Quinones from *Chirita eburnea*

Xiang-Hai Cai,[†,‡] Xiao-Dong Luo,*[,†] Jun Zhou,[†] and Xiao-Jiang Hao[†]

State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204, and Graduate School of Chinese Academy of Sciences, Beijing 100039, People's Republic of China

Received November 17, 2004

Five new quinone derivatives, (*R*)-7-hydroxy-α-dunnione (**1**), (*R*)-8-hydroxy-α-dunnione (**2**), (*R*)-7,8-dihydroxy-α-dunnione (**3**), (*R*)-7-methoxy-6,8-dihydroxy-α-dunnione (**4**), and 1,7-dihydroxy-2-hydroxymethylanthraquinone (**5**), along with seven known compounds, were isolated from *Chirita eburnea.* All structures were elucidated by spectroscopic techniques (NMR, MS, UV, and IR). The EtOAc fraction of the EtOH extract and compounds **3** and **4** showed free radical (DPPH) scavenging activity, with IC_{50} values of 101.7 ± 5.2 μg/mL, 124.82 ± 8.4 μM, and 45.72 ± 3.6 μM, respectively, compared with 86.91 ± 6.8 μM for ascorbate.

Chirita eburnea Hance, a species of the family Gesneriaceae, is distributed in Yunnan, Guangxi, Guangdong, and Sichuan Provinces of China.[1] It has been used as folk medicine to treat cough with bleeding and other immunodeficiency diseases.[2] In previous papers the naphthoquinones, α,*β*-dunnione and *β*-dunnione derivative were described from *Streptocarpus dunnii* and anthraquinones were obtained from other genera of the family Gesneriaceae.[3−5] We investigated *C. eburnea* because there were no chemical constituents published for this plant and no α-dunnione derivatives had been found. Four new α-dunnione derivatives (**1**−**4**), an anthraquinone, 1,7-dihydroxy-2-hydroxymethylanthraquinone (**5**), and seven known compounds, (*R*)-α-dunnione (**6**),[3] 1-hydroxy-2-hydroxymethylanthraquinone (**7**),[6] 1,4-dihydroxy-2-hydroxymethylanthraquinone (**8**),[7] 1,7-dihydroxy-2-methylanthraquinone (**9**),[8] 1,7-dihydroxy-6-methoxy-2-methylanthraquinone (**10**),[9] 1-hydroxy-2-methoxy-7-methylanthraquinone (**11**),[8] and 1,2-dihydroxy-6-methylanthraquinone (**12**),[10] were identified. The structures of the known compounds were identified by comparison of their MS and ^{1}H and ^{13}C NMR data with those reported, and new compounds were determined on the basis of spectroscopic evidence, especially HMBC spectra. The occurrence of α-dunnione in both this plant and *Streptocarpus dunnii* supports their close taxonomic relationship. Each compound except **6** was evaluated for its antioxidant properties using DPPH assay. This paper describes the isolation, identification, and antioxidant effects of these compounds.

Compound **1** possessed the molecular formula $C_{15}H_{14}O_4$ as inferred from EIMS, ^{1}H and ^{13}C NMR, and DEPT data. Its UV spectrum exhibited characteristic absorption peaks of the conjugated carbonyl moiety at 266, 307, 360, and 384 nm. The IR spectrum revealed absorption bands for hydroxyl (3350 cm^{-1}) and carbonyl groups (1680 cm^{-1}). The ^{1}H and ^{13}C NMR spectra of **1** showed signals of two conjugated carbonyl carbons [δ_C 182.2, 178.9], eight olefinic carbons, a quaternary carbon (δ_C 45.8), an oxygenated tertiary carbon (δ_C 91.6), and three methyls (δ_C 26.1, 20.7, 14.4). These data suggested that **1** was an α-dunnione derivative.[3] The ^{1}H NMR spectrum of **1** showed three protons arising from an aromatic moiety at δ_H 7.86 (1H, dd, J = 8.2, 0.25 Hz), 7.37 (1H, dd, J = 2.5, 0.25 Hz), and 7.17 (1H, dd, J = 8.2, 2.5 Hz). This ^{1}H NMR pattern indicated the location of the hydroxyl group at C-7 or C-6. Signals of δ_C 182.2 and 178.9 in the ^{13}C NMR spectrum of **1** could be assigned to C-4 and C-9, respectively, by comparison of the chemical shifts for C-4 (δ_C 182.2) and C-9 (δ_C 178.9) with those of α-dunnione,[3] which was also supported by correlation between δ_H 1.44 (CH_3-3α) and δ_C 182.2 in the HMBC spectrum. In the HMBC spectrum of **1** the cross-peaks [δ_H 7.86 with δ_C 182.2 (C-4), 162.6 and 134.6; δ_H 7.37 with δ_C 121.0, 126.7, and 178.9 (C-9)] suggested that the hydroxyl group was not located at C-6. The correlation patterns [δ_H 1.44 and 1.26 (3-CH_3) with δ_C 130.3 (C-3a), 91.6 (C-2), and 45.8 (C-3), respectively; δ_H 1.38 (2-CH_3) with δ_C 91.6 and 45.8; δ_H 1.26 with δ_C 26.1 (3-CH_3); δ_H 1.44 with δ_C 20.7 (3-CH_3)] in the HMBC spectrum also confirmed the structure of the 2,3,3-trimethylnaphtho[2,3-*b*]furan moiety. Compound **1** is thus 7-hydroxy-α-dunnione.

Compound **2** had the molecular formula $C_{15}H_{14}O_4$ according to its EIMS, ^{1}H and ^{13}C NMR, and DEPT data. The UV spectrum of **2** exhibited absorption peaks of a conjugated carbonyl moiety at 271, 314, 375, and 402 nm. Its IR spectrum indicated the presence of hydroxyl groups (3424 cm^{-1}) and carbonyl groups (1675, 1641 cm^{-1}). The ^{1}H and ^{13}C NMR spectra of **2** showed similarities to those of **1** with the exception of the location of the hydroxyl group. In the ^{1}H NMR spectrum, three doublets of doublets [δ_H 8.03 (1H, dd, J = 7.5, 2.5 Hz), 7.65 (1H, dd, J = 8.2, 7.5 Hz), 7.16 (1H, dd, J = 8.2, 2.5 Hz)] suggested that the three hydrogens were adjacent and that the hydroxyl group was at either C-5 or 8. The C-9 resonance shifted downfield from δ_C 178.1 to 183.3 in the ^{13}C NMR spectrum of **2** by comparison of the chemical shifts of α-dunnione,[3] which placed the hydroxyl at C-8 rather than C-5. Hence compound **2** is 8-hydroxy-α-dunnione.

Compound **3** possessed the molecular formula $C_{15}H_{14}O_5$ as inferred from EIMS, ^{1}H and ^{13}C NMR, and DEPT data. The UV spectrum of **3** exhibited absorption peaks of the conjugated carbonyl moiety at 268, 328, 380, and 421 nm. Its IR spectrum indicated the presence of hydroxyl (3235 cm^{-1}) and carbonyl groups (1660, 1634 cm^{-1}). ^{1}H and ^{13}C NMR spectra of **3** were very similar to those of **2** except for one more hydroxyl group. In the ^{1}H NMR spectrum of **3**, coupling constants of two doublets [δ_H 7.55 (1H, d, J = 8 Hz), δ_H 7.14 (1H, d, J = 8 Hz)] showed that two hydrogens were adjacent. The extra hydroxyl group was tentatively positioned at C-7. In the HMBC spectrum of **3**, correlations [δ_H 7.55 (H-5) with δ_C 180.9 (C-4), 150.1 (C-7), and 114.8

* To whom correspondence should be addressed. Tel: +86-871-5223188. Fax: +86-871-5150227. E-mail: xdluo@mail.kib.ac.cn.
† Kunming Institute of Botany.
‡ Graduate School of Chinese Academy of Sciences.

10.1021/np049632f CCC: $30.25
Published on Web 04/22/2005

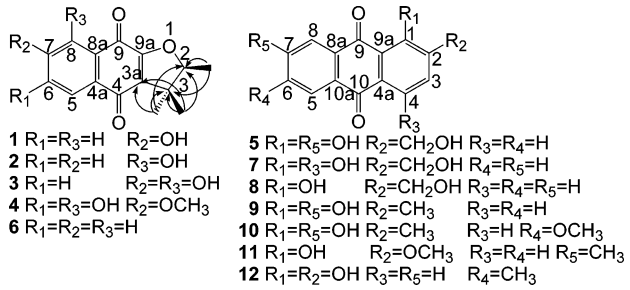

Figure 1. Structures of compounds **1**−**12**.

Table 1. Free Radical Scavenging Activity of EtOAc-Soluble Fraction, **3**, **4**, and Ascorbate in the DPPH Assay[a]

sample	IC_{50} (μM)
EtOAc-soluble fraction	101.7 ± 5.2 μg/mL
3	124.82 ± 8.4
4	45.72 ± 3.6
ascorbate	86.91 ± 6.8

[a] Results are given as the mean ± SD (n = 4).

(C-8a), δ_H 7.14 (H-6) with δ_C 125.3(C-4a) and 148.8 (C-8)] support the above conclusions. Compound **3** was thus established as 7,8-dihydroxy-α-dunnione.

Compound **4** had the molecular formula $C_{16}H_{16}O_6$, according to EIMS, ^{1}H and ^{13}C NMR, and DEPT data. The ^{1}H and ^{13}C NMR spectra of **4** were similar to those of **3** with the exception for one additional O-methyl group. In the HMBC spectra, the correlation of δ_H 7.03 with δ_C 181.2 (C-4), 157.4 (C-6), 139.1 (C-7), and 130.8 (C-4a) assigned δ_H 7.03 as H-5, and the correlation between δ_H 3.88 and δ_C 139.1 (C-7) placed the O-methyl group at C-7. The structure of **4** was thus established as 7-methoxy-6,8-dihydroxy-α-dunnione.

The CD spectrum of **4** showed a negative Cotton effect at 302 nm ($\theta = 4.2 \times 10^5$) contributed by a C-4 carbonyl group, with a positive Cotton effect at 380 nm ($\theta = 2.8 \times 10^5$) caused by a C-9 carbonyl group.[11−13] The absolute configuration of C-2 of **4** was determined as *R* from a positive Cotton effect of C-9 by using octant rules for ketone, which was supported by those of C-4. The optical rotation values of compounds **1**−**4** and **6** were −133°, −33.3°, −125°, −120°, and −90°, respectively, indicating that they had the same configuration. Thus compounds **1**−**4** and **6** were defined as (*R*)-7-hydroxy-α-dunnione (**1**), (*R*)-8-hydroxy-α-dunnione (**2**), (*R*)-7,8-dihydroxy-α-dunnione (**3**), (*R*)-7-methoxy-6,8-dihydroxy-α-dunnione (**4**), and (*R*)-α-dunnione (**6**). Full assignments of ^{1}H and ^{13}C NMR of **1**−**4** are determined by 2D NMR spectra (Table 2).

The molecular formula of **5** was established by ^{1}H NMR, ^{13}C NMR, DEPT, and EIMS spectra as $C_{15}H_{10}O_5$. Its UV spectrum exhibited characteristic absorption peaks of anthraquinone at 228 (4.05), 264 (4.15), 356 (3.60), and 425 (3.50) nm. The IR spectrum suggested the presence of hydroxyl (3400 cm^{-1}) and carbonyl groups (1685, 1670 cm^{-1}). The ^{1}H and ^{13}C NMR spectra of **5** showed the presence of two conjugated carbonyl carbons (δ_C 189.7, 181.1), six double bonds, a hydroxymethyl (δ_C 67.1), and two hydroxyl groups (δ_H 12.81, 5.45). These signals suggested that **5** was an anthraquinone, 1,7(or 6)-dihydroxy-2-hydroxymethylanthraquinone, by comparison with the ^{1}H NMR spectra of **7** and **8**.[6,7] The signals at δ_C 189.73 and 181.14 in **5** were assigned to C-9 and C-10, respectively, also by comparison with known compounds.[4,5] In the HMBC spectrum of **5**, correlations [δ_H 7.16 (H-3) with δ_C 135.7 (C-4a), 159.4 (C-1), δ_H 8.06 (H-4) with δ_C 138.4 (C-2), 181.1 (C-10), and 115.6 (C-9a), δ_H 8.38 (H-5) with δ_C 164.1 (C-7), 132.2 (C-8a), and 181.1, δ_H 7.47 (H-6) with δ_C 112.7 (C-8) and 126.1 (C-10a), δ_H 8.01 (H-8) with δ_C 122.6 (C-6), 126.1 and 189.7 (C-9)] supported that compound **5** was 1,7-dihydroxy-2-hydroxymethylanthraquinone.

Table 2. ^{13}C NMR Data for Compounds **1**−**5**[a]

	1	**2**	**3**	**4**	**5**
1					159.4 s
2	91.6 d	91.9 d	91.8 d	92.1 d	138.4 s
3	45.8 s	45.2 s	45.4 s	45.7 s	134.2 d
3a	130.3 s	131.8 s	132.8 s	131.4 s	
4	182.2 s	181.5 s	180.9 s	181.2 s	119.2 d
4a	126.7 s	133.6 s	125.3 s	130.8 s	135.7 s
5	128.9 d	118.9 d	119.4 d	109.4 d	130.2 d
6	121.0 d	136.9 d	120.5 d	157.4 s	122.6 d
7	162.6 s	123.8 d	150.1 s	139.1 s	164.1 s
8	112.7 d	161.8 s	148.8 s	157.5 s	112.7 d
8a	134.6 s	114.6 s	114.8 s	109.4 s	132.2 s
9	178.9 s	183.3 s	183.7 s	182.7 s	189.7 s
9a	159.1 s	158.4 s	157.8 s	159.8 s	115.6 s
10					181.1 s
10a					126.1 s
−CH_2OH					67.1 t
−OCH_3				60.8 q	
2β-CH_3	14.4 q	14.2 q	14.2 q	14.4 q	
3α-CH_3	26.1 q	25.7 q	25.7 q	25.9 q	
3β-CH_3	20.7 q	20.5 q	20.5 q	20.6 q	

[a] Compounds **1** and **2** were measured in acetone-d_6, **3** and **4** in $CDCl_3$, and **5** in pyridine-d_5.

For the screening and evaluation of antioxidant activity of crude extracts and each pure compound except **6**, a DPPH assay was adopted,[14−16] with ascorbate as a positive control. In the DPPH assay, the free radical scavenging activities of tested samples were expressed as IC_{50}. The EtOAc fraction and compounds **3** and **4** showed powerful free radical scavenging activity (Table 1) compared to ascorbate. Scavenger activities of other compounds were weak and not strongly linear to their concentrations. Compounds **3** and **4** showed stronger activities from the effects of the carbonyl group and the interactions from the two hydroxyl groups. The activity of **4** was more powerful than that for **3**, possibly because an additional O-methyl group increased the activity of the two hydroxyl groups. Those quinones are especially active compounds and may account for the plant's ability to treat the diseases mentioned above.

Experimental Section

General Experimental Procedures. Optical rotations were measured with a Horiba SEAP-300 spectropolarimeter. CD spectra were obtained using a JASCO J-810 spectropolarimeter (Japan Spectroscopic, Tokyo, Japan) in $CDCl_3$ solution. UV spectra were recorded on a Shimadzu double-beam 210A spectrophotometer. IR (KBr) spectra were obtained on Bio-Rac FTS-135 infrared spectrophotometer. ^{1}H, ^{13}C, and 2D NMR spectra were recorded on a DRX-500 MHz NMR spectrometer with TMS as internal standard. MS data were obtained on VG Autospec-3000 spectrometer, 70 eV for EI. Silica gel (200−300 mesh) for column chromatography and GF_{254} for TLC were obtained from Qingdao Marine Chemical Factory, Qingdao, People's Republic of China. Rp 18 silica gel (40−65 μm) was bought from Merck Co., Germany. 1,1-Diphenylpicrylhydrazyl (DPPH) was purchased from Sigma Co.

Plant Materials. The whole plant of *C. eburnea* was collected and identified by Dr. De-Shan Deng in August 2002 in Guangxi Province, People's Republic of China.

Extraction and Isolation. Air-dried whole plant (4.0 kg) was crushed and extracted with 90% aqueous EtOH (12 L × 4) at room temperature (48 h × 4) to yield an EtOH extract. After removal of the EtOH under reduced pressure, the viscous

concentration was partitioned with EtOAc (4 × 10 L) to afford an EtOAc extract (80 g). The EtOAc fraction was absorbed on 120 g of silica gel and chromatographed on a prepacked Si gel (1.0 kg) column, eluting with a mixture of $CHCl_3$−Me_2CO [from $CHCl_3$ to $CHCl_3$−Me_2CO (1:1)], to give eight fractions (I−VIII) according to differences in composition monitored by TLC (Si gel GF_{254}). Fraction III (15.8 g) was further purified by repeated column chromatography over silica gel (280 g) using petroleum ether−EtOAc and petroleum ether−$CHCl_3$, which gave three fractions (A−C) and compound **3** (10 mg). Fraction A (650 mg) was subjected to RP_{18} gel (80 g) CC, eluting with MeOH−H_2O (from 8:2 to 9:1) to afford **2** (120 mg) and **6** (6 mg). Repeated column chromatography of fraction B (1.0 g) afforded **1** (15 mg). Fraction IV (25.5 g) was loaded on column chromatography over silica gel (400 g), eluted by petroleum ether−Me_2CO (from 8:2 to 7:3) to obtain fractions D (95.6 mg) and E (76.5 mg), which were subjected to RP_{18} gel (80 g) and eluted with MeOH−H_2O (from 7:3 to 8:2) to afford **8** (13 mg) and **11** (14 mg), respectively. Fraction V (18.9 g) was rechromatographed on a Si gel (300 g) column and eluted with petroleum ether−Me_2CO (from 3:1 to 2:1) and $CHCl_3$−Me_2CO (from 5:1 to 4:1) to yield **7** (8 mg), **9** (10 mg), **10** (15 mg), and **12** (21 mg). Fraction VI (6.0 g) was also subjected to column chromatography over silica gel (100 g) using $CHCl_3$−Me_2CO (from 4:1 to 3:1) as eluent to afford fractions F and G, and fractions F (75.2 mg) and G (98.3 mg) were eluted by MeOH−H_2O (from 7:3 to 8:2) over RP_{18} gel (80 g) CC to afford **4** (18 mg) and **5** (21 mg), respectively.

(*R*)-7-Hydroxy-α-dunnione (1): red amorphous powder; $[\alpha]^{25}_D$ −133° (c 0.075, CH_3OH); UV (MeOH) λ_{max} (log ϵ) 266 (4.25), 307 (4.02), 360 (3.55), 384 (2.64) nm; IR (KBr) ν_{max} 3350, 2950, 1680, 1600, 1550 cm^{-1}; ^1H NMR (acetone-d_6, 500 MHz) δ 7.86 (1H, dd, J = 8.2, 0.25 Hz, H-5), 7.37 (1H, dd, J = 2.5, 0.25 Hz, H-8), 7.17 (1H, dd, J = 8.2, 2.5 Hz, H-6), 4.57 (1H, q, J = 6.4 Hz, H-2), 1.44 (3H, s, 3α-CH_3), 1.26 (3H, s, 3β-CH_3), 1.38 (3H, d, J = 6.4 Hz, 2β-CH_3); EIMS (70 eV) m/z 258 $[M]^+$ (60), 243 (100), 215 (10); ^{13}C NMR (acetone-d_6, 125 MHz), see Table 2.

(*R*)-8-Hydroxy-α-dunnione (2): red amorphous powder; $[\alpha]^{25}_D$ −33.3° (*c* 0.09, CH_3OH); UV (MeOH) λ_{max} (log ϵ) 232 (4.13), 271 (4.20), 314 (3.90), 375 (3.52), 402 (2.98) nm; IR (KBr) ν_{max} 3424, 2968, 1675, 1641, 1609, 1451 cm^{-1}; ^1H NMR (Me_2CO, 500 MHz) δ 11.63 (1H, s −OH), 8.03 (1H, dd, J = 7.5, 2.5 Hz, H-5), 7.65 (1H, dd, J = 8.2, 7.5 Hz, H-6), 7.16 (1H, dd, J = 8.2, 2.5 Hz, H-7), 4.57 (1H, q, J = 6.4 Hz, H-2), 1.46 (3H, s, 3α-CH_3), 1.26 (3H, s, 3β-CH_3), 1.42 (3H, d, J = 6.4 Hz, 2-CH_3); EIMS (70 eV) m/z 258 $[M]^+$ (21), 243 (100), 227 (50); ^{13}C NMR (acetone-d_6, 125 MHz), see Table 2.

(*R*)-α-7,8-Dihydroxy-α-dunnione (3): red amorphous powder; $[\alpha]^{25}_D$ −125° (*c* 0.10, CH_3OH); UV (MeOH) λ_{max} (log ϵ) 222 (4.12), 268 (4.01), 328 (3.74), 380 (3.36), 421 (3.05) nm; IR (KBr) ν_{max} 3235, 2807, 1660, 1634, 1600, 1548 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 11.84 (1H, br s, OH), 7.55 (1H, d, J = 8 Hz, H-5), 7.14 (1H, d, J = 8 Hz, H-6), 6.15 (1H, br s, −OH), 4.58 (1H, q, J = 6.5 Hz, H-2), 1.46 (3H, s, 3α-CH_3) 1.26 (3H, s, 3β-CH_3), 1.44 (3H, d, J = 6.5 Hz, 2-CH_3); EIMS (70 eV) m/z 274 $[M]^+$ (70), 259 (100), 245 (20); ^{13}C NMR ($CDCl_3$, 125 MHz), see Table 2.

(*R*)-7-Methyoxy-6,8-dihydroxy-α-dunnione (4): red amorphous powder, mp 136−138 °C; $[\alpha]^{25}_D$ −120° (*c* 0.10, CH_3OH); UV (MeOH) λ_{max} (log ϵ) 220 (4.13), 270 (3.95), 293 (3.50), 332 (3.77), 426 (3.12) nm; IR (KBr) ν_{max} 3315, 2805, 1670, 1635, 1600, 1550 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 12.30 (1H, br s, 8-OH), 7.03 (1H, q, J = 2.0 Hz, H-5), 4.58 (1H, q, 6.5 Hz, H-2), 3.88 (3H, s, −OCH_3), 1.41 (3H, s, 3α-CH_3), 1.22 (3H, s, 3β-CH_3), 1.38 (3H, d, J = 6.5 Hz, 2-CH_3); EIMS (70 eV) m/z 304 $[M]^+$ (75), 289 (100), 271 (20), 261 (15); ^{13}C NMR ($CDCl_3$, 125 MHz), see Table 2.

1,7-Dihydroxy-2-hydroxymethylanthraquinone (5): yellow amorphous powder; UV (MeOH) λ_{max} (log ϵ) 228 (4.05), 264 (4.15), 356 (3.60), 425 (3.50) nm; IR (KBr) ν_{max} 3400, 3235, 1685, 1670, 1602, 1550 cm^{-1}; ^1H NMR (C_5D_5N, 500 MHz) δ 12.81 (1H, br s, 1-OH), 8.38 (1H, dd, J = 8.5, 0.25 Hz, H-5), 8.06 (1H, d, J = 8.2 Hz, H-4), 7.16 (1H, d, J = 8.2 Hz, H-3), 8.01 (1H, dd, J = 2.5, 0.25 Hz, H-8), 7.47 (1H, dd, J = 8.5, 2.5 Hz, H-6), 5.45 (1H, br s, 7-OH), 4.70 (2H, s, −CH_2−OH); EIMS (70 eV) m/z 270 $[M]^+$ (62), 241 (100), 224 (30), 196 (25), 168 (30); ^{13}C NMR (C_5D_5N, 125 MHz), see Table 2.

Evaluation of DPPH Radical Scavenging Activity.[14−16] Antioxidant activities of the crude extract and each pure compound except **6** were assessed on the basis of the radical scavenging effect of the stable DPPH free radical. A 1.0 mL portion of a 200 μM DPPH MeOH solution was added to 1.0 mL of sample solutions of four different concentrations and allowed to react at room temperature. After 30 min the absorbance values were measured at 517 nm using a spectrophotometer and converted into the percentage antioxidant activity (AA) using the following formula:

$$(AA\ \%) = 100 - \{[(Abs_{sample} - Abs_{blank}) \times 100]/Abs_{control}\}$$

MeOH (1.0 mL) plus sample solution (1.0 mL) was used as a blank. DPPH solution plus MeOH was used as a negative control, and ascorbate as a positive control. The IC_{50} value is the concentration of test sample required to scavenge 50% DPPH free radical.

Acknowledgment. The authors are grateful to the National Natural Science Foundation of China (Project No. C 30370160), Yunnan Committee of Science and Technology (Project No. 2004C0009Z, 2000YP23), and The Chinese Academy of Sciences (XiBuZhiGuang Project) for financial support, and members of the analytical group in the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, for the spectral measurements. The authors are also grateful to Dr. D.-S. Deng for identification of plant samples.

References and Notes

(1) How, F. C. *Dictionary of the Families and Genera of Chinese Seed Plants*; Sciences Press: Beijing, 1982; p 114.
(2) *Compiling Groups of Compilation of Countrywide Herbal Medicine of China*; People's Medical Publishing House: Beijing, 1975; pp 153−154.
(3) Inoue, K.; Ueda, S.; Nayeshiro, H.; Inouye, H. *Chem. Pharm. Bull.* **1982**, *30*, 2265−2268.
(4) Chen, C. Y.; Lu, Y.; Chen, Z. N. *Acta Univ. Med. Second. Shanghai* **2001**, *21*, 488−491.
(5) Liu, G. M.; Chen, Z. N.; Yao, T. R.; Ding, W. G. *Acta Pharam. Sin.* **1990**, *25*, 699−704.
(6) Imre, S.; Tulus, R.; Sengun, I. *Tetrahedron Lett.* **1971**, *48*, 4681−4683
(7) Stockingt, J.; Srocka, U.; Zenk, M. H. *Phytochemistry* **1973**, *12*, 2389−2391.
(8) Pitre, S.; Srivastava, S. K. *Planta Med.* **1987**, *53*, 106−107.
(9) Schriposema, J. Ramos-Valdivia, A.; Verpoorte, R. *Phytochemistry* **1999**, *51*, 55−60.
(10) Boisvert, L.; Brassard, P. *J. Org. Chem*. **1988**, *53*, 4052−4059.
(11) Eyton, W. B. Ollis, W. D.; Sutherland, I. O.; Gottlieb, O. R.; Magalhaes, M. T.; Jackman L. M. *Tetrahedron* **1965**, *21*, 2683−2696.
(12) Ema, T.; Nemugaki, S.; Tsuboi, S.; Utaka, M. *Tetrahedron Lett.* **1995**, *36*, 5905−5908.
(13) Snatzke, G. *Tetrahedron* **1965**, *21*, 439−448.
(14) Chen, C. H.; Shaw, C. Y.; Chen, C. C.; Tsai, Y. C. H. *J. Nat. Prod.* **2002**, *65*, 740−741
(15) Peng, C. L.; Chen S. W.; Lin Z. F.; Lin G. Z. *Prog. Biochem. Biophys.* **2000**, *27*, 658−661.
(16) Zhang, Z. T.; Du, Y. J.; Liu, Q. G.; Liu, Y. *Nat. Prod. Res. Dev.* **2001**, *13*, 45−47.

NP049632F