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荸荠皮酚性成分及其抗氧化活性研究

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摘 要:从荸荠皮(*Eleocharis tuberosa*)70%丙酮提取物的乙酸乙酯部分共分离得到1个新化合物和8个已知化合物。通过波谱数据,分别鉴定为荸荠酚甲(**1**)、1,2′,4′,6′-四乙酰基-3,6-二阿魏酸蔗糖苷(**2**)、1,2′,6′-三乙酰基-3,6-二阿魏酸蔗糖苷(**3**)、丁香脂素(**4**)、阿魏酸(**5**)、咖啡酸(**6**)、对香豆酸(**7**)、肉桂酸(**8**)和对羟基苯甲酸(**9**)。测试了所得化合物的抗氧化活性。结果表明,化合物**5**和**6**具有较强的抗氧化活性。所有化合物均为首次从该植物中分离得到,化合物**1**为新化合物。

关键词:荸荠皮;酚性成分;抗氧化活性

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Phenolic Constituents and Antioxidant Activity of *Eleocharis tuberosa* Peels

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Abstract: Phenolic constituents were isolated from *Eleocharis tuberosa* via extraction with 70% aqueous acetone, purified by various column chromatographies, and identified on the basis of physical and spectral data. A new compound and eight known compounds were isolated, and identified as eleocharinol **A** (**1**), 1,2′,4′,6′-tetraacetyl-3,6-diferuloylsucrose (**2**), 1,2′,6′-triacetyl-3,6-diferuloylsucrose (**3**), (+)-syringaresinol (**4**), *trans*-ferulic acid (**5**), caffeic acid (**6**), *p*-coumaric acid (**7**), cinnamic acid (**8**) and **4**-hydroxylbenzoic acid (**9**). The potential antioxidant activity of the isolated compounds was evaluated using DPPH radical scavenging assay and reducing power assay. Compounds **5** and **6** showed strong antioxidant activities. To our knowledge, all the compounds were isolated from the peels of *E. tuberosa* for the first time and compound **1** is a new compound.

Key words: *Eleocharis tuberosa* peels; phenolic constituents; antioxidant activity

Introduction

Eleocharis tuberosa (Cyperaceae) is one of the most popular hydrophytic vegetables in China and other Asia countries. The corms are consumed as fruit, grain or vegetable, and prepared of starch and canning. *E. tuberosa* has also been used as a traditional medicine to treat pharyngitis, laryngitis, enteritis, cough, hepatitis and hypertension [1]. The peels of *E. tuberosa* contain puchiin, cytokinin, flavonoids and phenolics [1-3]. However, little research was reported about its chemical constituents. In recent years, fresh-cut *E. tuberosa* corms are in high demand because of their unique taste, medicinal properties. A large number of peels were wasted. It was reported that the extracts of *E. tuberosa* peels showed strong bactericidal [2] and antioxidant activities [3]. To comprehensive utilize it, the chemical constitutes of *E. tuberosa* peels were investigated. As a result, a new phenolic, named eleocharinol **A** (**1**) with 8 known phenolic compounds was isolated. The antioxidant properties of the isolated compounds, including reducing power and scavenging activities against DPPH radical, were evaluated.

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Experimental

Instrumentation

Optical rotations (OR) were recorded on a JASCO-20C digital polarimeter. Ultraviolet absorption (UV) spectra were determined on a Shimadzu UV-2401A spectrophotometer (Shimadzus, Kyoto). Infrared spectroscopy (IR) spectra were measured on a Tensor 27 spectrometer with KBr pellets. Nuclear Magnetic Resonance (NMR) spectra were collected on Bruker AV-400, DRX-500 and AVANCE III-600 spectrometers with tetramethylsilane as an internal standard. Electrospray ionization-mass spectrometry (ESI-MS) and high-resolution (HR) EI-MS were recorded with a Bruker HCT/Esquire and Waters AutoSpec-P776 mass spectrometer, respectively. Semi-preparative HPLC was performed on an Agilent 1100 liquid chromatography with a Zorbax SB-C18 column (Agilent Technologies, USA). Column chromatography (CC) was performed using silica gel or polyamides (100-200 and 200-300 mesh, Qingdao Marine Chemical Co. Ltd., Qingdao, China), MCI gel (75-150 μm; Mitsubishi Chemical Corporation, Japan), and Sephadex LH-20 (Amersham Pharmacia Biotech, Sweden).

Plant materials

Peels of fresh-cut *E. tuberosa* were collected in Hezhou, Guangxi province, People's Republic of China, in March 2012, and identified by Professor PAN Bai-ming of Hezhou University, Hezhou. A voucher specimen was kept in the laboratory for future reference.

Extraction and isolation

The air-dried and powdered peels of *E. tuberosa* (8.0 kg) were extracted three times with 70% aqueous acetone (32 L × 3), each for 24 h, at room temperature, and concentrated in *vacuo* to give a crude extract. The crude extract was suspended in water, followed by partitioning with EtOAc. The EtOAc fraction (120 g) was chromatographed on MPLC (MCI gel) eluted with a gradient of MeOH-H_2O (5∶5, 7∶3, 9∶1 and 10∶0) to afford four fractions (A-D). Fraction A (21.5 g) was chromatographed on MCI CC and then on polyamides CC to give compound **9** (13 mg) and compound **6** (330 mg). Fraction B (9.8 g) was purified by a polyamides CC and eluted with gradient $CHCl_3$-MeOH (from 5∶1 to 0∶1, *v/v*), followed by polyamides CC and silica CC with PE-acetone-H_2O (49∶49∶2) to produce compounds **5** (20 mg), TLC ($CHCl_3$-MeOH-H_2O = 90∶9∶1) to afford 8 (20 mg). Fraction C (31 g) was submitted to a polyamides CC and eluted with gradient $CHCl_3$-MeOH (from 5∶1 to 0∶1, *v/v*), then separated by Sephadex LH-20 CC, followed by semi-preparative HPLC to give compound **2** (120 mg), **3** (7 mg), and **4** (15 mg), by MIC CC to produce **7** (10 mg). Fraction D (28 g) was separated by CC on silica (PE-$CHCl_3$ = 8∶2) to give compound **1** (50 mg).

Antioxidant activity

Reducing power assay

A modification of the method described by Li Xia, *et al*[4] was used. A sample solution (1 mL, 0.1 mg/mL in ethanol) was added into a phosphate buffer (2.5 mL, 0.2 M, pH 6.6) and potassium ferricyanate (2.5 mL, 10 mg/mL). The mixtures were incubated at 50 °C for 20 min, and then 2.5 mL of trichloroacetic acid (100 mg/mL) was added and centrifuged at 2000 g for 10 min. The distilled water (2.5 mL) and ferric chloride (0.5 mL, 1.0 mg/mL) was added to 2.5 mL of the supernatant. The absorbance was measured at 700 nm using a spectrophotometer. Rutin with the same concentration was used as the reference sample. The increase in absorbance represented the increase in reducing power.

DPPH radical scavenging assay

The 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay was conducted according the reported method [5] with some modifications. The DPPH solution was prepared by dissolving 39.4 mg of DPPH with 500 mL of ethanol, and then was stored in a cool, dark area, until needed. 0.1 mL of blank (ethanol) or sample solutions in ethanol at different concentrations (from 0.05 mg/mL to 16 mg/mL) was each added to 3.9 mL of a DPPH solution, which was diluted to 0.080 mM with ethanol. The solution in the testing tubes was shaken vigorously and incubated in the dark for 30 min at 37 °C. Then, the absorbance of mixture was measured at 517 nm. The tests were carried out in triplicate. The antioxidant ac-

tivity was expressed as the antioxidant activity index (AAI), calculated as follows as:

$$I\% = [(A_{blank} - A_{sample})/A_{blank}] \times 100$$

$$AAI = \frac{\text{final concentration of DPPH}^{\cdot}\ (\mu g/mL)}{IC_{50}\ (\mu g/mL)}$$

The IC_{50} (concentration providing 50% inhibition) was calculated on a calibration curve by plotting the sample concentration and the corresponding scavenging effect. The sample would show poor, moderate, strong, or very strong antioxidant activity when AAI values were less than 0.5, between 0.5 and 1.0, between 1.0 and 2.0, or larger than 2.0, respectively.

Results and Discussion

Structural elucidation

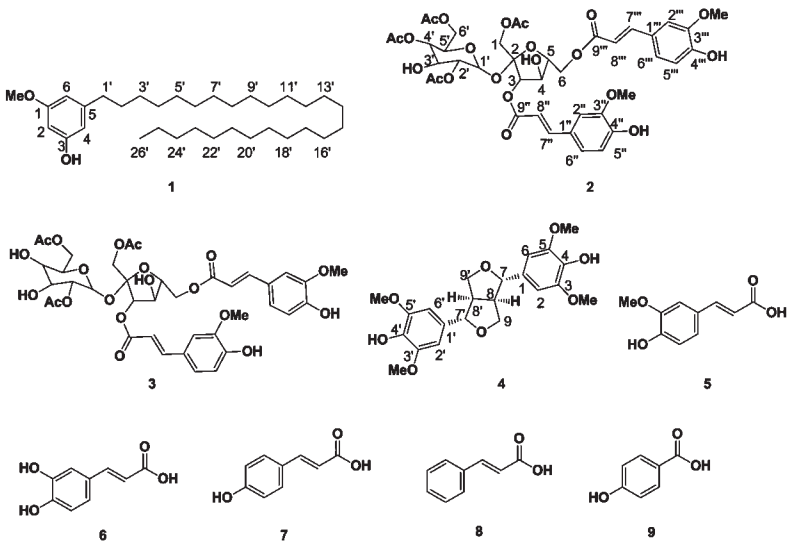

Fig. 1 Compounds isolated from *E. tuberosa*

Compound 1 Compound **1** had the molecular formula $C_{33}H_{60}O_2$ as deduced from HR-EI-MS at *m/z* 488.4608 $[M]^+$ (calcd 488.4593), in accordance to four degrees of unsaturation. Its UV spectrum showed the typical absorptions of a phenolic group at 203 and 275 nm and its IR spectrum revealed band for saturated long-chain groups (2918, 2850, 1467, 720 cm^{-1}). The ^1H NMR spectrum showed a hydroxyl group [4.97 (1H, s, 3-OH)], three aromatic singlets [δ_H 6.33 (1H, s, H-6), 6.26 (1H, s, H-4), and 6.24 (1H, d, J = 1.7 Hz, H-2)], and a extraordinary saturated multiplet [1.34-1.25 (46H, overlapped, H-3′ to 25′)]. The ^{13}C NMR spectra revealed the presence of 16 overlapped carbons. All of the saturated carbons were secondary carbons, except for two of methyl groups [55.2 (q, 1-OCH_3) and 14.1 (q, C-26′)], and suggested it contained a long-chain alkyl. In ^1H-^1H COSY spectrum, the multiplet at δ_H 1.57 (2H, m, H-2′) was coupled with H-1′ [2.51 (2H, t, J = 7.7 Hz)] and H-3′ [1.31 (overlapped)], and the triplets at 0.88 [(3H, t, J = 6.6 Hz, H-26′)] showed cross-peaks with H-25′ [1.28 (overlapped)]. In the HMBC spectrum, the singlet at δ_H 6.24 (H-2) was coupled with C-1 (δ_C 160.7), C-3 (δ_C 156.4), and C-4 (δ_C 107.8), and the protons at δ_H 6.26 (H-4) and δ_H 6.33 (H-6) also showed obvious cross-peaks with their C_α and C_β, respectively. The signals at δ_C 31.9 and δ_C 22.7 were assigned to C-24′ and C-25′, respectively, on the basis of HMBC correlations. As a result, all proton and carbon signals were fully assigned based on HMQC, HMBC and H-H COSY spectral analysis, and the positions of the substitution and saturated long-chain skeleton were determined. Consequently, the structure of compound **1** was determined as 3-hexacosyl-5-methoxyphenol, and named as Eleocharinol **A**.

Data of compound **1**: White amorphous solid ($CHCl_3$); $[\alpha]_D^{16.0}$: -12.48 (*c* 1.01, MeOH); UV (MeOH) λ_{max} (log ε) 275.20 (3.05), 203.40 (4.33) nm; IR (KBr) ν_{max} 3426, 2918, 2850, 1624, 1467, 1148, 1057, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) and ^{13}C

NMR (100 MHz, $CDCl_3$) data, see Table 1; ESI-MS (positive-ion mode) *m/z* 489 $[M+H]^+$; HR-EI-MS *m/z* 488.4608 $[M]^+$ (calcd for $C_{33}H_{60}O_2$, 488.4593).

Table 1 ^{1}H and ^{13}C NMR spectroscopic data for compound 1[a] (δ in ppm)

Position	δ_H (*J* in Hz)	δ_C mult	HMBC (H→C)	^{1}H-^{1}H COSY
1		160.7, s		
2	6.24 (d, 1.7)	98.6, d	1, 3, 4, 6	
3		156.4, s		
4	6.26 (s)	107.8, d	2, 3, 6, 1′	
5		145.8, s		
6	6.33 (s)	106.7, d	1, 2, 4, 1′	
1′	2.51 (t, 7.7, 2H)	36.0, t	4, 5, 6, 2′	2′
2′	1.57 (m, 2H)	31.2, t	5, 1′, 3′	1′, 3′
3′	1.31 (overlapped, 2H)	29.5, t	2′	2′
4′to23′	1.30-1.25 (overlapped, 40H)	29.7, 29.6, 29.4, 29.3, each t	overlapped	overlapped
24′	1.26 (overlapped, 2H)	31.9, t	25′	overlapped
25′	1.28 (overlapped, 2H)	22.7, t	26′	26′
26′	0.88 (t, 6.6, 3H)	14.1, q	24′, 25′	25′
1-OCH_3	3.77 (s, 3H)	55.2, q	1	
3-OH	4.97 (s)			

[a] Recorded at 400 MHz and 100 MHz for ^{1}H and ^{13}C NMR in $CDCl_3$, respectively.

Compound 2 Colorless amorphous solid (MeOH); ^{1}H NMR (400 MHz, MeOD-d_4) δ: 4.22 (3H, m, H-1, 5′), 5.38 (1H, d, *J* = 7.7 Hz, H-3), 4.45 (3H, m, H-4, 4′, 5), 4.10 (3H, m, H-6, 3′), 5.67 (1H, d, *J* = 3.4 Hz, H-1′), 4.80 (1H, m, H-2′), 4.66 (2H, m, H-6′), 7.25 (1H, s, H-2″), 6.80 (2H, d, *J* = 8.1 Hz, H-5″, 5‴), 7.09 (2H, d, *J* = 9.8 Hz, H-6″, 6‴), 7.69 (1H, d, *J* = 15.9 Hz, H-7″), 6.44 (1H, d, *J* = 15.2 Hz, H-8″), 7.18 (1H, s, H-2‴), 7.64 (1H, d, *J* = 16.0 Hz, H-7‴), 6.40 (1H, d, *J* = 15.5 Hz, H-8‴), 1.85 (3H, s, 1-$OCOCH_3$), 2.01 (3H, s, 2′-$OCOCH_3$), 2.08 (3H, s, 4′-$OCOCH_3$), 2.10 (3H, s, 6′-$OCOCH_3$), 3.89 (6H, s, 3″, 3‴-OCH_3); ^{13}C NMR (100 MHz, MeOD-d_4) δ: 66.6 (t, C-1), 103.9 (s, C-2), 79.5 (d, C-3), 73.9 (d, C-4), 81.5 (d, C-5), 64.1 (t, C-6), 90.5 (d, C-1′), 73.8 (d, C-2′), 70.0 (d, C-3′), 72.2 (d, C-4′), 69.8 (d, C-5′), 64.7 (t, C-6′), 127.7 (s, C-1″), 111.7 (d, C-2″), 149.5 (s, C-3″), 151.1 (s, C-4″), 116.6 (d, C-5″), 124.7 (d, C-6″), 148.3 (d, C-7″), 115.1 (d, C-8″), 168.8 (s, C-9″), 127.5 (s, C-1‴), 111.6 (d, C-2‴), 149.4 (s, C-3‴), 150.7 (s, C-4‴), 116.5 (d, C-5‴), 124.4 (d, C-6‴), 147.3 (d, C-7‴), 114.3 (d, C-8‴), 168.0 (s, C-9‴), 171.8 (s, 1-$OCOCH_3$), 20.7 (q, 1-$OCOCH_3$), 172.1 (s, 2′-$OCOCH_3$), 20.8 (q, 2′-$OCOCH_3$), 172.2 (s, 4′-$OCOCH_3$), 20.9 (q, 4′-$OCOCH_3$), 172.7 (s, 6′-$OCOCH_3$), 21.0 (q, 6′-$OCOCH_3$), 56.5 (q, 3″, 3‴-OCH_3); ESI-MS (negative-ion mode) *m/z* 861 $[M-H]^-$. The NMR data were in accordance with the reported data [6,7]. Therefore, compound **2** was characterized as 1, 2′, 4′, 6′-tetraacetyl-3, 6-diferuloyl-sucrose.

Compound 3 Colorless amorphous solid; ^{1}H NMR (500 MHz, MeOD-d_4) δ: 4.17-4.10 (6H, m, H-1, 3′, 5′, 6′), 5.44 (1H, d, *J* = 8.4 Hz, H-3), 4.52-4.40 (4H, m, H-4, 5, 6), 5.63 (1H, d, *J* = 3.6 Hz, H-1′), 4.60 (1H, m, H-2′), 3.33 (1H, overlapped in water peak, H-4′), 7.27 (1H, s, H-2″), 6.81 (2H, d, *J* = 8.1 Hz, H-5″, 5‴), 7.12 (1H, d, *J* = 9.4 Hz, H-6″), 7.71 (1H, d, *J* = 15.9 Hz, H-7″), 6.47 (1H, d, *J* = 15.9 Hz, H-8″), 7.22 (1H, s, H-2‴), 7.11 (1H, d, *J* = 8.4 Hz, H-6‴), 7.66 (1H, d, *J* = 15.9 Hz, H-7‴), 6.42 (1H, d, *J* = 16.0 Hz, H-8‴), 2.07 (3H, s, 1-$OCOCH_3$), 2.09 (3H, s, 2′-

$OCOCH_3$), 2.12 (3H, s, 6′-$OCOCH_3$), 3.90 (6H, s, 3″, 3‴-OCH_3); ^{13}C NMR (125 MHz, MeOD-d_4) δ: 66.3 (t, C-1), 103.6 (s, C-2), 79.1 (d, C-3), 74.3 (d, C-4), 81.3 (d, C-5), 65.1 (t, C-6), 90.6 (d, C-1′), 72.2 (d, C-2′), 73.8 (d, C-3′), 71.9 (s, C-4′), 72.1 (d, C-5′), 65.2 (t, C-6′), 127.8 (s, C-1″), 115.2 (d, C-2″), 147.2 (s, C-3″, 3‴), 151.1 (s, C-4″), 116.6 (d, C-5″, 5‴), 124.5 (d, C-6″), 149.5 (d, C-7″), 112.1 (d, C-8″), 168.8 (s, C-9″), 127.5 (s, C-1‴), 114.4 (d, C-2‴), 150.9 (s, C-4‴), 124.3 (d, C-6‴), 148.3 (d, C-7‴), 111.9 (d, C-8‴), 168.3 (s, C-9‴), 172.1 (s, 1-$OCOCH_3$), 20.7 (q, 1-$OCOCH_3$), 172.4 (s, 2′-$OCOCH_3$), 20.9 (q, 2′-$OCOCH_3$), 172.9 (s, 6′-$OCOCH_3$), 21.0 (q, 6′-$OCOCH_3$), 56.6 (q, 3″, 3‴-OCH_3); ESI-MS (positive-ion mode) *m/z* 843 [M + Na]$^+$. The spectral data were matched with literature [6,7], hence it was identified as 1, 2′, 6′-triacetyl-3, 6-diferuloylsucrose.

Compound 4 Colorless needle (MeOH); ^{1}H NMR (500 MHz, MeOD-d_4) δ: 6.65 (4H, s, H-2, 2′, 6, 6′), 4.70 (2H, d, *J* = 3.9 Hz, H-7, 7′), 3.13 (2H, m, H-8, 8′), 4.25 (2H, dd, *J* = 8.8, 6.6Hz, H-9a, 9′a), 3.88 (2H d, *J* = 3.0 Hz, H-9b, 9′b), 3.83 (12H, s, -OCH_3 ×4); ^{13}C NMR (125 MHz, MeOD-d_4) δ: 133.2 (s, C-1, 1′), 104.4 (d, C-2, 2′, 6, 6′), 149.3 (s, C-3, 3′, 5, 5′), 136.0 (s, C-4, 4′), 87.6 (d, C-7, 7′), 55.5 (d, C-8, 8′), 72.8 (t, C-9, 9′), 56.8 (q, -OCH_3 ×4); ESI-MS (positive-ion mode) *m/z* 441, [M + Na]$^+$. Compound **4** was identified as (+)-syringaresinol by a comparison of its spectral data with the reported[8].

Compound 5 White amorphous powders (MeOH); ^{1}H NMR (400 MHz, MeOD-d_4) δ: 7.16 (1H, s, H-2), 6.78 (1H, d, *J* = 8.1 Hz, H-5), 7.04 (1H, d, *J* = 8.1 Hz, H-6), 7.56 (1H, d, *J* = 15.9 Hz, H-7), 6.29 (1H, d, *J* = 15.9 Hz, H-8), 3.87 (3H, s, 3-OMe); ^{13}C NMR (100 MHz, MeOD-d_4) δ: 127.8 (s, C-1), 111.6 (d, C-2), 150.4 (s, C-3), 149.3 (s, C-4), 116.4 (d, C-5), 124.0 (d, C-6), 146.8 (d, C-7), 116.1 (d, C-8), 171.1 (s, C-9), 56.4 (q, 3-OCH_3); ESI-MS (negative-ion mode) *m/z* 193 [M-H]$^-$. The NMR data were in accordance with those reported in literature [6], and compound **5** was identified as *trans*-ferulic acid.

Compound 6 White amorphous powders (MeOH); ^{1}H NMR (400 MHz, MeOD-d_4) δ: 7.03 (1H, d, *J* = 2.0 Hz, H-2), 6.77 (1H, d, *J* = 8.2 Hz, H-5), 6.93 (1H, dd, *J* = 8.2, 1.9 Hz, H-6), 7.53 (1H, d, *J* = 15.9 Hz, H-7), 6.22 (1H, d, *J* = 15.9 Hz, H-8); ^{13}C NMR (100 MHz, MeOD-d_4) δ: 127.8 (s, C-1), 115.0 (d, C-2), 146.8 (s, C-3), 149.5 (s, C-4), 116.5 (d, C-5), 122.9 (d, C-6), 147.0 (d, C-7), 115.5 (d, C-8), 171.1 (s, C-9); ESI-MS (negative-ion mode) *m/z* 179 [M-H]$^-$. Comparing the NMR data with references [9], compound 6 was determined to be caffeic acid.

Compound 7 White amorphous powder (MeOH); ^{1}H NMR (400 MHz, MeOD-d_4) δ: 7.44 (2H, d, *J* = 8.4 Hz, H-2, 6), 6.80 (2H, d, *J* = 8.5 Hz, H-3, 5), 7.58 (1H, d, *J* = 15.8 Hz, H-7), 6.29 (1H, d, *J* = 15.9 Hz, H-8); ^{13}C NMR (100 MHz, MeOD-d_4) δ: 127.3 (s, C-1), 131.0 (d, C-2, 6), 116.8 (d, C-3, 5), 161.0 (s, C-4), 146.3 (d, C-7), 116.1 (d, C-8), 171.5 (s, C-9); ESI-MS (negative-ion mode) *m/z* 163 [M-H]$^-$. Compound **7** was identified as *p*-coumaric acid by comparison of the spectral data [6].

Compound 8 White amorphous powder (MeOH); ^{1}H NMR (400 MHz, MeOD-d_4) δ: 7.50 (2H, d, *J* = 7.1 Hz, H-2, 6), 7.40 (1H, d, *J* = 16.0 Hz, H-7), 7.37-7.26 (3H, m, H-3, 4, 5), 6.50 (1H, d, *J* = 15.9 Hz, H-8); ^{13}C NMR (100 MHz, MeOD-d_4) δ: 137.2 (s, C-1), 128.5 (d, C-2, 6), 129.8 (d, C-3, 5), 130.1 (d, C-4), 141.1 (d, C-7), 126.6 (d, C-8), 175.6 (s, C-9); ESI-MS (negative-ion mode) *m/z* 147 [M-H]$^-$. The spectral data were agreed with the literature values of cinnamic acid [10].

Compound 9 White amorphous powder (MeOH); ^{1}H NMR (500 MHz, Pyridine-d_5) δ: 8.45 (2H, d, *J* = 8.5 Hz, H-2, 6), 7.24 (2H, d, *J* = 8.4 Hz, H-3, 5); ^{13}C NMR (100 MHz, MeOD-d_4) δ: 118.3 (s, C-1), 132.8 (d, C-2, 6), 116.1 (d, C-3, 5), 163.2 (s, C-4), 169.4 (s, CO); ESI-MS (negative-ion mode) *m/z* 137 [M-H]$^-$. The NMR data were in accordance with 4-hydroxylbenzoic acid[11].

Antioxidant activity

All the isolated compounds were evaluated for antioxidant activities by reducing power assay and DPPH radical scavenging assay. The results were showed in Table 2. In terms of reducing power, compounds **5** and **6** showed very strong reducing power. The reducing power of compound **9** was moderate, and those of the others were poor. In the DPPH radical scavenging assay, compounds **4**, **5**, **6**, and **9** showed very strong DPPH radical scavenging activities. The DPPH radical scavenging activities of compounds **2** and **3** were moderate, and those of the others were poor.

Table 2 Reducing Power and DPPH Radical Scavenging Activity of Isolated Compounds

Samples	Reducing power	DPPH radical scavenging activity	
	Abs	IC_{50} (μg/mL)	AAI
1	0.00	–	–
2	0.08	38.37	0.80
3	0.08	28.60	1.08
4	0.00	5.40	5.69
5	0.24	9.11	3.38
6	0.70	3.97	7.74
7	0.02	96.09	0.32
8	0.02	–	–
9	0.16	8.49	3.62
Rutin	0.35	4.15	7.40

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