咖啡酰基奎宁酸(**1**)、4-*O*-咖啡酰基奎宁酸(**2**)、5-*O*-咖啡酰基奎宁酸(**3**)、4-*O*-galloylquinic acid(**4**)、5-*O*-galloylquinic acid(**5**)。化合物**1**～**5**均为首次从本属植物中分离得到。通过抗氧化能力指数检测(ORAC法),所有的化合物均表现出较强的抗氧化活性。

关键词: 红背山麻杆; 化学成分; 提取与分离; 奎宁酸; 抗氧化活性

Alchornea trewioides belongs to the family of *Alchornea*, and there are about 70 species of distributed around the world, including over 6 species in China (Editorial Committee in Flora of China, 1996). Many

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species of the *Alchornea* have been used to treat prostate gland, shigella, lumbocrural pain, inflammation and other diseases in Traditional Chinese Medicine. In our previous studies, phenylethanoid glycosides, flavonoid glycosides, and phenolic acids from the *A. trewioides* have been reported, and the antioxidant activity was comparated, too (Lu, 2012; Qin, 2012; Lu, 2011; Huang, 2014). To continue to invested the chemical composition of *A. trewioides*, five quinic acids were isolated and identified from 80% acetone extracts of the fresh leaves of *A. trewioides*. All these quinic acids (**1**-**5**) were isolated from the *Alchornea* for the first time. All compounds were observed to show the stronger antioxidation activity.

1 Materials and Methods

Both ^{1}H-and ^{13}C-NMR spectra were determined using acetone-d_6 at on Bruker Avance 500 spectrometer(500 MHz for ^{1}H and 125 MHz for ^{13}C)(Bruker Biospin AG, Faellanden, Switzerland) or a JEOL JNM-AL 400 spectrometer(400 MHz for ^{1}H and 100 MHz for ^{13}C)(JEOL Ltd., Tokyo, Japan) machine. Coupling constants are expressed in Hz and chemical shifts are given on a δ(ppm) scale with TMS as an internal standard. MCI gel CHP 20P(75－150 μm; Mitsubishi Chemical, Tokyo, Japan), Sephadex LH-20(25－100 μm; GE Healthcare Bio-Science AB, Uppsala, Sweden), Chromatorex ODS(100－200 mesh, Fuji Silysia Chemical Ltd., kasugai, Japan), and Toyopearl Butyl-650C(TOSOH Co., Tokyo, Japan) were used for column chromatography. The precoated Kieselgel 60 F_{254} plates(0.2 mm thick; Merck, Darmstadt, Germany) with toluene-ethyl formate-formic acid(1∶7∶1, v/v) as the solvent, and spots were detected by UV illumination(254 nm) and by spraying with 2% ethanolic $FeCl_3$ for TLC.

The fresh leaves of *A. trewioides* were collected from Guangxi Institute of Botany, Guangxi, People's Republic of China, in August 2011, and identified by Prof. Wei Fa'nan. The voucher specimen(2011 0920) had been deposited in the Guangxi key laboratory of functional phytochemicals research and utilization, Guangxi Institute of Botany.

2 Extraction and Separation

The fresh leaves of *A. trewioides*(5.35 kg) were cut into small pieces and extracted with 80% acetone (v/v) at room temperature. After filtration, the plant debris remaining was extracted with the same manner for further two times. The filtrate was combined, concentrated under reduced pressure, and removed chlorophylls and waxes by filtration. The extract(610 g) was partitioned into Et_2O and water-soluble fractions. The water-soluble fraction was separated by Sephadex LH-20 column chromatography(10 cm i.d.×40 cm) with 0－100% MeOH(10% stepwise elution, each 2 L) and 60% acetone, to afford 9 fractions(Fr. 1-9). Fraction 2 (14.9 g) was purified on a column of MCI gel CHP 20P(6 cm i.d.×40 cm) with 0－100% MeOH (10% stepwise elution, each 0.5 L) to give fr.2-1(3.21 g), fr. 2-2(4.58 g), and fr.2-3(6.02 g). Fraction 2-2 was further purified on a column of Chromatorex ODS (5 cm i.d.×40 cm) with 0－100% MeOH containing 0.1% TFA(10% stepwise elution, each 300 mL) to give **1**(9 mg), **2**(46 mg), and **4**(12 mg). Fraction **3**(6.51 g) was further purified on a column of MCI gel CHP 20P(4 cm i.d.×40 cm) with 0－100% MeOH(20% stepwise elution, each 500 ml), Toyopearl Butyl-650C(4 cm i.d. ×40 cm) with 0－100% MeOH(10% stepwise elution, each 50 mL), and Sephadex LH-20(4 cm i.d.×40 cm) with 0－100% MeOH(10% stepwise elution, each 200 mL) to afford **3**(26 mg) and **5**(18 mg).

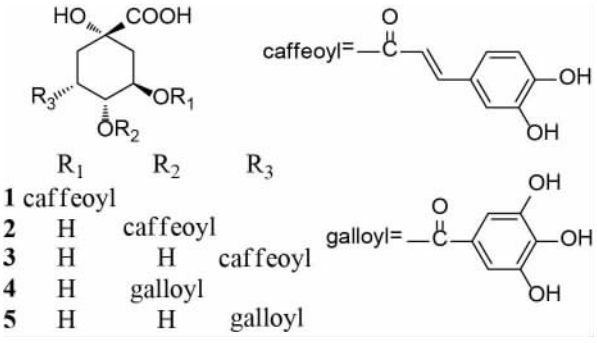

Fig. 1 Chemical structures of compounds **1**-**5**

3 Results and Analysis

3-*O*-Caffeoylquinic acid (**1**)　White amorphous powder, $C_{16}H_{18}O_9$. ^{1}H-NMR (500 MHz, CD_3OD) δ: 2.00 (1H, dd, J = 8.5, 13.1 Hz, H-2ax), 2.17－2.25 (3H, m, H-2eq, 6ax, 6eq), 3.69 (1H, dd, J = 3.1, 8.5 Hz, H-4), 4.21 (1H, ddd, J = 3.1, 8.5, 8.5 Hz, H-5), 5.39 (1H, ddd, J = 3.1, 3.1, 5.2 Hz, H-3), 6.32 (1H, d, J = 16.0 Hz, H-8′), 6.80 (1H, d, J = 8.5 Hz, H-5′), 6.94 (1H, dd, J = 2.0, 8.5 Hz, H-6′), 7.07 (1H, d, J = 2.0 Hz, H-2′), 7.60 (1H, d, J = 16.0 Hz, H-7′); ^{13}C-NMR (125 MHz, CD_3OD) δ: 37.6 (C-2), 41.5 (C-6), 68.1 (C-5), 72.9 (C-3), 74.8 (C-4), 75.4 (C-1), 115.1 (C-2′), 115.7 (C-8′), 116.5 (C-5′), 122.9 (C-6′), 127.9 (C-1′), 146.5 (C-3′), 146.8 (C-7′), 149.2 (C-4′), 169.1 (C-9′), 178.3 (C-7) (Nakatani *et al*., 2008).

4-*O*-Caffeoylquinic acid (**2**)　White amorphous powder, $C_{16}H_{18}O_9$. ^{1}H-NMR (500 MHz, CD_3OD) δ: 2.00 (1H, dd, J = 8.5, 13.1 Hz, H-2ax), 2.07-2.22 (3H, m, H-2eq, 6ax, 6eq), 4.29 (1H, ddd, J = 3.1, 8.5, 8.5 Hz, H-5), 4.29 (1H, ddd, J = 3.1, 3.1, 5.2 Hz, H-3), 4.81 (1H, dd, J = 3.1, 8.5 Hz, H-4), 6.41 (1H, d, J = 16.0 Hz, H-8′), 6.79 (1H, d, J = 8.5 Hz, H-5′), 6.98 (1H, dd, J = 2.0, 8.5 Hz, H-6′), 7.07 (1H, d, J = 2.0 Hz, H-2′), 7.67 (1H, d, J = 16.0 Hz, H-7′); ^{13}C-NMR (125 MHz, CD_3OD) δ: 38.1 (C-2), 41.6 (C-6), 65.7 (C-5), 70.1 (C-3), 76.8 (C-1), 79.4 (C-4), 115.2 (C-2′), 115.7 (C-8′), 116.5 (C-5′), 122.9 (C-6′), 128.0 (C-1′), 146.6 (C-3′), 146.9 (C-7′), 149.2 (C-4′), 169.1 (C-9′), 178.5 (C-7) (Nakatani *et al*., 2008).

5-*O*-Caffeoylquinic acid (**3**)　White amorphous powder, $C_{16}H_{18}O_9$. ^{1}H-NMR (500 MHz, CD_3OD) δ: 2.03-2.24 (4H, m, H-2ax, H-2eq, 6ax, 6eq), 3.73 (1H, dd, J = 3.0, 8.5 Hz, H-5), 4.17 (1H, ddd, J = 3.1, 3.1, 5.2 Hz, H-3), 5.34 (1H, ddd, J = 4.4, 8.5, 8.5 Hz, H-4), 6.28 (1H, d, J = 16.0 Hz, H-8′), 6.78 (1H, d, J = 8.5 Hz, H-5′), 6.95 (1H, dd, J = 2.0, 8.5 Hz, H-6′), 7.05 (1H, d, J = 2.0 Hz, H-2′), 7.56 (1H, d, J = 16.0 Hz, H-7′); ^{13}C-NMR (125 MHz, CD_3OD) δ: 38.2 (C-2), 38.8 (C-6), 71.3 (C-3), 72.0 (C-5), 73.5 (C-4), 76.2 (C-1), 115.2 (C-2′), 115.3 (C-8′), 116.5 (C-5′), 123.0 (C-6′), 127.8 (C-1′), 146.7 (C-3′), 147.1 (C-7′), 149.5 (C-4′), 168.7 (C-9′), 177.1 (C-7) (Tamura *et al*., 2004).

4-*O*-Galloylquinic acid (**4**)　White amorphous powder, $C_{14}H_{16}O_{10}$. ^{1}H-NMR (500 MHz, acetone-d_6) δ: 2.07-2.30 (4H, m, H-2ax, 2eq, 6ax, 6eq), 4.41-4.46 (2H, m, H-3, 5), 4.92 (1H, d, J = 8.5 Hz, H-4), 7.19 (2H, s, H-2′, 6′); ^{13}C-NMR (125 MHz, acetone-d_6) δ: 37.5 (C-2), 41.7 (C-6), 64.3 (C-3), 68.5 (C-5), 75.6 (C-1), 78.5 (C-4), 109.5 (C-2′, 6′), 121.1 (C-1′), 138.0 (C-4′), 145.1 (C-3′, 5′), 166.0 (C-7′), 175.1 (C-7) (Nishimura *et al*., 1984).

5-*O*-Galloylquinic acid (**5**)　White amorphous powder, $C_{14}H_{16}O_{10}$. ^{1}H-NMR (400 MHz, acetone-d_6) δ: 2.00-2.35 (4H, m, H-2ax, H-2eq, 6ax, 6eq), 3.79 (1H, dd, J = 3.2, 8.5 Hz, H-4), 4.14 (1H, ddd, J = 3.2, 3.2, 5.2 Hz, H-3), 5.42 (1H, m, H-5), 7.12 (2H, s, H-2′, 6′); ^{13}C-NMR (100 MHz, acetone-d_6) δ: 36.6 (C-6), 40.3 (C-2), 68.3 (C-3), 72.6 (C-5), 73.9 (C-4), 75.2 (C-1), 110.6 (C-2′, 6′), 121.9 (C-1′), 138.6 (C-4′), 145.8 (C-3′, 5′), 1676 (C-7′), 169.6 (C-7) (Nishimura *et al*., 1984).

Oxygen radical absorbance capacity (ORAC) of the all compounds were also compared (Table 1) and compounds **1**-**5** were observed to show the strongest antioxidation activity (Prior *et al*., 2005). Comparison of the values for **1**-**5** suggested that quinic acid with coumaroyl group compounds gave rise to a larger ORAC value among quinic acid esters. (Measurement of the ORAC values method reference to Huang *et al*., 2011)

Table 1　ORAC values of compounds **1**-**5**

Compound	mmol Trolox equivalent /g
3-*O*-Caffeoylquinic adid(**1**)	13.26
4-*O*-Caffeoylquinic adid(**2**)	11.23
5-*O*-Caffeoylquinic adid(**3**)	13.77
4-*O*-Galloylquinic adid(**4**)	6.37
5-*O*-Galloylquinic adid(**5**)	5.63

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