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Antioxidant *C*-glycosyl flavones from the leaves of *Sasa kurilensis* var. *gigantea*

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Abstract

C-glycosyl flavones, kurilensin A (**1**) and B (**2**), together with two known compounds, tricin-4′-*O*-β-D-glucopyranoside (**3**) and tricin-5-*O*-β-D-glucopyranoside (**4**), were isolated from hot-water extracts of the leaves of *Sasa kurilensis*. The structure of the compounds was determined by spectroscopic analyses including 1D, 2D NMR and MS. The absolute configuration of sugar moieties in **1** and **2** was determined by chiral HPLC analyses of the benzoyl derivatives of acid hydrolysis. Compounds **1** and **2** exhibited higher radical scavenging activity than ascorbic acid in the 1,1-diphenyl-2-pycrylhydrazyl (DPPH) assay system.

Keywords: *Sasa kurilensis*; Gramineae; Flavone glycoside; Kurilensin; Benzoyl derivative; Chiral HPLC analysis; Antioxidant activity

1. Introduction

The genus *Sasa* belongs to the bamboo grasses and is widely distributed in Asian countries including Japan, Korea, China and Russia (Okabe et al., 1975). *Sasa* leaves are known traditionally to have antimicrobial activity in Japan, and have been used clinically for treating hypertension, arteriosclerosis, cardiovascular disease and cancer (Shibata et al., 1975). It is well known that plants of the genus *Sasa* biosynthesize triterpenoids, flavone glycosides and flavonolignans (Ohmoto and Ikuse, 1970; Yoon et al., 2000; Nakajima et al., 2003). Several studies have been carried out to identify some active constituents, including anti-inflammatory and lipid peroxidation factors, from bamboo leaves belonging to the genus *Sasa* (Okabe et al., 1975). *Sasa kurilensis* (Rupr.) Makino et Shibata var. *gigantea* Tatewaki (Gramineae) is also one of the bamboo grasses. It is a native Japanese plant that grows mainly in the northern part of the Japanese archipelago, Saghalien and Korean peninsula, and is a major source of *Sasa* leaves in traditional medicine in Japan. However, the bioactive compounds contained in the plant have not yet been clarified.

In this paper, we report the isolation and structural elucidation of four flavonoid glycosides, including two new *C*-glycosyl flavones kurilensin A (**1**) and B (**2**), as well as their radical scavenging activities against 1,1-diphenyl-2-pycrylhydrazyl (DPPH) radical formation.

2. Results and discussion

Since *Sasa* leaves have been used as decoction in some herbal prescriptions for diseases in Japan, Korea and China (Shibata et al., 1975). In this study, we therefore attempted to establish the identity of biologically active constituent(s) from the hot-water extract of this plant. The lyophilized powder of the hot-water extract of the leaves of *S. kurilensis* was absorbed on a Diaion HP-20 resin, and fractions were successively eluted with aqueous MeOH. A fraction was eluted with 50% and 80% aqueous MeOH, which exhibited

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strong radical scavenging activities in the DPPH assay. This fraction was subjected to bioassay-guided fractionation with several column chromatographic steps, repeated, and further purified by reversed-phase HPLC to yield four compounds (**1**–**4**) (see Fig. 1).

Compound **1** was obtained as an amorphous yellow powder, and its molecular formula $C_{26}H_{28}O_{14}$ was established from high-resolution fast atom bombardment MS (HRFABMS), which gave a pseudomolecular ion peak at *m/z* 563.1424 $[M-H]^-$. UV maxima occurred at 350 nm (band I) and 292 nm (band II), characteristic of a flavonoid system. The ^{1}H NMR spectrum (in CD_3OD) showed the presence of a luteolin skeleton, which was suggested by the aromatic protons at δ 7.40 (1H, *dd*, $J = 2.0$, 8.8 Hz), δ 7.39 (1H, *d*, $J = 2.0$ Hz), δ6.94 (1H, *d*, $J = 8.8$ Hz), δ 6.59 (*1H, s*), δ 6.58 (*1H, s*) (Markham and Chari, 1982). The complete assignments of all proton and carbon resonances of the sugar moieties were based on the TOCSY, COSY, HMQC and HMBC experiments. In the TOCSY and COSY data, the presence of a rhamnopyranose moiety was suggested by a characteristic methyl doublet at δ 0.68 ($J = 6.4$ Hz), anomeric proton a doublet at δ 5.12 ($J = 1.5$ Hz) and four other ^{1}H signals (δ 3.89, 3.44, 3.13, 2.53). Six additional ^{1}H resonances were observed at δ 4.81, 4.00, 3.95, 3.90, 3.76, 3.70, indicating the presence of a second sugar moiety, which was identified as arabinofuranose from analysis of the ^{1}H NMR spectroscopic data and NOE correlation between H-3″ (3.96 ppm) and H-5″ (3.70, 4.00 ppm). The HMBC spectrum of **1** showed the anomeric proton signal H-1″ (δ 4.81) of an arabinofuranose moiety coupled to C-6 (δ 109.9) of a luteolin moiety, and another anomeric proton signal H-1‴ (δ 5.12) of a rhamnopyranose moiety coupled to C-2″ (δ 76.3) of an arabinofuranose moiety (Fig. 2). The absolute configuration of the rhamnopyranose moiety was determined as the L-form on the basis of chiral HPLC analysis of a benzoyl derivative of acid hydrolysis of **1** (Kasai et al., 2005) (see Scheme 1). The optical rotation was also identical between the synthetic model of L-rhamnopyranose tetrabenzoate (**5**) $[\alpha]_D + 75.0$ (c 1.6, $CHCl_3$) and a benzoyl derivative of acid hydrolysis of **1** $[\alpha]_D + 76.0$ (c 0.005, $CHCl_3$). Thus, compound **1** was determined to be luteolin 6-*C*-α-arabinofuranosyl-(1 → 2)-α-L-rhamnopyranoside, a new flavone glycoside named "kurilensin A".

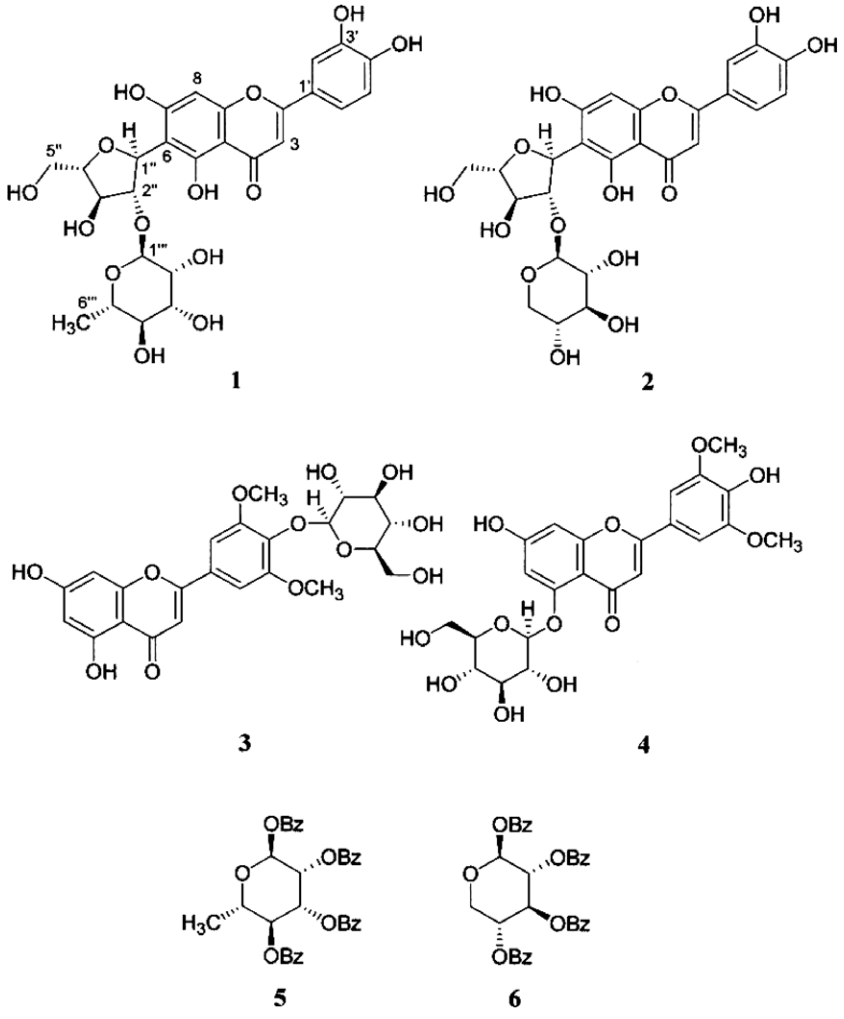


Fig. 1. Chemical structures of compounds **1**–**4**.

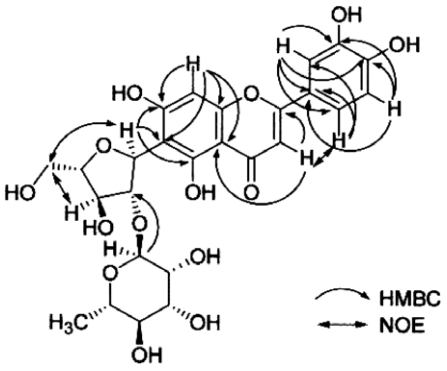


Fig. 2. HMBC and NOE correlations of compound **1**.

Compound **2** was obtained as an amorphous yellow powder, and its molecular formula $C_{25}H_{26}O_{14}$ was established from HRFABMS, which gave a pseudomolecular ion peak at *m/z* 549.1200 $[M-H]^-$. UV maxima occurred at 349 nm (band I) and 292 nm (band II), characteristic of a flavonoid system. The ^1H NMR spectrum (in CD_3OD) showed the presence of a luteolin skeleton, which was suggested by the aromatic protons at δ 7.39 (1H, *dd*, $J = 2.0$, 8.8 Hz), δ 7.38 (1H, *d*, $J = 2.0$ Hz), δ 6.91 (1H, *d*, $J = 8.8$ Hz), δ 6.55 (1H, *s*), δ 6.47 (1H, *s*). In the ^1H NMR spectrum of **2**, two anomeric protons appeared at δ 4.26 (1H, *d*, $J = 7.3$ Hz) and 4.82 (1H, s), which indicated the presence of two sugar moieties identified as arabinofuranose and xylopyranose from analysis of their ^1H–^1H coupling constants (Aquino et al., 2001). The ^1H and ^{13}C NMR spectroscopic data of the two sugar moieties were assigned by the TOCSY, COSY and HMQC experiments, respectively. The HMBC spectrum of **2** showed the anomeric proton signal H-1″ (δ 4.82) of an arabinofuranose moiety coupled to C-6 (δ 109.2) of a luteolin moiety. Another anomeric proton signal H-1‴ (δ 4.26) of a xylopyranose moiety was inferred to be linked at C-2″ (δ 80.2). This substitution pattern agreed with the deshielding effect observed for the C-2″ signal. The absolute configuration of the xylopyranose moiety was determined as the D-form, on the basis of chiral HPLC analysis of a benzoyl derivative of acid hydrolysis of **2** (Kasai et al., 2005). Thus, compound **2** was determined to be luteolin 6-*C*-α-arabinofuranosyl-(1 → 2)-β-D-xylopyranoside, a new flavone glycoside named "kurilensin B".

The known compounds tricin-4′-*O*-β-D-glucopyranoside (**3**) and tricin-5-*O*-β-D-glucopyranoside (**4**) have also been isolated from *S. kurilensis*. These were identified by comparing their spectroscopic data with those reported in the literature (Wilson, 1985; Hong et al., 2004).

Some flavonoid *C*-glycosides including orientin, isoorientin, vitexin and isovitexin have been isolated from the genus *Sasa* (Fu et al., 2005). Furthermore, Park et al. (2007) recently reported that the antioxidative flavonoid *C*-glycoside derivatives, isoorientin and isoorientin 2″-*O*-α-L-rhamnoside, were isolated from the 80% aqueous MeOH extracts of the leaves of *Sasa borealis*. Their structures were similar to that of compounds **1** and **2** from *S. kurilensis*. It is therefore suggested that flavone *C*-glycosides with a luteolin 6-*C*-arabinose moiety are unusual for this plant.

Flavonoids are a major class of secondary polyphenolic metabolites of wide occurrence in the natural plants. There is a beneficial health effect because of their antioxidant properties and their inhibitory role in various stages of tumor development in animal studies (Hollman and Katan, 1999).

For these reasons, the antioxidant activity of the four compounds isolated from *S. kurilensis* was evaluated by DPPH radical scavenging (Table 2). Since ascorbic acid has been reported to have radical scavenging activity (McCune and Johns, 2002), this compound was used as a positive control in this experiment. In the DPPH assay, the two new compounds **1** and **2** exhibited free radical scavenging activity, with IC_{50} values of 6.0 and 5.1 μM, this activity was stronger than that of the positive control ascorbic acid (12 μM) (Table 2). However, the known compounds **3** and **4** did not scavenge DPPH radical at any concentration (Table 2). It is therefore possible that the presence of the two methoxyl group at C-3′ and C-5′ instead of free hydroxyl group is detrimental for the radical scavenging activity (Rice-Evans et al., 1996; Burda and Oleszek, 2001).

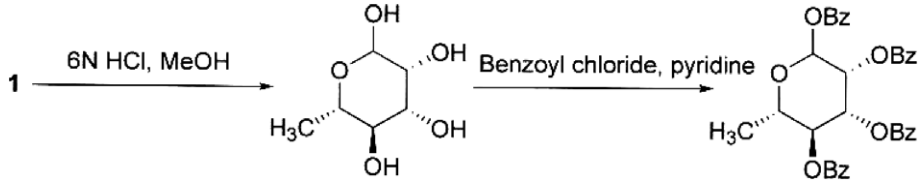
2.1. Concluding remarks

In summary, this is believed to be the first report identifying two new antioxidant constituents, kurilensin A (**1**) and B (**2**), of the leaves of *S. kurilensis*, which have potential to scavenge the DPPH free radical.

3. Experimental

3.1. General

Optical rotations were determined with a Horiba SEPA-3000 high-sensitivity polarimeter. UV spectra were mea-



Scheme 1. Acid hydrolysis of **1** and benzoylation of the sugar unit.

Table 1
^{13}C and ^{1}H NMR spectroscopic data for **1** and **2**[a]

Position	Kurilensin A (**1**)		Kurilensin B (**2**)	
	δ_C	δ_H	δ_C	δ_H
2	166.3		166.2	
3	103.9	6.59 (1H, *s*)	103.7	6.55 (1H, *s*)
4	184.1		183.8	
5	164.1		nd	
6	109.9		109.2	
7	164.9		nd	
8	95.1	6.58 (1H, *s*)	95.4	6.47 (1H, *s*)
9	158.8		158.8	
10	105.3		104.7	
1'	123.5		123.4	
2'	114.2	7.39 (1H, *d*, 2.0)	114.0	7.38 (1H, *d*, 2.0)
3'	146.9		147.2	
4'	151.1		150.0	
5'	116.9	6.94 (1H, *d*, 8.8)	116.8	6.91 (1H, *d*, 8.8)
6'	120.5	7.40 (1H, *dd*, 2.0, 8.8)	120.3	7.39 (1H, *dd*, 2.0, 8.8)
1''	74.2	4.81 (1H)[b]	74.6	4.82 (1H)[b]
2''	76.3	3.76 (1H, *brs*)	80.2	3.98 (1H, *brs*)
3''	71.3	3.96 (1H, *brs*)	70.7	3.98 (1H, *brs*)
4''	77.7	3.76 (1H, *m*)[b]	75.9	3.80 (1H, *dd*, 2.9, 8.8)
5''	71.7	3.70 (1H, *d*, 12.2)	71.8	3.71 (1H, *d*, 12.7)
		4.00 (1H, *dd*, 1.5, 12.2)		4.00 (1H, *m*)[b]
1'''	102.4	5.12 (1H, *d*, 1.5)	106.8	4.26 (1H, *d*, 7.3)
2'''	71.9	3.89 (1H, *dd*, 1.5, 3.4)	75.6	3.08 (1H, *t*, 7.3)
3'''	72.2	3.44 (1H, *dd*, 3.4, 9.3)	71.0	3.19 (1H, *t*, 7.3, 8.8)
4'''	73.3	3.13 (1H, *t*, 9.3)	77.5	3.23 (1H, *m*)[b]
5'''	69.9	2.53 (1H, *dd*, 6.4, 9.3)	66.8	2.75 (1H, *t*, 9.8)
				3.29 (1H, *m*)[b]
6'''	17.9	0.68 (3H, *d*, 6.4)		

nd, not determined.
[a] Values in parentheses indicate coupling constants in Hz.
[b] Coupling constants not clearly defined or obscured by overlap.

Table 2
DPPH radical scavenging activity of compounds isolated from hot-water extracts of *S. kurilensis*

Compounds	IC_{50} (μM)[a]
1	6.0
2	5.1
3	na[b]
4	na[b]
Ascorbic acid	12

[a] IC_{50} values were determined by regression analysis and expressed as the mean of three replicates.
[b] na, no activity.

sured on a Shimadzu UV-1600 UV–Vis spectrometer, whether the IR spectra were recorded on a Shimadzu IR-460 IR spectrophotometer. NMR spectra were obtained using a JEOL GSX-500 spectrometer and a JEOL EX-270 spectrometer in CD_3OD and $CDCl_3$, respectively. Chemical shifts were referenced to the residual solvent peaks CD_3OD (δ_H 3.30 and δ_C 49.8) and $CDCl_3$ (δ_H 7.26 and δ_C 77.0). Mass spectra were measured on a JEOL SX-102 mass spectrometer. Diaion HP-20 (Mitsubishi Chemical), Sephadex LH-20 (25–100 μm, Sigma), silica gel (63–210 μm, Kanto Chemical) and ODS (63–212 μm, Wako) and were used for open column chromatography (cc). Further purification was performed by HPLC equipped with a reversed-phase column (column: SunFire™ Prep C_{18} 5 μm; 10 × 250 mm; Waters). TLC utilized silica gel 60 F_{254} (Merck) and RP-18 F_{254S} (Merck).

3.2. Plant material

Fresh leaves of *S. kurilensis* were collected on Mt. Hakkoda in Aomori Prefecture in 2005, kindly provided and taxonomically identified by HABA laboratory (Tokyo, Japan) and Nippon Haruma (Aomori, Japan), and deposited in a database at the Graduate School of Natural Science and Technology, Kanazawa University, under Registration No. S-2005-02.

3.3. Extraction and isolation

The fresh leaves (8.5 kg) of *S. kurilensis* were extracted with hot H_2O (18 l) at 90 °C for 30 min. After filtration and removal of the solvent by freeze drying, a residue powder (550 g) was obtained, which was passed through a Diaion HP-20 column with a step-wise gradient of aqueous MeOH. Fractions (33 g) eluted with 30% and 50% aqueous

MeOH were subjected to ODS cc with a step-wise gradient of aqueous MeOH (10, 30, 50, 70 and 100%), to give nine fractions. A biologically active fraction 4 (3.5 g) was further separated by silica gel cc with a step-wise gradient of $CHCl_3$ and MeOH (7:1, 5:1, 3:1, 2:1 and 0:1), to give four fractions. Fraction 1 (440 mg) was applied to a Sephadex LH-20 column with MeOH, and H_2O (1:1, v/v) as eluent, then further purified by ODS HPLC with CH_3CN H_2O (1:4, v/v) to give kurilensin A (**1**) (20.0 mg) and kurilensin B (**2**) (3.6 mg). Fraction 3 (168 mg) was purified by Sephadex LH-20 cc with MeOH H_2O (1:1, v/v) and further purified by ODS HPLC with CH_3CN in H_2O (1:3, v/v) to give tricin-4′-*O*-β-D-glucopyranoside (**3**) (0.4 mg) and tricin-5-*O*-β-D-glucopyranoside (**4**) (5.8 mg).

3.4. Kurilensin A (*1*)

Amorphous yellow powder; $[\alpha]_D$–34.0 (MeOH, *c* 0.13); UV (MeOH) λ_{max} (log ε) 350 (3.9), 292 (3.5) nm; IR ν_{max} (KBr) 2988, 2862, 2783, 2517, 1506, 1474, 1458, 1398, 1339, 1115, 1051, 1005 cm^{-1}; for ^1H NMR (500 MHz, CD_3OD) and ^{13}C NMR (125 MHz, CD_3OD) spectroscopic data, see Table 1; HRFABMS *m/z* 563.1424 $[M-H]^-$ (calculated for $C_{26}H_{27}O_{14}$, 563.1422).

3.5. Kurilensin B (*2*)

Amorphous yellow powder; $[\alpha]_D$–28.1 (MeOH, *c* 0.11); UV (MeOH) λ_{max} (log ε) 349 (3.8), 292 (3.5) nm; IR ν_{max} (KBr) 3734, 2824, 2519, 2235, 2046, 1717, 1420, 1115, 1009 cm^{-1}; for ^{1}HNMR (500 MHz, CD_3OD) and ^{13}CNMR (125 MHz, CD_3OD) spectroscopic data, see Table 1; HRFABMS *m/z* 549.1200 $[M-H]^-$ (calculated for $C_{25}H_{25}O_{14}$, 549.1204).

3.6. Determination of stereochemistry of the secondary sugar unit in *1* and *2* by chiral HPLC

Compound **1** or **2** (2.0 mg) in MeOH (0.5 ml) was treated with 6 N HCl (3.0 ml) for 24 h at 80 °C, and evaporated. Each residue was purified by Sephadex LH-20 cc (eluting with H_2O (1:9, v/v) MeOH → MeOH) to give aglycones and sugar moieties, respectively. Benzoyl chloride (0.1 ml) was added to the ice-cooled solution of each sugar moiety in dry pyridine (0.5 ml), and each mixture was stirred at room temperature for 40 h. MeOH (0.1 ml) was added dropwise to each of the reaction mixtures, stirred for 30 min, and then diluted with EtOAc and aqueous Na_2CO_3, and the layers were separated. Each organic layer was washed with brine, and the combined aqueous layers were extracted with EtOAc. Each of the combined organic extracts were dried over $MgSO_4$, and concentrated. Each residual dark brown oil was purified by silica gel cc (eluting with hexane/EtOAc 5:1) to give the corresponding benzoyl derivatives of the sugar moieties. The benzoyl derivatives of each hydrolysis products of **1** or **2** were subjected to chiral HPLC analyses using CHIRALPAK IB (Daisel Chemical Industries, 4.6 × 250 mm; MeOH, 1.0 ml/min; UV detection at 254 nm). The retention time of each of the benzoyl derivatives of the hydrolysis products of **1** or **2** was found to be 8.2 and 9.1 min, respectively. Furthermore, the retention times of synthetic benzoyl derivatives of L-rhamnopyranose (**5**), D-xylopyranose (**6**) and L-xylopyranose were found to be 8.2 and 9.1 and 8.6 min, respectively.

3.7. L-rhamnopyranose tetrabenzoate (*5*) and D-xylopyranose tetrabenzoate (*6*)

Benzoyl chloride (0.5 ml) was added to each ice-cooled solution of ether L-rhamonopyranose (18.0 mg) or D-xylopyranose (15.0 mg) in dry pyridine (1.0 ml), and each mixture was stirred at room temperature for 15 h. MeOH (1.0 ml) was added dropwise to the reaction mixture, stirred for 30 min, and then diluted with EtOAc and aqueous Na_2CO_3, and the layers were separated. Each organic layer was washed with brine, and the combined aqueous layers for each were extracted with EtOAc. Each combined organic extracts were dried over $MgSO_4$, and concentrated, was the corresponding residual dark brown oil were individually purified by silica gel cc (eluting with hexane/EtOAc 5:1) to give either **5** (53 mg, 91%) or **6** (52 mg, 92%) as a colorless oil, respectively. **5**: $[\alpha]_D$ + 75.0 ($CHCl_3$; *c* 1.6); ^1H NMR (270 MHz, $CDCl_3$) δ 1.44 (3H, *d*, *J* = 6.4 Hz), 4.37 (1H, *dd*, *J* = 6.4, 9.8 Hz), 5.81 (1H, t, *J* = 9.8 Hz), 5.88 (1H, *dd*, *J* = 1.9, 3.4 Hz), 6.00 (1H, *dd*, *J* = 3.4, 10.3 Hz), 6.57 (1H, *d*, *J* = 1.5 Hz), 7.27–8.21 (20H, m); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 17.7, 69.3, 69.7, 69.8, 71.1, 91.3, 128.3, 128.4, 128.6, 128.7, 128.8, 128.8, 129.0, 129.7, 129.7, 130.0, 130.1, 130.1, 133.3, 133.4, 133.6, 133.9, 164.0, 165.3, 165.6, 165.7; EIMS *m/z* 580 $[M]^+$.

6: ^1H NMR (270 MHz, $CDCl_3$) δ 3.97 (1H, t, *J* = 10.7 Hz), 4.23 (1H, *dd*, *J* = 5.4, 10.7 Hz), 5.48 (1H, m), 5.57 (1 H, *dd*, *J* = 3.4, 10.3 Hz), 6.21 (1H, t, *J* = 10.3 Hz), 6.70 (1H, *d*, *J* = 3.9 Hz), 7.15–7.57 (12H, m), 7.79–8.08 (8H, m); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 61.2, 69.4, 69.9, 70.2, 90.2, 128.4, 128.4, 128.6, 128.7, 128.8, 128.9, 129.0, 129.7, 129.8, 129.8, 129.9, 133.3, 133.4, 133.5, 133.8, 164.5, 165.3, 165.4, 165.8; EIMS *m/z* 566 $[M]^+$.

3.8. DPPH radical scavenging activity

The DPPH assay was performed by a method previously reported by Marsden (1958) and Zhang et al. (2007). In brief, 100 μl test samples at different concentrations in MeOH and 8.0×10^{-5} M DPPH (Wako) in MeOH (300 μl) were added to a 96-well microtiter plate. The plate was shaken for 1 min on a plate shaker, and incubated for 30 min at room temperature in the dark. After incubation, the absorbance was recorded at 517 nm. The tested samples at different concentrations without DPPH solution were used as a blank control to eliminate the influence of sample

color. Ascorbic acid was used as a positive control, and DPPH solution in MeOH served as a negative control. All tests were independently performed in triplicate and the definition of IC_{50} values in the tested compounds is concentration required to scavenge 50% DPPH free radicals. The DPPH radical scavenging activity was calculated according to the following equation: DPPH radical scavenging activity (%) $= [\{Abs_C - (Abs_S - Abs_B)/Abs_C\}] \times 100$.

Abs_B is the absorbance of the blank control, Abs_C is the absorbance of the negative control and ABS_S is the absorbance of the presence of the sample in DPPH solution.

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