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Isolation and Identification of Lignans from Caulis Bambusae in Taenia with Antioxidant Properties

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Supporting Information

ABSTRACT: Caulis Bambusae in Taenia is a medicinal preparation from *Bambusa tuldoides* Munro consisting of skinless slices of the stem (bamboo shavings) and used as a traditional health food in tea, wine, and soup in Asia. Three novel lignans, (−)-7′-*epi*-lyoniresinol 4,9′-di-*O*-*β*-D-glucopyranoside (**7**), (−)-lyoniresinol 4,9′-di-*O*-*β*-D-glucopyranoside (**8**), bambulignan A (**10**), and seven known lignan compounds (**1**−**6** and **9**) were isolated from Caulis Bambusae in Taenia. The structures of the lignans were determined by detailed spectroscopic analysis (HRESIMS, HSQC, HMBC, NOE). All the isolated lignans were tested for antioxidant activities by DPPH and FARP assays. The results showed that the compounds (+)-lyoniresinol 9′-*O*-*β*-D-glucopyranoside (**1**) and (−)-7′-*epi*-lyoniresinol 9′-*O*-*β*-D- glucopyranoside (**9**) have strong free radical scavenging activity and reducing power.

KEYWORDS: *Bambusa tuldoides, Caulis Bambusae in Taenia, (−)-7′-epi-lyoniresinol 4, 9′-di-O-β-D-glucopyranoside, (−)-lyoniresinol 4, 9′-di-O-β-D-glucopyranoside, bambulignan A, antioxidant activities, DPPH, FARP*

■ INTRODUCTION

Bambusa tuldoides Munro is a widely distributed and cultivated bamboo species in southern China.[1] Sliced stem without the skin named "Caulis Bambusae in Taenia" or "Bamboo shavings" is used in traditional Chinese medicine and food. In Asia, Caulis Bambusae in Taenia has been used as a health food additive[2] and folk medicine for the treatments of tumors,[3] fatigue,[4] epilepsy,[5] insomnia,[6] and nausea and vomiting in pregnancy.[7] In China, Caulis Bambusae in Taenia is a functional food certified by the Ministry of Health. More than 100 patents concerning addition of Caulis Bambusae in Taenia in foods, including tea,[8,9] wine,[10,11]and soup[12,13] have been issued.

Studies on the chemical constituents and activity of *B. tuldoides* revealed the occurrence of molecules such as triterpenoids and polyphenols. However, less than five of these compounds have been isolated and identified.[2,3,14] Although chemical and activity studies on crude extracts from *B. tuldoides* have been conducted, detailed chemical constituent analysis remains to be reported. As part of a research program studying the chemical diversity found in bamboo, with an emphasis on determining biological effects, the ethanol extract of Caulis Bambusae in Taenia has been investigated. Herein, we describe the isolation, structural elucidation, and biological assay of three novel lignans and seven known lignans from the *n*-butanol fraction of the extract.

Identification of the active compounds in Caulis Bambusae in Taenia and their biological effects are important in understanding how this medicinal product can be used to aid human health. The isolated lignans were tested by 1,1-diphenyl-2-picrylhydrazyl (DPPH) and ferric reducing/antioxidant power (FRAP) assays to evaluate their antioxidant activities.

■ MATERIALS AND METHODS

Plant Material. Dried Caulis Bambusae in Taenia, cultivated and processed in Guangzhou City (Guangdong Province, China), was purchased from Shucheng Market for Chinese Medicinal Material in Anhui, China. A voucher specimen was deposited in the State Forestry Administration Key Open Laboratory, International Centre for Bamboo and Rattan, Beijing 100102, China.

General Instrumental Equipment. Preparative HPLC was carried out on a Shimadzu LC-6AD instrument with an SPD-20A detector, using a YMC-Pack ODS-A column (250 × 20 mm, 5 μm). HPLC-DAD analysis was performed using a 1200 series system (Agilent Technologies, Waldbronn, Germany) with an Apollo C_{18} column (250 × 4.6 mm, 5 μm, Grace Davison, Chicago, IL). Optical rotations were measured with a JASCO P-2000 polarimeter, and CD (Circular Dichroism) spectra were recorded on a JASCO J-815 CD spectrometer. IR spectra were taken on a Thermo Nicolet FT-IR NEXUS 670 spectrophotometer with KBr pellets. NMR spectra were run on INOVA 500 spectrometers. HRESIMS and ESI-MS spectra were obtained using an Agilent 6540 high resolution quadrupole time-of-flight (Q-TOF) mass spectrometer. DPPH and FARP assays were performed on PerkinElmer Lambda 35 UV−vis spectrometer.

Chemicals and Reagents. Column chromatography was performed with macroporous resin (Diaion HP-20, Mitsubishi Chemical Corp., Tokyo, Japan), Rp-18 (50 μm, YMC, Kyoto, Japan), Sephadex LH-20 (Pharmacia Fine Chemicals, Uppsala, Sweden). 1,1-Diphenyl-2-picrylhydrazyl (DPPH) was purchased from Aladdin Industry Corporation Shanghai. Trolox was purchased from Tokyo Chemical Industry Co., Ltd. 2,6-Di-*tert*-butyl-*p*-cresol (BHT), *tert*-butylhydroquinone (TBHQ), and pyrogallic acid were

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Table 1. NMR Spectroscopic Data (measured at 500 MHz) for Compounds 7, 8, and 10 (in DMSO) from the *n*-Butanol Fraction of an Extract from the Medicinal Preparation of Caulis Bambusae in Taenia

	compound **7**		compound **8**			compound **10**	
no.	δ_C	δ_H, J in Hz	δ_C	δ_H, J in Hz		δ_C	δ_H, J in Hz
1	132.5		134.7			128.3	
2	126.8		125.8			104.8	6.24, 2H, s
3	151.4		151.8			147.9	
4	136.9		137.2			135.1	
5	150.7		151.3			147.9	
6	108.7	6.63, 1H, s	108.5	6.65, 1H, s		104.8	6.24, 2H, s
7	33.4	2.93, 2.68, 2H, dd, 12.0, 6.0	32.7	2.65, 2.56, 2H, dd, 11.5, 4.5		80.5	4.40, 1H, d, 4.0
8	33.5	1.76, 1H, m	39.7	1.55, 1H, m		39.6	3.04, 1H, m
9	63.2	3.40, 3.33, 2H, m	64.4	3.42, 3.37, 2H, m		68.9	4.26, 2H, m
1′	133.1		133.8			133.2	
2′	108.7		106.1			127.1	7.09, 7.07, 2H, d, 8.5
3′	147.6		148.0			115.1	6.65, 6.63, 2H, d, 8.5
4′	134.3		137.8			156.7	
5′	147.6		148.0			115.1	6.65, 6.63, 2H, d, 8.5
6′	108.7		106.1			127.1	7.09, 7.07, 2H, d, 8.5
7′	39.7	4.53, 1H, d, 4.5	40.8	4.24, 1H, d, 5.0		71.2	4.99, 1H, d, 3.0
8′	40.9	2.02, 1H, m	44.0	2.10, 1H, m		49.0	2.68, 1H, m
9′	69.0	3.62, 3.45, 2H, m	70.4	3.76, 3.48, 2H, m		178.1	
3-OCH_3	60.2	3.28, 3H, s	60.7	3.44, 3H, s	3,5-OCH_3	56.3	3, 69, 6H, m
5-OCH_3	56.5	3.79, 3H, s	56.6	3.78, 3H, s			
3′,5′-OCH_3	56.6	3.63, 6H, s	56.5	3.64, 6H, s			
		4-*O*-glucose					7-*O*-glucose
1″	103.4	4.87, 1H, d, 7.0	103.3	4.90, 1H, d, 7.0		101.5	4.10, 1H, d, 8.0
2″	74.8	3.11, 1H, m	74.7	3.13, 1H, m		74.8	3.01, 1H, m
3″	77.6	3.10, 1H, m	77.4	3.11, 1H, m		77.3	3.15, 1H, m
4″	70.4	3.12, 1H, m	70.4	3.14, 1H, m		70.5	3.13, 1H, m
5″	76.9	3.18, 1H, m	76.9	3.19, 1H, m		77.6	2.98, 1H, m
6″	61.3	3.61, 3.43, 2H, m	61.3	3.61, 3.42, 2H, m		61.0	3.57, 3.48, 2H, m
		9′-*O*-glucose					
1‴	103.5	4.19, 1H, d, 7.5	103.6	4.12, 1H, d, 7.5			
2‴	74.9	3.16, 1H, m	74.0	3.15, 1H, m			
3‴	77.8	3.12, 1H, m	77.3	3.13, 1H, m			
4‴	70.9	3.05, 1H, m	70.5	3.03, 1H, m			
5‴	77.3	3.02, 1H, m	77.0	3.01, 1H, m			
6‴	61.7	3.70, 3.48, 2H, m	61.6	3.70, 3.49, 2H, m			

purchased from Sinopharm Chemical Reagent Co., Ltd. 2,4,6-Tripyridyl-*s*-triazine was obtained from XiYa Reagent Company, ChengDu. Sodium acetate anhydrous was obtained from Beijing Chemical Works in China.

Analytical Techniques. The HPLC analysis was a binary elution system consisting of solvent A (methanol) and solvent B (water containing 0.2% acetic acid) with an Rp-18 column. The flow rate was 1 mL/min, and the column temperature was set at 30 °C. The injection volume was 10 μL. The DAD detection wavelength was monitored at 220 nm. LC-MS analysis was carried out to confirm the molecular weight of compounds with an Rp-18 column at ESI-MS. The mobile phases were solvent A (methanol) and solvent C (water containing 0.1% formic acid). The flow rate was 0.2 mL/min. The column temperature was set at 30 °C, and the effluent was monitored at 220 nm. The mass spectrometer was equipped with a JetStream technology ESI ion source. The source parameters were as follows in negative ionization mode: Gas temperature: 350 °C, drying gas flow: 8 L/min, nebulizer: 35 psig, sheath gas temperature: 350 °C, sheath gas flow: 11 L/min, VCap: 3500 V, nozzle voltage (expt): 1000 V, fragmentor: 200 V, 250 V, 300 V, 350 V, 400 V, skimmer: 65 V, OCT 1 RF Vpp: 750 V, collision energy: 10 eV, 15 eV,20 eV, 25 eV, 30 eV. The ^{1}H NMR spectra, ^{13}C NMR spectra, and 2D NMR (HSQC, HMBC, and NOE) spectra were recorded on INOVA 500 spectrometers using DMSO-d_6 as solvent, and tetramethylsilane (TMS) as an internal standard. Chemical shifts are expressed in δ (ppm), and coupling constants are reported in hertz. The concentration of compounds is 10 mg/mL, NMR acquisition duration is 2 min for ^{1}H NMR and 2 h for ^{13}C NMR, and the width range of the NMR spectrum is 0−14 ppm for ^{1}H NMR and 0−220 ppm for ^{13}C NMR.

Extraction, Isolation, and Purification of Compounds from Caulis Bambusae in Taenia. Dried Caulis Bambusae in Taenia (20 kg) was extracted three times with 95% aqueous ethanol at room temperature (1 day each in 20 L). The filtrates were combined and concentrated under reduced pressure for removal of the organic solvent. The concentrated aqueous fraction was extracted with ethyl acetate and *n*-butanol, which yielded an ethyl acetate fraction, *n*-butanol fraction, and water fraction. The *n*-butanol fraction (200 g) was separated on a macroporous resin column using a gradient of water−ethanol (100:0, 85:15, 70:30, 50:50, 5:95), giving five fractions. The 30% ethanol fraction (53.9 g) was applied to an Rp-18 column and eluted with gradient of water−methanol (100:0, 95:5, 90:10, 85:15, 80:20, 75:25, 70:30, 50:50, 0:100), to give nine fractions (1−9). Fraction 6 (4 g) was further subjected to repeated column chromatography (CC) over Sephadex LH-20, eluting with water, and preparative HPLC eluting with methanol−water (15:85), to yield compounds **1** (840 mg), **2** (13 mg), **3** (21 mg), and **4**(12 mg). Fraction 5 (2.5 g) was separated by Sephadex LH-20 (water) CC, to

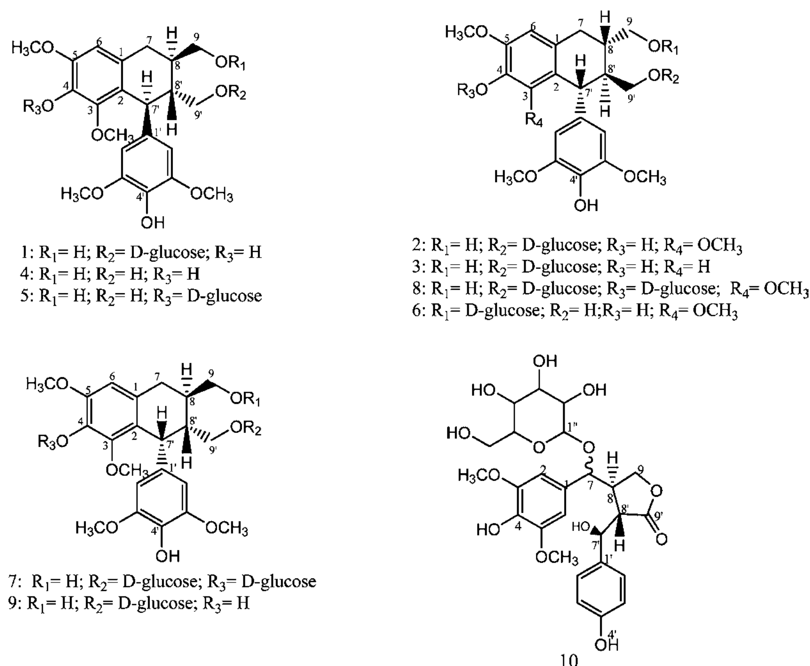

Figure 1. Compounds **1**−**10** isolated from Caulis Bambusae in Taenia.

give compounds **5** (25 mg), **7** (14 mg), and **8** (15 mg). Fraction 2 (1.5 g) was reapplied over Sephadex LH-20 (water) and preparative HPLC, eluting with methanol−water (10:90), which yielded compounds **6** (14 mg), **9** (13 mg), and **10** (10 mg).

(−)-7′-epi-Lyoniresinol 4,9′-Di-O-β-D-glucopyranoside (7). White amorphous powder; $[\alpha]_D$ −73.1° (*c* 0.46, methanol). ESI-MS: *m/z* 743 [M − H]⁻. HRESIMS ($C_{34}H_{48}O_{18}$) *m/z* 743.2761 [M − H]⁻ (calculated for 743.2768). IR (KBr) cm^{-1}: ν_{max} 3433, 2924, 1630, 1401, 1111, 561. UV λ_{max} (methanol) (log ε): 274.8 nm. ^1H and ^{13}C NMR (500 MHz) (DMSO-d_6), see Table 1.

(−)-Lyoniresinol 4,9′-Di-O-β-D-glucopyranoside (8). White amorphous powder; $[\alpha]_D$ −15.5° (*c* 2.0, methanol). ESI-MS: *m/z* 743 [M − H]⁻. HRESIMS ($C_{34}H_{48}O_{18}$) *m/z* 743.2779 [M − H]⁻ (calculated for 743.2768). IR (KBr) cm^{-1}: ν_{max} 3423, 2928, 1611, 1458, 1413, 1223, 1110, 1075, 534. UV λ_{max} (methanol) (log ε): 274.8 nm. ^1H and ^{13}C NMR (500 MHz) (DMSO-d_6), see Table 1.

Bambulignan A (10). White amorphous powder; $[\alpha]_D$ +3.78° (*c* 0.6, methanol). ESI-MS: *m/z* 551 [M − H]⁻. HRESIMS ($C_{26}H_{32}O_{13}$) *m/z* 551.1769 [M − H]⁻ (calculated for 551.1770). IR (KBr) cm^{-1}: ν_{max} 3432, 2929, 1714, 1617, 1517, 1400, 1223, 1113, 1077, 536. UV λ_{max} (methanol) (log ε): 231.0, 274.8 nm. ^1H and ^{13}C NMR (500 MHz) (DMSO-d_6), see Table 1.

Antioxidant Activity. The antioxidant activities of the isolated compounds **1**−**10** from Caulis Bambusae in Taenia were measured by two methods and compared.

DPPH Radical Scavenging Activity. The ability of samples to scavenge the DPPH radical (diphenylpicrylhydrazine) were monitored according to the method of Shimada[15] with minor modifications. Briefly, a 0.3 mL aliquot of compound **1**−**10** (1.0 mg in 1.0 mL 95% ethanol) was added to 0.4 mL of the yellow-colored 1 mmol/L DPPH ethanol solution. The mixture was vortexed for 1 min and then left to stand at room temperature for 30 min in the dark, The absorbance was read at 517 nm with a Lambda 35 UV/visible spectrophotometer, which had been set to zero using a 95% ethanol solution. A decrease of the absorbance indicates an increase of DPPH radical scavenging activity. All samples were carried out in triplicate with BHT and TBHQ as positive controls. The ability to scavenge the DPPH radical was calculated using the following equation:[16]

$$\text{scavenging effect (\%)} = [1 - (A_{sample} - A_{sample\ blank})/A_{control}] \times 100$$

where $A_{control}$ is the absorbance of the control (DPPH solution without sample), A_{sample} is the absorbance of the test sample (DPPH solution plus test sample), and $A_{sample\ blank}$ is the absorbance of the sample only (sample without DPPH solution).

Ferric Reducing/Antioxidant Power (FRAP) Assay. The ferric reducing/antioxidant power of each sample was measured according to the method of Benzie and Strain[17] with some modification. The stock solutions included 300 mM acetate buffer (5.1 g of CH_3COONa and 20 mL of CH_3COOH), 10 mM TPTZ (2,4,6-tripyridyl-*s*-triazine) solution in 40 mM HCl, and 20 mM $FeCl_3{\cdot}6H_2O$ solution. The fresh FARP working solution was prepared by mixing 25 mL of acetate buffer, 2.5 mL of TPTZ solution, and 2.5 mL of $FeCl_3{\cdot}6H_2O$ solution and then warmed at 37 °C before using. A 0.05 mL aliquot of compound **1**−**10** (1.0 mg in 1.0 mL 95% ethanol) was added to 0.5 mL of FARP working solution and 2.45 mL of distilled water. The mixture was shaken vigorously and then left to stand at 37 °C for 10 min in the water bath, The absorbance was read at 593 nm with a Lamda 35 UV/visible spectrophotometer, which had been set to zero using distilled water. High absorbance is an indication of high ferric reducing/antioxidant power. Each sample was run in triplicate. The standard control was 1.0 mmol/L $FeSO_4$, and trolox was used as a positive control.

RESULTS AND DISCUSSION

Isolation and Characterization. Repeated column chromatography over Sephadex LH-20, macroporous resin, Rp-18, and preparative HPLC of the 95% ethanol extract from Caulis Bambusae in Taenia led to isolation of three novel compounds, (−)-7′-*epi*-lyoniresinol 4,9′-di-*O*-*β*-D-glucopyranoside (**7**), (−)-lyoniresinol 4,9′-di-*O*-*β*-D-glucopyranoside (**8**), and bambulignan A (**10**), together with seven known compounds. The known ones were identified as (+)-lyoniresinol 9′-*O*-*β*-D-glucopyranoside (**1**),[18−20] (−)-lyoniresinol 9′-*O*-*β*-D-glucopyranoside (**2**),[21] (−)-5′-methoxyisolariciresinol 9′-*O*-*β*-glucopyranoside (**3**),[22] (+)-lyoniresinol (**4**),[23] (+)-lyoniresinol 4-*O*-*β*-D-glucopyranoside (**5**),[24] (−)-lyoniresinol 9-*O*-*β*-D- glucopyranoside (**6**),[25]and (−)-7′-*epi*-lyoniresinol 9′-*O*-*β*-D-glucopyranoside (**9**)[25] (Figure 1), by comparison of their spectroscopic and physical data with those previously reported

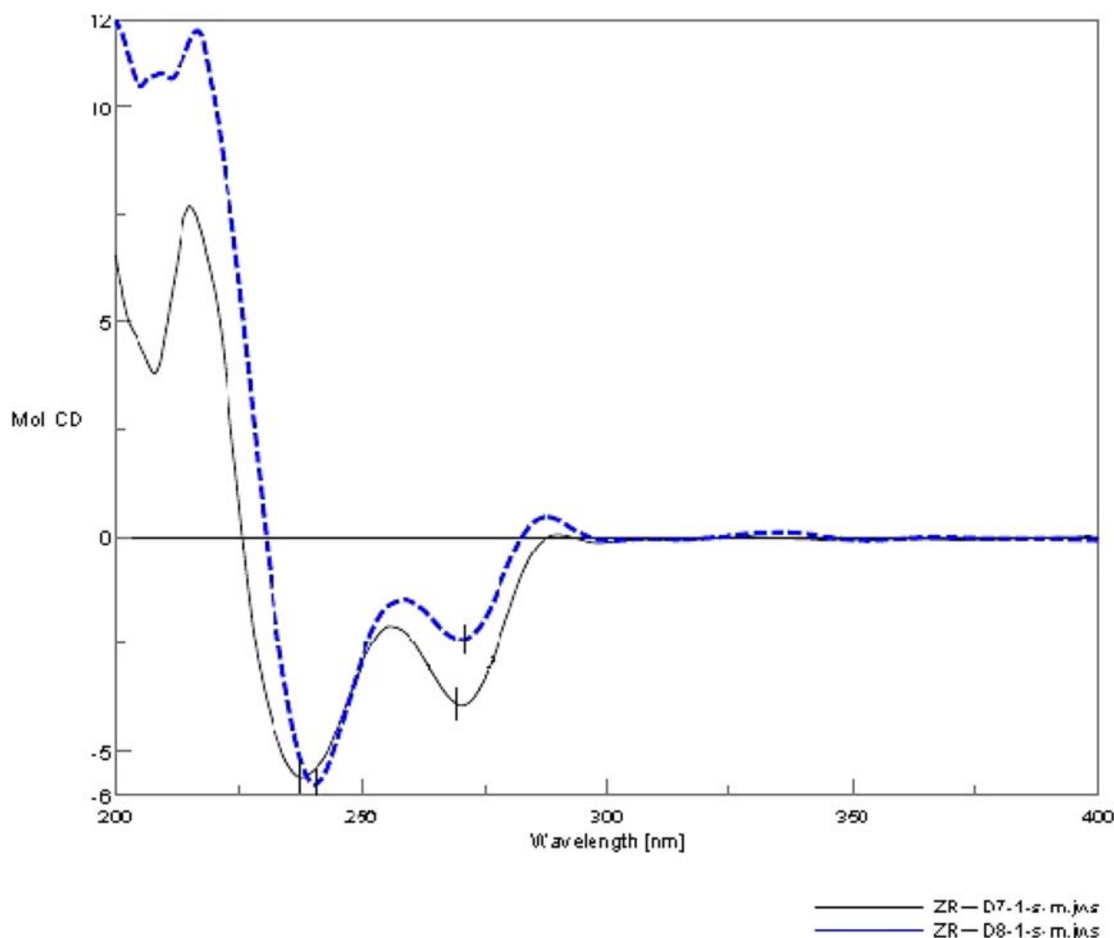

Figure 2. Circular dichroism (CD) curves of the novel compounds **7** and **8** from Caulis Bambusae in Taenia.

in the literature. This was the first isolation of all 10 compounds from Caulis Bambusae in Taenia.

Compound **7** was obtained as a white powder, $[\alpha]_D$ −73.1° (c = 0.46, MeOH, 20 °C), and its molecular formula was determined as $C_{34}H_{48}O_{18}$ by negative HRESIMS (m/z 743.2761 $[M - H]^-$, calcd for 743.2768). All the spectra of compounds **7**, **8**, and **10** are shown in Supporting Information, and NMR assignments are gathered in Table 1. The IR spectrum showed absorption bands for hydroxyl group (3433 cm^{-1}), methylene (2924 cm^{-1}), and aromatic rings (1630 and 1401 cm^{-1}). The ^1H NMR and ^{13}C NMR spectra of compound **7** exhibited signals characteristic of an aryltetralin-type lignan glucoside.[26] In the HSQC spectrum, two anomeric proton signals at δ 4.87 (1H, d, J = 7.0) and δ 4.19 (1H, d, J = 7.5) correlated with corresponding carbon signals at δ 103.4 and δ 103.5 in the ^1H and ^{13}C NMR spectrum, which suggested compound **7** has two terminal β-D-glucopyranosyl units. In the HMBC analysis, the presence of a cross-peak between the anomeric proton δ 4.19 (H-1″) and δ 69.0 (C-9′) revealed the location of the glucosidic linkage at the C-9′ position. In the ^{13}C NMR spectrum (Table 1), the signals of **7** was similar to (+)-lyoniresinol 4,9′-di-O-β-D-glucopyranoside[26,27] except for change of chemical shift at C-7,7′,8,8′. Therefore, the relative configuration of compound **7** should be lyoniresinol 4,9′-di-O-β-D-glucopyranoside. The absolute configuration of compound **7** was determined by examination of the circular dichroism (CD) spectra (Figure 2). In the CD spectrum, the negative Cotton effects at 240 and 270 nm were observed (Figure 2). Comparison to published CD spectra of (+)-lyoniresinol, (−)-lyoniresinol, and (−)-4-*epi*-lyoniresinol,[25] the absolute configuration of the aryl substituent at C-7′ is R for compound **7**. Furthermore, compared with ^{13}C NMR spectra of (−)-lyoniresinol and (−)-4-*epi*-lyoniresinol,[25] the signals of compound **7** at C-7/8 and 7′/8′ were the same as (−)-4-*epi*-lyoniresinol C-7/8 and 7′/8′. The result showed that the structure of compound **7** was (−)-4-*epi*-lyoniresinol 4,9′-di-O-β-D- glucopyranoside.

Compound **8** was also obtained as a white powder, $[\alpha]_D$ −15.5° (c = 2.0, MeOH, 20 °C), and its molecular formula was determined to be $C_{34}H_{48}O_{18}$ by negative HRESIMS (m/z 743.2779 $[M - H]^-$, calcd for 743.2768). The IR and UV spectra of **7** and **8** showed similar absorption patterns. In the ^1H and ^{13}C NMR spectra (Table 1), the signals of compound **8** were similar to those of compound **7** except for a field shift at C-7,7′,8,8′. For compound **8**, the observed C-8 was +6.2 ppm and C-8′ was +3.1 ppm in the ^{13}C NMR spectrum (Table 1). Furthermore, the CD spectrum showed negative Cotton effects at 240 and 270 nm in **8** (Figure 2), which indicated the absolute configuration of the aryl substituent at C-7′ is R. Comparison of the ^{13}C NMR spectra of (−)-lyoniresinol and compound **8** showed that C-7/8 and 7′/8′ were similar. Therefore, the absolute configuration of **8** was concluded to be that of (−)-lyoniresinol. The structure was determined to be (−)-lyoniresinol 4,9′-di-O-β-D-glucopyranoside.

Compound **10** was obtained as a white amorphous powder, and HRESIMS afforded a quasimolecular ion $[M - H]^-$ at m/z

551.1769 (calculated for 551.1770). The ESIMS suggested the molecular formula to be $C_{26}H_{32}O_{13}$. The IR spectrum showed absorption bands for hydroxyl group (3432 cm^{-1}), aromatic rings (1617 and 1400 cm^{-1}), and carbonyl group (1614 cm^{-1}). The ^{1}H NMR spectrum revealed the presence of six aromatic protons at δ 7.09 (2H), δ 6.65 (2H), δ 6.24 (2H) and two aryl-substituted methoxyl groups at δ 3.69, showing a typical pattern for a 3,5-dimethoxy-4-hydroxyphenyl group and a 4-hydroxyphenyl group. Furthermore, the anomeric proton at δ 4.10 (d, *J* = 8.0) indicated a *β*-glycoside linkage for the D-glucose moiety, and there were two aromatic moieties and a *β*-D-glucopyranosyl unit in the lignan.[28,29] In the ^{13}C NMR spectrum, besides the 3,5-dimethoxy-4-hydroxyphenyl and 4-hydroxyphenyl groups, six carbon signals at δ 178.1 (carbonyl), δ 80.5, δ 71.2, δ 68.9 (oxygenated carbons), and δ 49.0, δ 39.6 (methine carbons), and a *β*-D-glucopyranosyl unit at δ 101.5, δ 74.8, δ 77.3, δ 70.5, δ 77.6, δ 61.0 were also observed. In the HMBC spectrum, the anomeric protons δ 4.10 (H-1″), δ 6.24 (H-2,6), δ 2.68 (H-8′), and δ 4.26 (H-9) were correlated to δ 80.5 (C-7), implying that the *O*-glycoside was linked to δ 80.5 (C-7). Both δ 4.99 (H-7′) and δ 2.68 (H-8′) were correlated to δ 178.1 (C-9′), δ 4.99 (H-7′) was also correlated to δ 133.2 ppm (C-1′) and δ 127.1 ppm (C-2′,6′), which confirmed that the furanone was linked to the 4-hydroxyphenyl group (Figure 3). The NOESY experiment on compound **10** showed correlations between δ 2.68 (H-8′, m) and δ 4.40 (H-7, d), δ 4.99 (H-7′, d) and between δ 4.40 (H-7, d) and δ 3.04 (H-8, m), and we presume that C-8 and C-8′ may be *R*′ and *R*′. The CD spectrum showed negative Cotton effects at 257 and 287 nm. Comparison with podorhizol and analogous compounds[30,31] suggested that the configurations of C-8 and C-8′ are 8*S* and 8′*R*. Regarding the configuration of C-7′, it has been reported that a proton of 5′-methoxypodorhizol appeared at δ 5.28 (*J* = 3.0 Hz) in 5′-methoxypodorhizol.[32] In compound **10**, a C-7′ proton appears at δ 4.99 (*J* = 3.0 Hz), revealing that the configuration of C-7′ is *S*. Therefore, the structure of compound **10** was assigned a *O*-glucopyranosyl unit connected to the C-7 position, and a 4-hydroxyphenyl group is included in the partial structures of **10**, so the compound has been named bambulignan A (Figure 1).

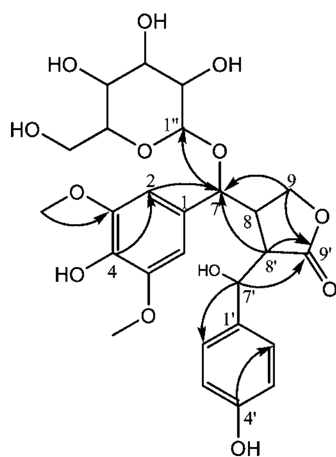

Figure 3. Key HMBC correlations of compound **10**.

Free Radical Scavenging Activities of Isolated Compounds. *DPPH Radical Scavenging Assay.* DPPH is a useful reagent for investigating the free radical-scavenging activities of compounds.[33] The DPPH (diphenylpricrylhydrazine) method is based on the reduction of DPPH solution in the presence of a hydrogen-donating antioxidant to the nonradical form DPPH-H.[34] The isolated compounds **1**−**10** and the controls TBHQ, BHT, and trolox were assayed for antioxidant effects in the DPPH free radical scavenging assay and FRAP assay.[35,36]

The DPPH free radical scavenging ability of each sample is shown in Figure 4. All compounds exhibited DPPH radical scavenging activity. The scavenging actions of compounds **1** and **9** were higher than that of the controls (TBHQ, BHT). All compounds except compound **7** showed potent DPPH radical scavenging activity.

Ferric Reducing/Antioxidant Power (FRAP) Assay. Studies have indicated that antioxidant effects are related to the development of reductones.[33,34,37] Reductones were reported to be terminators of free radical chain reactions and can be measured by the FRAP (ferric reducing/antioxidant power) method. These reductants may limit free radical damage in biological systems.[35,36] Thus, the reductive (H acceptor) activities of the antioxidant compounds from Caulis Bambusae in Taenia were assayed using the FRAP method. The abilities of the isolated compounds **1**−**10** and trolox for reducing the $FeCl_3$ are seen in Figure 5. All 10 compounds possessed the ability to reduce iron(III). Compound **4** showed the strongest reducing power. Compounds **1** and **9** also had notable reducing

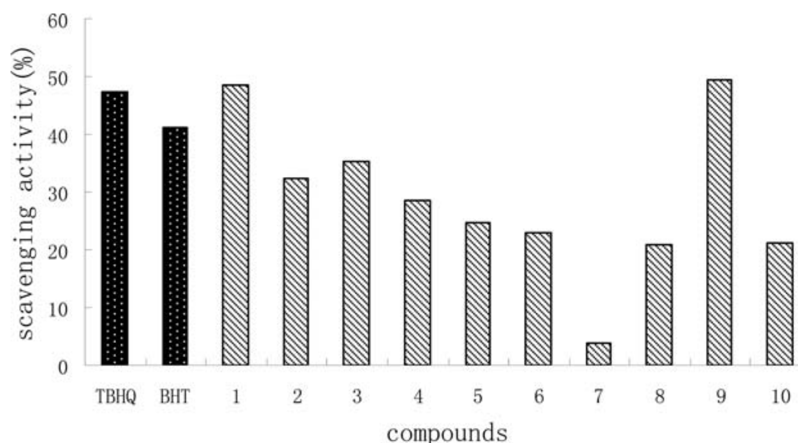

Figure 4. DPPH free radical scavenging ability of the isolated lignan compounds from Caulis Bambusae in Taenia and the positive controls BHT and TBHQ.

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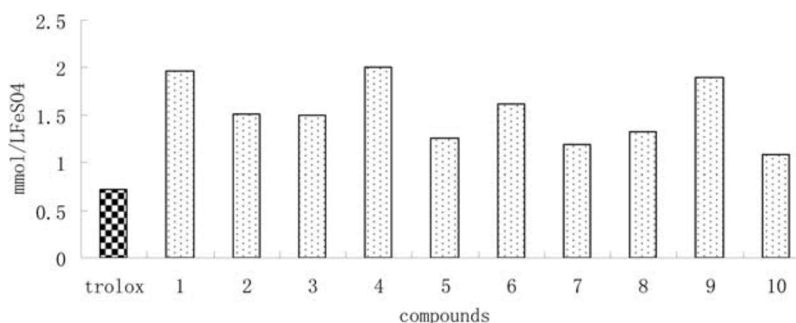

Figure 5. Ferric reducing/antioxidant power of isolated lignan compounds from Caulis Bambusae in Taenia and the positive control trolox.

power. Interestingly, all compounds reported reducing power higher than that of the control (trolox).

According to the results of the DPPH free radical scavenging and FRAP reducing power assays, the antioxidant activities of compounds **1** and **9** were better than that of the other compounds. Because free hydroxyl groups in phenolic compounds are mainly responsible for antioxidant activity,[38] it is worth noting that compounds **1** and **9** both contain multiple phenolic hydroxyl groups, and their configuration also has a certain effect for the antioxidant activity.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H, ^{13}C, HSQC, and HMBC spectra of (−)-7′-*epi*-lyoniresinol 4,9′-di-*O*-*β*-D-glucopyranoside (**7**), ^{1}H, ^{13}C, and HMBC spectra of (−)-lyoniresinol 4,9′-di-*O*-*β*-D-glucopyranoside (**8**), ^{1}H, ^{13}C, HSQC, HMBC, and NOESY spectra of bambulignan A (**10**) in DMSO. IR, HRESIMS, and CD spectra of (−)-7′-*epi*-lyoniresinol 4,9′-di-*O*-*β*-D-glucopyranoside (**7**), (−)-lyoniresinol 4,9′-di-*O*-*β*-D-glucopyranoside (**8**), and bambulignan A (**10**). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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