Antioxidant Flavonoid Glycosides from Aerial Parts of the Fern *Abacopteris penangiana*

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Five new flavan-4-ol glycosides, abacopterins E–I (**5**–**9**), and seven known flavonoid glycosides (**3** and **10**–**15**) were isolated from the aerial parts of the fern *Abacopteris penangiana*. Their structures were elucidated on the basis of extensive spectroscopic analysis, including HSQC, HMBC, ^{1}H–^{1}H COSY, and ROESY, and chemical evidence. The isolated glycosides were evaluated for their antioxidant activity using the TEAC assay, and compounds **3**, **5**–**8**, **10**, **11**, **14**, and **15** showed TEAC values of 1.03–1.91 mM.

Ferns are rich in flavonoids, and many types of flavonoids have been discovered from various fern species.[1] Previous phytochemical investigation revealed that some ferns contain unusual flavan-4-ol glycosides and flavones modified in the B-ring.[2–5] *Abacopteris penangiana* (Hook.) Ching (Thelypteridaceae) is widely distributed in the south of China and has been used as a folk medicine to treat upper respiratory tract infections and dysentery.[6,7] With the purpose of seeking bioactive substances from thelypteridaceous ferns and obtaining evidence for classification of *A. penangiana*, we previously investigated a methanol extract of rhizomes of this species and reported the isolation of four flavan-4-ol glycosides, abacopterins A–D (**1**–**4**).[8] In this paper, we report our study of the aerial parts of *A. penangiana* and the isolation, structural elucidation, and antioxidant activity of five new flavan-4-ol glycosides (**5**–**9**) and seven known flavonoid glycosides (**3** and **10**–**15**).

The EtOAc-soluble fraction of an acetone–H_2O (4:1) extract of the aerial parts of *A. penangiana* was subjected to various chromatographic techniques to afford **3**, **5**–**10**, **14**, and **15**. Repeated column chromatography of the *n*-BuOH-soluble fraction led to the isolation of known flavan-4-ol glycosides **11**–**13**.

Abacopterin E (**5**) was isolated as white needles and had the molecular formula $C_{23}H_{26}O_9$ determined by HRESIMS (*m/z* 469.1454, $[M + Na]^+$, calcd 469.1475) and ^{13}C NMR. The spectroscopic data of **5** were similar to those of abacopterin C (**3**).[8] The only difference between these two compounds was the disappearance of a methoxy group, located at C-4′ in **5**, which was replaced by an OH group. ^{1}H and ^{13}C NMR assignments (Tables 1 and 2) were performed using HSQC, ^{1}H–^{1}H COSY, and HMBC experiments. Thus, the structure of **5** was assigned as (2*S*,4*S*)-7,4′-dihydroxy-6,8-dimethyl-4,2″-oxidoflavan-5-*O*-*β*-D-glucopyranoside.

Abacopterin F (**6**) was isolated as white needles with the molecular formula $C_{23}H_{26}O_9$ deduced from the HREIMS spectrum (*m/z* 446.1580 $[M]^+$, calcd 446.1577) and ^{13}C NMR data. Compound **6** had the same molecular formula as **5**, and its UV, IR, and NMR spectra were very similar to those of **5**, indicating that **6** and **5** are structurally related. Comparison of the ^{1}H and ^{13}C NMR spectra of **6** with those of **5** revealed that the coupling constants of H-4 (δ 5.34, d, J = 3.2 Hz) and H_2-3 (δ 2.37, brd, J = 14.0 Hz; 2.14, ddd, J = 14.0, 12.0, 3.2 Hz) were different from those of **5** (Table 1), and the chemical shifts of C-2, C-4, and C-2″ shifted upfield about 3, 7, and 8 ppm, respectively (Table 2). The spectroscopic data suggested that **6** was an isomer of **5**, which had different configurations at C-2 and C-4. To confirm the configurations at C-2 and C-4, the CD spectrum of **6** was compared with that of **5**. A positive Cotton effect at 282 nm ($\Delta\varepsilon$ +1.05) was observed in the CD spectrum of **6**, suggesting the stereochemical relationship between H-2 and H-4 was *trans*.[9] NOE correlation of H-1″ to H-4, observed in the ROESY spectrum of **6**, indicated that the configuration at C-4 was *R*; therefore, the configuration at C-2 was deduced to be *S*. Thus, compound **6** was characterized as (2*S*,4*R*)-7,4′-dihydroxy-6,8-dimethyl-4,2″-oxidoflavan-5-*O*-*β*-D-glucopyranoside, a conclusion supported by comparing its spectroscopic data with those of eruberin A (**10**).[2]

Abacopterin G (**7**) was obtained as white needles with the molecular formula $C_{24}H_{28}O_{10}$ determined by HRESIMS (*m/z* 499.1567 $[M + Na]^+$, calcd 499.1580) and ^{13}C NMR. The ^{1}H and ^{13}C NMR data of **7** (Tables 1 and 2) were similar to those of **6**. Obvious differences were the appearance of a methoxy group (δ 3.34, s, CH_2-OCH_3-6) and the disappearance of a methyl group in ring A. Thus, **7** was determined to be (2*S*,4*R*)-7,4′-dihydroxy-6-methoxymethyl-8-methyl-4,2″-oxidoflavan-5-*O*-*β*-D-glucopyranoside.

Abacopterin H (**8**) was obtained as white needles and had the molecular formula $C_{25}H_{30}O_{10}$ as deduced from the HRESIMS spectrum (*m/z* 513.1718 $[M + Na]^+$, calcd 513.1737) and ^{13}C NMR data. The ^{1}H and ^{13}C NMR data of **8** were similar to those of **7**, except for additional signals of a methoxy group. An HMBC correlation of OMe-4′ (δ 3.67, s) to C-4′ (δ 159.9) established the location of the methoxy at C-4′. Thus **8** was assigned as (2*S*,4*R*)-7-hydroxy-4′-methoxy-6-methoxymethyl-8-methyl-4,2″-oxidoflavan-5-*O*-*β*-D-glucopyranoside.

Abacopterin I (**9**) was obtained as white needles. The molecular formula $C_{30}H_{38}O_{14}$ was deduced from ^{13}C NMR data and HRESIMS data. The spectroscopic data indicated that **9** was a flavan-4-ol glycoside with two sugar units. Comparison of the ^{1}H and ^{13}C NMR spectra of **9** with those of eruberin B (**12**)[3] clearly revealed that the aglycon of **9** was identical to that of **12**. On hydrolysis with acid, **9** yielded D-glucose as determined by GLC. HMBC correlations of H-1″ (δ 5.58) to C-5 (δ 151.3) and H-1‴ (δ 5.41) to C-7 (δ 156.1) indicated that the two D-glucose units were attached to C-5 and C-7. Correlation of H-2″ (δ 4.02) to C-4 (δ 65.8) indicated that C-2″ of the D-glucose located at C-5 formed an ether linkage to C-4 of the aglycon. Comparing the coupling constants of H-2 and H_2-3, CD, and ROESY data with those of **6**, the configurations at C-2 and C-4 were established as 2*S* and 4*R*. On the basis of the above, **9** was concluded to be (2*S*,4*R*)-6,8-dimethyl-4′-methoxy-4,2″-oxidoflavan-5,7-di-*O*-*β*-D-glucopyranoside.

The known compounds abacopterin C (**3**),[8] eruberin A (**10**),[2] triphyllin B (**11**),[3,4] eruberin B (**12**),[3] triphyllin A (**13**),[8] astragalin (**14**),[11] and contigoside B (**15**)[12] were identified by comparison of their spectroscopic data with those reported in the literature.

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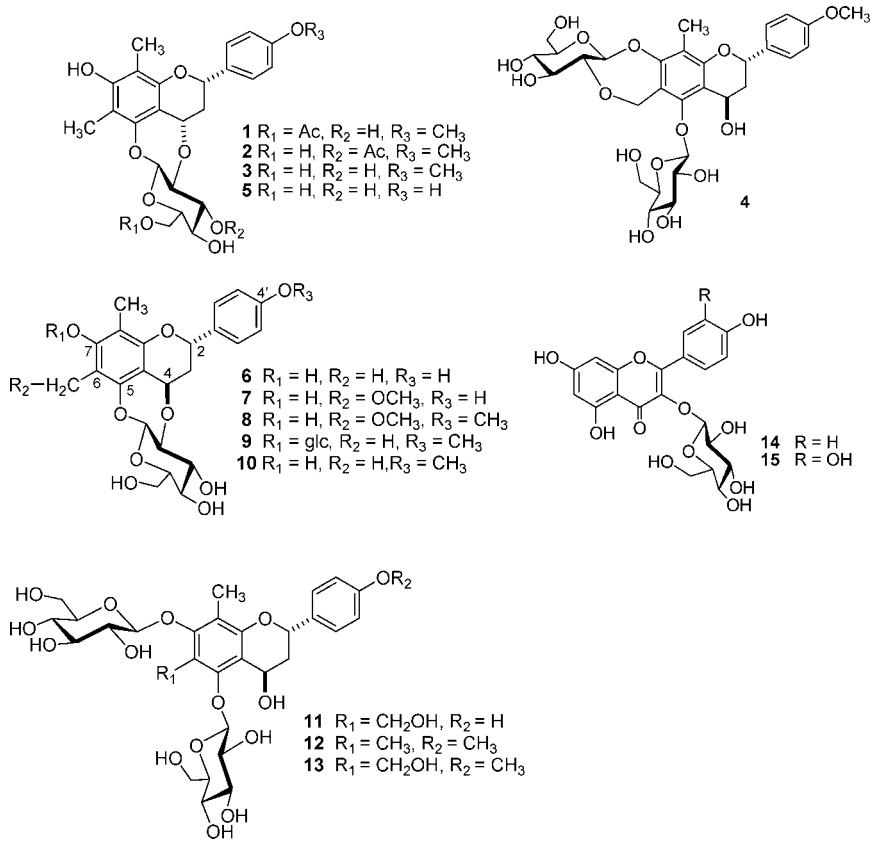

Table 1. ^{1}H NMR Data of Compounds **5**–**9** in Pyridine-d_5 (δ values; J in Hz, in parentheses)

position	**5**	**6**	**7**	**8**	**9**
2	4.99 brd (12.0)	5.12 brd (12.0)	5.09 brd (12.0)	5.06 brd (12.0)	4.98 brd (12.0)
3	2.55 dd (12.0, 8.0)	2.37 brd (14.0)	2.34 brd (14.0)	2.31 brd (14.0)	2.27 brd (14.0)
	2.41 brd (12.0)	2.14 ddd (14.0, 12.0, 3.2)	2.10 ddd (14.0, 12.0, 2.9)	2.06 ddd (14.0, 12.0, 2.9)	1.96 ddd (14.0, 12.0, 3.0)
4	5.26 brt (8.0)	5.34 d (3.2)	5.27 d (2.9)	5.27 d (2.9)	5.19 d (3.0)
Me-6	2.60 s	2.58 s			2.87 s
Me-8	2.44 s	2.49 s	2.41 s	2.41 s	2.65 s
C*H*$_2$-OCH$_3$-6			5.11 brd (11.4)	5.12 brd (11.4)	
			4.97 brd (11.4)	4.97 brd (11.4)	
CH$_2$-OC*H*$_3$-6			3.34 s	3.34 s	
2′,6′	7.52 d (8.6)	7.23 d (8.6)	7.32 d (8.4)	7.30 d (8.7)	7.25 d (8.7)
3′,5′	7.24 d (8.6)	7.17 d (8.6)	7.17 d (8.4)	6.98 d (8.7)	6.97 d (8.7)
OMe-4′				3.67 s	3.76 s
O-glc-5					
1″	4.95 d (7.4)	5.65 d (8.2)	5.62 d (8.4)	5.63 d (8.2)	5.58 d (8.4)
2″	4.08 dd (9.0, 7.4)	4.07 m	4.05 m	4.03 m	4.02 m
3″	4.25 brt (9.0)	4.12 m	4.02 m	4.01 m	4.01 m
4″	4.41 brt (9.0)	4.09 m	4.07 m	4.06 m	3.96 brt (8.5)
5″	4.03 m	4.36 m	4.34 m	4.36 m	4.34 m
6″	4.58 brd (12.0)	4.60 brd (11.6)	4.58 brd (11.3)	4.58 brd (12.2)	4.55 brd (11.1)
	4.47 dd (12.0, 5.0)	4.38 m	4.35 m	4.34 m	4.36 m
O-glc-7					
1‴					5.41 d (7.4)
2‴					4.32 m
3‴					4.30 m
4‴					4.28 m
5‴					3.87 m
6‴					4.38 m
					4.35 m

The antioxidant activity of compounds **3** and **5**–**15** was studied in the TEAC assay.[10] This method measures the relative ability of substances to scavenge the radical cation 2,2′-azinobis(3-ethylbenzothiozoline-6-sulfonate) (ABTS$^{\bullet+}$), compared with that of the synthetic antioxidant Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), an aqueous soluble vitamin E analogue. The activity of the tested samples was expressed as TEAC values. TEAC value is defined as the concentration of Trolox solution with antioxidant potential equivalent to a 1 mM concentration of the test sample. The TEAC values of **3** and **5**–**15** are listed in Table 3. In the TEAC assay, flavonol glycosides **14** and **15** exhibited higher antioxidant activity than those of flavan-4-ol glycosides **3**, **5**–**8**, **10**, and **11**, and compound **15** showed the highest antioxidant activity (1.91 mM). However, free-radical scavenging activity of all of these compounds was lower than that of the reference antioxidant compound quercetin (3.74 mM). Compounds **9**, **12**, and **13** were not active. The structure–antioxidant activity relationships of flavan-4-ol glycosides **3** and **5**–**13** were analyzed. The methylation of OH-

Table 2. ^{13}C NMR Data (δ values) of Compounds **5–9** (pyridine-d_5)

position	5	6	7	8	9
2	77.3	74.1	74.3	74.0	73.8
3	38.3	37.5	37.2	37.2	37.1
4	73.5	66.1	65.9	65.8	65.8
5	152.5	151.1	151.5	151.5	151.3
6	111.2	110.4	109.9	110.0	116.5
7	155.2	156.4	157.2	157.3	156.1 \
8	109.3	108.7	109.1	109.1	117.3
9	152.8	152.3	154.4	154.2	152.0
10	113.4	104.6	104.3	104.3	109.0
Me-6	10.3	10.5			11.1
Me-8	9.7	8.5	9.0	9.0	10.7
*C*H$_2$-OCH$_3$-6			65.7	65.7	
CH$_2$-O*C*H$_3$-6			57.4	57.4	
1′	132.0	132.1	131.8	133.4	133.4
2′,6′	128.3	128.5	128.5	128.2	128.2
3′,5′	116.3	116.2	116.2	114.2	114.2
4′	158.9	158.8	158.9	159.9	159.9
OMe-4′				55.2	55.2
O-glc-5					
1″	103.2	102.3	102.0	102.0	102.2
2″	87.3	79.6	79.5	79.5	79.6
3″	76.0	76.1	76.0	76.1	76.1
4″	71.0	71.5	71.3	71.3	71.7
5″	79.9	76.7	76.5	76.5	76.5
6″	62.3	62.8	62.7	62.7	62.8
O-glc-7					
1‴					106.0
2‴					75.8
3‴					78.3
4‴					71.4
5‴					78.5
6‴					62.8

Table 3. Antioxidant Activity of Compounds **3** and **5–15** in the TEAC Assay

compound	ABTS TEAC (mM)[a]	compound	ABTS TEAC (mM)[a]
3	1.10 ± 0.03	**10**	1.36 ± 0.04
5	1.44 ± 0.02	**11**	1.17 ± 0.04
6	1.32 ± 0.04	**12**	[b]
7	1.51 ± 0.06	**13**	[b]
8	1.03 ± 0.07	**14**	1.46 ± 0.04
9	[b]	**15**	1.91 ± 0.09
quercetin	3.74 ± 0.06		

[a] TEAC values were calculated at 15 min. [b] No activity observed.

4′ in **3** and **8** led to their lower antioxidant activity than that of **5**, **6**, and **7**, and glucosylation of OH-7 and methylation of OH-4′ in **9**, **12**, and **13** clearly resulted in loss of their antioxidant activity. Thus, free OH groups at C-7 and C-4′ of the flavan skeleton are structural requirements for their antioxidant activity.

Experimental Section

General Experimental Procedures. Experimental details have been reported previously.[8]

Plant Material. The aerial parts of *Abacopteris penangiana* (Hook.) Ching were collected in Jiangxi Province (People's Republic of China), in June 2004, and they were identified by Prof. Cen-Ming Tan, Institute of Forest Science, Jiujiang, Jiangxi Province, People's Republic of China. The voucher specimen (PZX0311) was deposited in the College of Pharmacy, Tongji Medical Center, Huazhong University of Science and Technology.

Extraction and Isolation. The dried aerial parts (8.0 kg) were ground and extracted with acetone–H_2O (4:1) three times (20 L each). The extract was concentrated under vacuum to give a residue that was suspended in H_2O (2.5 L) and extracted with petroleum (2.5 L × 3), $CHCl_3$ (2.5 L × 3), and EtOAc (2.5 L × 3), successively. The EtOAc extract (25.0 g) was subjected to silica gel column chromatography (CC), eluting with a $CHCl_3$–MeOH gradient (10:1, 5:1, 2:1) to afford 12 major fractions. Fraction 2 (0.8 g) was purified by Sephadex LH-20 CC with $CHCl_3$–MeOH (1:2), followed by silica gel CC with petroleum–acetone (4:3) to give **8** (30 mg). Fraction 3 (2.0 g) was passed through a silica gel column ($CHCl_3$–MeOH, 12:1) and then subjected to RP C_{18} CC (MeOH–H_2O, 3:2 → 2:1) to give **3** (36 mg) and **10** (27 mg). Fraction 4 (1.2 g) was chromatographed on Sephadex LH 20 using $CHCl_3$–MeOH (2:3) as eluent and then on silica gel using petroleum–acetone (1:1) as eluent, to yield **7** (25 mg). Fraction 5 (2.3 g) was separated using a Sephadex LH 20 column ($CHCl_3$–MeOH, 1:2), then further purified on RP C_{18} (MeOH–H_2O, 3:2) followed by silica gel (petroleum–acetone, 3:4) to yield **5** (29 mg) and **6** (17 mg). Compound **14** (45 mg) was isolated from fraction 7 (1.3 g) by CC on Sephadex LH 20 ($CHCl_3$–MeOH, 1:2) and then RP C_{18} (MeOH–H_2O, 1:1). Fraction 9 (1.9 g) and fraction 10 (2.3 g) were separately purified by RP C_{18} CC (MeOH–H_2O, 2:3 → 1:1) to give **9** (40 mg) and **15** (30 mg), respectively. The *n*-BuOH extract (30 g) was chromatographed on silica gel (1.0 kg), eluting with a $CHCl_3$–MeOH–H_2O gradient (5:1:0.1, 4:1:0.15, 2:1:0.2, 1:1:0.5), to yield 10 fractions. Fraction 2 (1.2 g) was passed through a Sephadex LH 20 column (MeOH–H_2O, 4:1) and then subjected to silica gel CC (EtOAc–MeOH, 7:1 → 6:1) to give **12** (15 mg). Fraction 7 (3.5 g) was chromatographed on Sephadex LH 20, using MeOH–H_2O (4:1) as eluent, then further purified on silica gel eluting with $CHCl_3$–MeOH–H_2O (4:1:0.15) to yield **11** (100 mg) and **13** (30 mg).

Abacopterin E (5): white needles; mp 228–231 °C; $[\alpha]^{20}_D$ –8 (*c* 0.49, MeOH); CD (*c* 0.0020, MeOH), λ ($\Delta\varepsilon$) 225 (−6.15), 280 (−0.99) nm; UV (MeOH) λ_{max} (log ε) 232 (4.03), 276 (3.37) nm; IR (KBr) ν_{max} 3401, 2920, 1616, 1520, 1469, 1240, 1133, 1115, 1075, 834 cm^{-1}; ^1H NMR (pyridine-d_5, 400 MHz), see Table 1; ^{13}C NMR (pyridine-d_5, 100 MHz), see Table 2; HRESIMS (positive ion mode) *m/z* 469.1454 $[M + Na]^+$ (calcd for $C_{23}H_{26}O_9Na$, 469.1475).

Abacopterin F (6): white needles; mp 201–204 °C; $[\alpha]^{20}_D$ +99 (*c* 0.18, MeOH); CD (*c* 0.0030, MeOH), λ ($\Delta\varepsilon$) 221 (−1.53), 239 (+1.13), 282 (+1.05) nm; UV (MeOH) λ_{max} (log ε) 232 (4.00), 276 (3.37) nm; IR (KBr) ν_{max} 3401, 2925, 1616, 1519, 1476, 1339, 1231, 1142, 1061, 837 cm^{-1}; ^1H NMR (pyridine-d_5, 400 MHz), see Table 1; ^{13}C NMR (pyridine-d_5, 100 MHz), see Table 2; EIMS *m/z* 446 $[M]^+$ (2), 285 (100), 267 (10), 191 (18), 166 (19), 131 (5), 107 (10), 91 (3), HREIMS *m/z* 446.1580 $[M]^+$ (calcd for $C_{23}H_{26}O_9$, 446.1577).

Abacopterin G (7): white needles; mp 235–238 °C; $[\alpha]^{20}_D$ +72 (*c* 0.24, MeOH); CD (*c* 0.0020, MeOH), λ ($\Delta\varepsilon$) 222 (−1.46), 239 (+3.08), 281 (+1.12) nm; UV (MeOH) λ_{max} (log ε) 233 (3.92), 275 (3.31) nm; IR (KBr) ν_{max} 3413, 2928, 1616, 1520, 1458, 1241, 1152, 1070, 839 cm^{-1}; ^1H NMR (pyridine-d_5, 400 MHz), see Table 1; ^{13}C NMR (pyridine-d_5, 100 MHz), see Table 2; HRESIMS (positive ion mode) *m/z* 499.1567 $[M + Na]^+$ (calcd for $C_{24}H_{28}O_{10}Na$, 499.1580).

Abacopterin H (8): white needles; mp 248–250 °C; $[\alpha]^{20}_D$ +74 (*c* 0.48, MeOH); CD (*c* 0.0048, MeOH), λ ($\Delta\varepsilon$) 221 (−1.22), 239 (+1.19), 281 (+0.15) nm; UV (MeOH) λ_{max} (log ε) 233 (4.09), 274 (3.36) nm; IR (KBr) ν_{max} 3429, 2930, 1614, 1517, 1461, 1249, 1152, 1072, 832 cm^{-1}; ^1H NMR (pyridine-d_5, 400 MHz), see Table 1; ^{13}C NMR (pyridine-d_5, 100 MHz), see Table 2; HRESIMS (positive ion mode) *m/z* 513.1718 $[M + Na]^+$ (calcd for $C_{25}H_{30}O_{10}Na$, 513.1737).

Abacopterin I (9): colorless needles; mp 196–198 °C; $[\alpha]^{20}_D$ +71 (*c* 0.20, MeOH); CD (*c* 0.0036, MeOH), λ ($\Delta\varepsilon$) 250 (+0.56), 283 (+1.83) nm; UV (MeOH) λ_{max} (log ε) 230 (4.06), 276 (3.46), 281 (3.48) nm; IR (KBr) ν_{max} 3428, 2925, 1615, 1517, 1462, 1249, 1155, 1071, 837 cm^{-1}; ^1H NMR (pyridine-d_5, 400 MHz), see Table 1; ^{13}C NMR (pyridine-d_5, 100 MHz), see Table 2; HRESIMS (positive ion mode) *m/z* 645.2133 $[M + Na]^+$ (calcd for $C_{30}H_{38}O_{14}Na$, 645.2159).

Acidic Hydrolysis of Compounds 5–9. Compounds **5–9** (each 2 mg) were hydrolyzed with 9% HCl (1.5 mL) at 90 °C for 5 h, respectively. After being cooled to 2–4 °C, the reaction mixture was filtered and the filtrate was freeze-dried. The dried material was dissolved in dry pyridine (100 μL), and 200 μL of 0.1 M L-cysteine methyl ester hydrochloride was added. The mixture was stirred at 60 °C for 1 h, then 150 μL of HMDS-TMCS (hexamethyldisilazane–trimethylchlorosilane, 2:1) was added and the mixture was stirred at 60 °C for another 30 min After centrifugation, the supernatant was analyzed by GLC. D-Glucose for compounds **5–9** was detected by co-injection of each hydrolysate with a standard D-glucose derivative, giving a single peak at 23.61 min The derivative obtained using standard L-glucose had a retention time of 24.56 min.[13]

ABTS Radical Cation Scavenging Activity. Free-radical scavenging activity was performed using the TEAC assay.[10] ABTS was dissolved in water to a concentration of 7 mM, and then potassium persulfate was added to reach a 2.45 mM final concentration. The

reaction mixture was stored in the dark at room temperature for 16 h, then the $ABTS^{\bullet+}$ solution was diluted with water to an absorbance of 0.700 ± 0.003 at 734 nm. The reaction was initiated by the addition of 1.98 mL of diluted $ABTS^{\bullet+}$ to 20 μL of each sample solution. The decrease of absorbance at 734 nm was recorded for each sample after 15 min (0 to 20 μM final concentration after addition of $ABTS^{\bullet+}$). Assays were performed in triplicate, and solvent blanks were run during each assay. The percentage inhibition of absorbance was calculated for each concentration and was plotted as a function of concentration of compound or standard, 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox). The antioxidant activities of compounds **3** and **5**–**15** are expressed as TEAC (Trolox equivalent antioxidant capacity) values in comparison with TEAC activity of the reference compound quercetin.

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