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PHENOL GLUCOSIDE GALLATES FROM *MALLOTUS JAPONICUS**

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Key Word Index—*Mallotus japonicus*; Euphorbiaceae; phenol glucoside gallates; 4-hydroxy-2-methoxyphenol; 4-hydroxy-3-methoxyphenol; 3,4,5-trimethoxyphenol; 2,6-dimethoxy-4-hydroxyphenol.

Abstract—Five phenol glucoside gallates were isolated from *Mallotus japonicus*, and their structures characterized by chemical and spectroscopic means as 4-hydroxy-2-methoxyphenol 1-*O*-β-D-(6′-*O*-galloyl)glucoside, 4-hydroxy-3-methoxyphenol 1-*O*-β-D-(2′,6′-di-*O*-galloyl)glucoside, 4-hydroxy-3-methoxyphenol 1-*O*-β-D-(2′,3′,6′-tri-*O*-galloyl)glucoside, 3,4,5-trimethoxyphenol 1-*O*-β-D-(2′,6′-di-*O*-galloyl)glucoside and 4-hydroxy-2,6-dimethoxyphenol 1-*O*-β-D-(6′-*O*-galloyl)glucoside. In addition, the occurrence of several flavan-3-ols and prodelphinidins was demonstrated.

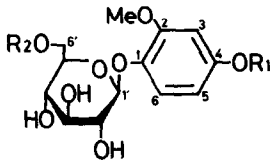
INTRODUCTION

As part of our chemical studies on tannins and related compounds in crude drugs, we previously reported on the structure elucidation of 17 gallotannins and related compounds from the bark and the leaves of *Mallotus japonicus* [1]. Further examination of the bark has now led to the isolation of five new phenol glucoside gallates (**1–5**), together with 4-hydroxy-3-methoxyphenol 1-*O*-β-D-(6′-*O*-galloyl)glucopyranoside (**6**), four flavan-3-ols (**7–10**) and three prodelphinidins (**11–13**). In this paper, we describe the isolation and characterization of these compounds.

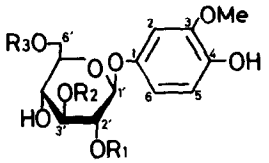
RESULTS AND DISCUSSION

The aqueous acetone extract of the fresh bark of *Mallotus japonicus* was subjected to a combination of Sephadex LH-20, MCI-gel CHP-20P and Avicel cellulose chromatography using various solvent systems to afford 13 compounds (**1–13**). Among them, compounds **6–13** were identified as 4-hydroxy-3-methoxyphenol 1-*O*-β-D-(6′-*O*-galloyl)glucoside (**6**) [2], (+)-catechin (**7**) [3], (+)-gallocatechin (**8**) [4], (−)-epicatechin 3-*O*-gallate (**9**) [5], (−)-epigallocatechin 3-*O*-gallate (**10**) [6] and prodelphinidins B-3(**11**) [Nonaka, G. *et al.*, unpublished data], B-2 3′-*O*-gallate (**12**) [6] and B-4 3′-*O*-gallate (**13**) [Hashimoto, F. *et al.*, unpublished data], by comparison of their physical and spectral data with those of authentic samples.

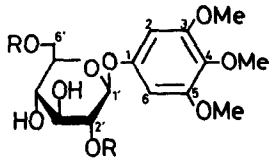
Compound **1** showed a prominent $[M-H]^-$ ion peak at *m/z* 453 in the negative FABMS. The ^1H and ^{13}C NMR spectra indicated the presence of a galloyl group [δ7.19 (2H, *s*); δ110.2 (2C), 120.9, 140.3, 145.8 (2C), 167.7] and a sugar moiety (δ4.83 (1H, *d*, $J=7$ Hz); δ102.5]. On enzymatic hydrolysis with tannase, **1** gave gallic acid and a hydrolysate (**1a**), whose ^1H NMR spectrum showed, together with sugar resonances, signals due to ABX-type aromatic protons [δ6.36 (1H, *dd*, $J=3$, 9 Hz), 6.54 (1H, *d*, $J=3$ Hz), 7.03 (1H, *d*, $J=9$ Hz) and a methoxyl group [δ3.82 (3H, *s*)]. On subsequent acid hydrolysis with 0.8 M HCl, **1a** yielded glucose and an



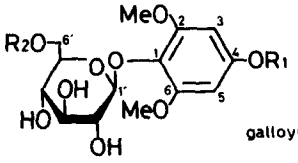
1 R1=H, R2=galloyl
1a R1=R2=H
1c R1=Me, R2=H



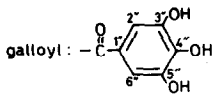
2 R1=R3=galloyl, R2=H
2a R1=R2=R3=H
3 R1=R2=R3=galloyl
6 R1=R2=H, R3=galloyl



4 R=galloyl



5 R1=H, R2=galloyl
5a R1=R2=H
5b R1=Me, R2=H



galloyl :

* Part 82 in the series 'Tannins and Related Compounds'. For Part 81 see ref. [1].

aglycone (**1b**), which was identified as 4-hydroxy-2-methoxyphenol [2] by direct comparison with an authentic sample previously prepared from **6**. The ^{1}H NMR shifts to lower fields [δ4.39 (1H, *dd*, J = 6,12 Hz), 4.64 (1H, *dd*, J = 2,12 Hz)] of the glucose C-6 methylene proton signals in **1** confirmed the location of the galloyl group at this position. Methylation of **1a** with diazomethane afforded the monomethyl ether (**1c**). The ^{1}H–^{1}H NOESY spectrum of **1c** clearly showed that two methoxyl groups [δ3.76, 3.85 (each 3H, *s*)] are adjacent to the C-3 aromatic proton [δ6.60 (1H, *d*, J = 3 Hz)]. Thus, the glucosyl residue is linked at C-1. The configuration of the glucose anomeric centre was confirmed to be β from the ^{1}H NMR coupling constant of anomeric signal [δ4.83 (1H, *d*, J = 7 Hz)]. Accordingly, **1** is 4-hydroxy-2-methoxyphenol 1-*O*-β-D-(6′-*O*-galloyl)glucopyranoside.

Compound **2** (negative FABMS *m/z*: 605 [M − H]$^-$) gave ^{1}H NMR spectrum exhibiting the presence of two galloyl groups [δ7.18, 7.20 (each 2H, *s*)], an aromatic ring with one methoxy group [δ3.63 (3H, *s*), 6.51 (1H, *dd*, J = 3, 9 Hz), 6.53 (1H, *d*, J = 3 Hz), 6.67 (1H, *d*, J = 9 Hz)] and a sugar moiety. Hydrolysis of **2** with tannase furnished gallic acid and a glycoside (**2a**). The latter was shown by direct physical and spectral comparison to be identical with 4-hydroxy-3-methoxyphenol 1-*O*-β-D-glucopyranoside [2] obtained by similar tannase hydrolysis of **6**. The galloyl groups were determined to be located at the C-6 and C-2 positions of the glucose moiety by the downfield shifts of the corresponding signals [δ4.46 (1H, *dd*, J = 6, 12 Hz), 4.70 (1H, *dd*, J = 2, 12 Hz), 5.14 (1H, *t*, J = 7 Hz)] in the ^{1}H NMR spectrum of **2**. Consequently, **2** is 4-hydroxy-3-methoxyphenol 1-*O*-β-D-(2′,6′-di-*O*-galloyl)glucopyranoside.

Compound **3** (negative FABMS *m/z*: 757 [M − H]$^-$) liberated gallic acid and 4-hydroxy-3-methoxyphenol 1-*O*-β-D-glucopyranoside (**2a**) on treatment with tannase. The ^{1}H NMR spectrum of **3** showed the occurrence of three galloyl groups [δ7.07 (2H, *s*), 7.21 (4H, *s*)] in the molecule. In addition, the signals due to a methylene and two methines bearing the galloyl group [δ4.55 (1H, *dd*, J = 6, 12 Hz), 4.74 (1H, *dd*, J = 2, 12 Hz), 5.43 (1H, *t*, J = 7 Hz), 5.63 (1H, *t*, J = 7 Hz)] are shifted downfield, and these signals could be assigned to H-6′, H-2′ and H-3′ by examination of the ^{1}H–^{1}H COSY spectrum. Thus, **3** is 4-hydroxy-3-methoxyphenol 1-*O*-β-D-(2′,3′,6′-tri-*O*-galloyl)glucopyranoside.

Compound **4** exhibited an [M − H]$^-$ ion peak at *m/z* 649 in the negative FABMS. Acid hydrolysis of **4** with 0.8M HCl yielded gallic acid, glucose and an aglycone. The ^{1}H NMR spectrum of **4** showed the presence of two galloyl groups [δ7.16, 7.17 (each 2H, *s*)] and glucose with β-configuration (δ5.30, J = 7 Hz). The observation of two equivalent methoxyl groups [δ3.62 (6H, *s*)] and two aromatic protons [δ6.47 (2H, *s*)], indicated that the aglycone moiety possesses a symmetrical substitution system. The ^{1}H–^{1}H NOESY spectrum of **4** showed that the aromatic protons and the sugar anomeric proton [δ5.30 (1H, *d*, J = 7 Hz)] are close to each other, and that **4** is a 3,4,5-trimethoxyphenol glucoside digallate. The chemical shifts of the glucose signals in the ^{1}H and ^{13}C NMR spectra of **4**, were consistent with those observed in **2**. Thus, the galloyl groups are located at the C-2 and C-6 positions of the glucose moiety. Accordingly, **4** is 3,4,5-trimethoxyphenol 1-*O*-β-D-(2′,6′-di-*O*-galloyl) glucopyranoside.

Compound **5** (negative FABMS *m/z*: 483 [M − H]$^-$) furnished gallic acid, glucose and an aglycone on hydrolysis with 0.8 M HCl. The ^{1}H and ^{13}C NMR spectra of **5** showed the presence of one galloyl group [δ7.15 (2H, *s*)], one glucose moiety [δ64.5, 71.0, 74.6 (2C), 76.6, 104.7], an aromatic ring with a symmetrical substitution [δ6.16 (2H, *s*); δ94.1 (2C), 128.2, 154.1 (2C), 154.7] and two methoxyl groups [δ3.59 (6H, *s*)]. From these spectral data, **5** appears to be a glucoside gallate of 4-hydroxy-2,6-dimethoxyphenol (2,6-dimethoxy-1,4-benzenediol). On enzymatic hydrolysis with tannase, **5** gave gallic acid and a hydrolysate (**5a**). Subsequent methylation of **5a** with diazomethane yielded the monomethyl ether (**5b**). The ^{1}H–^{1}H NOESY spectrum of **5b** showed that one isolated methoxyl proton [δ3.79 (3H, *s*)] is in close proximity to the aromatic protons [δ6.29 (2H, *s*)], indicating that **5b** is 2,4,6-trimethoxyphenol glucoside. The location of the galloyl group in **5** was confirmed to be at the C-6′ position by comparison of the ^{1}H and ^{13}C NMR sugar signal patterns with those of **1**, while the β-configuration of the anomeric centre was concluded from the coupling constant of the H-1′ signal [δ4.72 (1H, *d*, J = 7 Hz)]. Thus, **5** is 4-hydroxy-2,6-dimethoxyphenol 1-*O*-β-D-(6′-*O*-galloyl) glucopyranoside.

EXPERIMENTAL

The instruments used to obtain physical data were the same as described in our previous paper [1].

Plant material. The bark of *Mallotus japonicus* was collected at Fukuoka prefecture, Japan, in May, 1987. Voucher specimens are deposited at the Herbarium, Faculty of Pharmaceutical Sciences, Kyushu University.

Extraction and isolation. The fresh bark (43.5 kg) of *M. japonicus* was chopped into small pieces and extracted × 3 with 80% aq. Me_2CO at room temp. After concn under red. pres., the resulting ppt. was removed by filteration. The filtrate was applied to a column of Sephadex LH-20. Elution with H_2O containing increasing proportions of MeOH yielded five fractions: I (860 g), II (580 g), III (420 g), IV (140 g) and V (250 g). Fraction I was rechromatographed over MCI-gel CHP-20P (H_2O–MeOH), Sephadex LH-20 (80% aq. MeOH, EtOH) and Avicel cellulose (H_2O) to give **1** (98 mg), **5** (111 mg) and **6** (278 mg). Fraction II was repeatedly chromatographed over Sephadex LH-20 (EtOH, 60% aq. MeOH), MCI-gel CHP-20P (H_2O–MeOH) and Fuji gel ODS G-3 (H_2O–MeOH) to afford **2** (128 mg) and **4** (253 mg). On similar CC, fraction III furnished **3** (58 mg), **7** (15.1 g), **8** (16.1 g), **9** (1.7 g), **10** (6.7 g) and **11** (352 mg), while fraction IV gave **12** (667 mg) and **13** (1.1 g).

General procedure for enzymatic hydrolysis. A soln of the sample (30 mg) in H_2O (2 ml) was treated with tannase at room temp. for 3 hr. The reaction mixture was directly applied to a column of MCI-gel CHP-20P. Elution with H_2O–MeOH (1:0–0:1) furnished gallic acid and a hydrolysate.

General procedure for methylation. A soln of the sample (5–10 mg) in MeOH (2 ml) was treated with CH_2N_2 with ice-cooling for 1 hr. The solvent was evapd off and the residue purified by silica gel CC using $CHCl_3$–MeOH–H_2O (90:10:1–40:10:1).

General procedure for acid hydrolysis. A soln of the sample (5–20 mg) in 0.8 M HCl (1–3 ml) was heated at 90° for 1 hr, and the reaction mixture extracted × 3 with EtOAc. The EtOAc layer was washed with H_2O, dried (Na_2SO_4) and concd to dryness. The residue was subjected to CC over Bondapak C_{18}/Porasil B using H_2O–MeOH (1:0–0:1) to yield gallic acid and an aglycone. The aq. layer was neutralized with Amberlite IRA-400 and concd to dryness. The residue dissolved in MeOH was checked by

Avicel SF cellulose chromatography [*n*-BuOH–pyridine–H_2O (6:4:3)].

4-Hydroxy-2-methoxyphenol 1-*O*-β-D-(6′-*O*-*galloyl*)*glucoside* (**1**). An amorphous powder, $[\alpha]_D^{13}$ −36.6° (Me_2CO–H_2O; *c* 1.3). Negative FABMS *m/z*: 453 $[M-H]^-$. ^1H NMR (Me_2CO-d_6 + D_2O): δ3.80 (3H, *s*, OMe), 4.39 (1H, *dd*, *J* = 6, 12 Hz, H-6′), 4.64 (1H, *dd*, *J* = 2, 12 Hz, H-6′), 4.83 (1H, *d*, *J* = 7 Hz, H-1′), 6.31 (1H, *dd*, *J* = 3, 9 Hz, H-5), 6.52 (1H, *d*, *J* = 3 Hz, H-3), 7.03 (1H, *d*, *J* = 9 Hz, H-6), 7.19 (2H, *s*, galloyl H). ^{13}C NMR: see Table 1. (Found: C, 49.76; H, 5.24. $C_{20}H_{22}O_{12}\cdot 3/2H_2O$ requires: C, 49.90; H, 5.20%).

4-Hydroxy-2-methoxyphenol 1-*O*-β-D-*glucoside* (**1a**). An amorphous powder. Negative FABMS *m/z*: 301 $[M-H]^-$. ^1H NMR (Me_2CO-d_6 + D_2O): δ3.82 (3H, *s*, OMe), 4.85 (1H, *d*, *J* = 8 Hz, H-1′), 6.36 (1H, *dd*, *J* = 3, 9 Hz, H-5), 6.54 (1H, *d*, *J* = 3 Hz, H-3), 7.03 (1H, *d*, *J* = 9 Hz, H-6). (Found: C, 49.18; H, 6.19. $C_{13}H_{18}O_8\cdot H_2O$ requires: C, 48.75; H, 6.25%).

4-Hydroxy-2-methoxyphenol (**1b**). Colourless prisms (H_2O), mp 75–76°. ^1H NMR (Me_2CO-d_6): δ3.76 (3H, *s*, OMe), 6.26 (1H, *dd*, *J* = 3, 8 Hz, H-5), 6.46 (1H, *d*, *J* = 3 Hz, H-3), 6.64 (1H, *d*, *J* = 8 Hz, H-6).

2,4-Dimethoxyphenol 1-*O*-β-D-*glucoside* (**1c**). An amorphous powder, $[\alpha]_D^{20}$ −62.2° (H_2O; *c* 0.2). ^1H NMR (Me_2CO-d_6 + D_2O): δ3.76, 3.85 (each 3H, *s*, OMe), 4.79 (1H, *d*, *J* = 7 Hz, H-1′), 6.44 (1H, *dd*, *J* = 3, 9 Hz, H-5), 6.60 (1H, *d*, *J* = 3 Hz, H-3), 7.13 (1H, *d*, *J* = 9 Hz, H-6).

4-Hydroxy-3-methoxyphenol 1-*O*-β-D-(2′,6′-*di*-*O*-*galloyl*)*glucoside* (**2**). A powder (H_2O), mp 244–246°, $[\alpha]_D^{26}$ −46.3° (Me_2CO; *c* 0.5). Negative FABMS *m/z*: 605 $[M-H]^-$. ^1H NMR (Me_2CO-d_6): δ3.63 (3H, *s*, OMe), 4.46 (1H, *dd*, *J* = 6, 12 Hz, H-6′), 4.70 (1H, *dd*, *J* = 2, 12 Hz, H-6′), 5.14 (1H, *t*, *J* = 7 Hz, H-2′), 5.18 (1H, *d*, *J* = 7 Hz, H-1′), 6.51 (1H, *dd*, *J* = 3, 9 Hz, H-6), 6.53 (1H, *d*, *J* = 3 Hz, H-2), 6.67 (1H, *d*, *J* = 9 Hz, H-5), 7.18, 7.20 (each 2H, *s*, galloyl H). ^{13}C NMR: see Table 1. (Found: C, 49.39; H, 4.62. $C_{27}H_{26}O_{16}\cdot 3H_2O$ requires: C, 49.09; H, 4.85%).

4-Hydroxy-3-methoxyphenol 1-*O*-β-D-*glucoside* (**2a**). Colourless needles (H_2O), mp 208–210°, $[\alpha]_D^{16}$ −53.3° (MeOH; *c* 0.6). ^1H NMR (Me_2CO-d_6 + D_2O): δ3.82 (3H, *s*, OMe), 4.82 (1H, *d*, *J* = 7 Hz, H-1′), 6.57 (1H, *dd*, *J* = 3, 9 Hz, H-6), 6.75 (1H, *d*, *J* = 9 Hz, H-5), 6.81 (1H, *d*, *J* = 3 Hz, H-2).

4-Hydroxy-3-methoxyphenol 1-*O*-β-D-(2′,3′,6′-*tri*-*O*-*galloyl*)*glucoside* (**3**). An amorphous powder, $[\alpha]_D^{26}$ −103.5° (Me_2CO; *c* 0.5). Negative FABMS *m/z*: 757 $[M-H]^-$. ^1H NMR (Me_2CO $-d_6$): δ3.65 (3H, *s*, OMe), 4.55 (1H, *dd*, *J* = 6, 12 Hz, H-6′), 4.74 (1H, *dd*, *J* = 2, 12 Hz, H-6′), 5.36 (1H, *d*, *J* = 7 Hz, H-1′), 5.43 (1H, *t*, *J* = 7 Hz, H-2′), 5.63 (1H, *t*, *J* = 7 Hz, H-3′), 6.55 (1H, *dd*, *J* = 3, 9 Hz, H-6), 6.56 (1H, *d*, *J* = 3 Hz, H-2), 6.71 (1H, *d*, *J* = 9 Hz, H-5), 7.07 (2H, *s*, galloyl H), 7.21 (4H, *s*, galloyl H). ^{13}C NMR: see Table 1. (Found: C, 52.48; H, 4.26. $C_{34}H_{30}O_{20}\cdot H_2O$ requires: C, 52.85; H, 4.12%).

3,4,5-Trimethoxyphenol 1-O-β-D-(2′,6′-*di*-O-*galloyl*)*glucoside* (**4**). Colourless needles (H_2O), mp 269–271°, $[\alpha]_D^{26}$ −33.5° (Me_2CO; *c* 0.5). Negative FABMS *m/z*: 649 $[M-H]^-$. ^1H NMR (Me_2CO-d_6): δ3.60 (3H, *s*, OMe), 3.62 (6H, *s*, OMe), 4.46 (1H, *dd*, *J* = 5, 12 Hz, H-6′), 4.70 (1H, *dd*, *J* = 2, 12 Hz, H-6′), 5.18 (1H, *t*, *J* = 8 Hz, H-2′), 5.30 (1H, *d*, *J* = 8 Hz, H-1′), 6.26 (2H, *s*, H-2 and H-6), 7.16, 7.17 (each 2H, *s*, galloyl H). ^{13}C NMR: see Table 1. (Found: C, 49.60; H, 4.76. $C_{29}H_{30}O_{17}\cdot 3H_2O$ requires: C, 49.43; H, 5.11%).

Table 1. ^{13}C NMR spectral data of compounds **1**–**5** at 25.05 MHz (δ values)

C	1*	2*	3†	4†	5*
Aglycone					
1	148.5	151.8	151.6	154.9	128.2
2	150.4	103.6	103.6	96.2	154.1
3	104.4	148.5	148.6	154.5	94.1
4	153.3	142.9	143.1	134.9	154.7
5	107.4	115.7	115.8	154.5	94.1
6	118.1	109.9	110.0	96.2	154.1
OMe	56.3	56.0	56.1	56.3(×2)	56.6(×2)
				60.5	
Glucose					
1′	102.5	101.7	101.4	101.2	104.7
2′	74.0	74.8	72.7	74.8	74.6
3′	76.6	75.4	76.0	75.6	76.6
4′	71.0	71.4	69.6	71.4	71.0
5′	74.5	75.1	75.1	75.3	74.6
6′	64.6	64.5	64.2	64.4	64.5
Galloyl					
1″	120.9	121.2	120.6	121.6	120.1
		121.4	120.8	121.7	
			121.1		
2″,6″	110.2(×2)	109.9(×4)	110.0(×6)	109.9(×2)	110.3(×2)
				110.1(×2)	
3″,5″	145.8(×2)	146.0(×4)	145.8(×6)	146.0(×4)	145.7(×2)
4″	140.3	139.0(×2)	139.1(×2)	138.9(×2)	139.2
COO	167.7	166.4	166.2	166.0	168.0
		167.1	166.8	166.7	
			167.1		

*In Me_2CO-d_6 + D_2O.
†In Me_2CO-d_6.

4-Hydroxy-2,6-dimethoxyphenol 1-O-β-D-(6′-O-*galloyl*)*glucoside* (**5**). Colourless needles (H_2O), mp 242–243°, $[\alpha]_D^{26}$ −36.6° (MeOH–H_2O; *c* 0.3). Negative FABMS *m/z*: 483 $[M-H]^-$. ^1H NMR (Me_2CO-d_6 + D_2O): δ3.59 (6H, *s*, OMe), 4.37 (1H, *dd*, *J* = 6, 12 Hz, H-6′), 4.56 (1H, *dd*, *J* = 2, 12 Hz, H-6′), 4.72 (1H, *d*, *J* = 7 Hz, H-1′), 6.16 (2H, *s*, H-3 and H-5), 7.15 (2H, *s*, galloyl H). ^{13}C NMR: see Table 1. (Found: C, 50.03; H, 5.25. $C_{21}H_{24}O_{13}\cdot H_2O$ requires: C, 50.20; H, 5.18%).

4-Hydroxy-2,6-dimethoxyphenol 1-O-β-D-*glucoside* (**5a**). An amorphous powder, $[\alpha]_D^{20}$ −21.9° (H_2O; *c* 0.3). Negative FABMS *m/z*: 331 $[M-H]^-$. ^1H NMR (Me_2CO-d_6 + D_2O): δ3.80 (6H, *s*, OMe), 4.70 (1H, *d*, *J* = 7 Hz, H-1′), 6.21 (2H, *s*, H-3 and H-5). (Found: C, 49.99; H, 6.11. $C_{14}H_{20}O_9$ requires: C, 50.60; H, 6.02%).

2,4,6-Trimethoxyphenol 1-O-β-D-*glucoside* (**5b**). An amorphous powder, $[\alpha]_D^{20}$ −20.0° (H_2O; *c* 0.1). ^1H NMR (Me_2CO-d_6 + D_2O): δ3.79 (3H, *s*, OMe), 3.85 (6H, *s*, OMe), 4.70 (1H, *d*, *J* = 8 Hz, H-1′), 6.29 (2H, *s*, H-3 and H-5).

4-Hydroxy-3-methoxyphenol 1-O-β-D-(6′-O-*galloyl*)*glucoside* (**6**). An amorphous powder (H_2O), $[\alpha]_D^{25}$ −31.3° (Me_2CO; *c* 0.5). ^1H NMR (Me_2CO-d_6 + D_2O): δ3.74 (3H, *s*, OMe), 4.66 (1H, *dd*, *J* = 2, 12 Hz, H-6′), 4.89 (1H, *d*, *J* = 7 Hz, H-1′), 6.61 (1H, *dd*, *J* = 2, 8 Hz, H-6), 6.70 (1H, *d*, *J* = 2 Hz, H-2), 6.74 (1H, *d*, *J* = 8 Hz, H-5), 7.19 (2H, *s*, galloyl H). ^{13}C NMR: see Table 1.

(+)-*Catechin* (**7**). Colourless needles (H_2O), mp 175–176°, $[\alpha]_D^{24}$ +8.6° (Me_2CO; *c* 0.9). ^1H NMR (Me_2CO-d_6): δ2.52 (1H, *dd*, *J* = 8, 16 Hz, H-4), 2.92 (1H, *dd*, *J* = 6, 16 Hz, H-4), 3.99 (1H, *m*, H-3), 4.66 (1H, *d*, *J* = 8 Hz, H-2), 5.80, 6.02 (each 1H, *d*, *J* = 2 Hz, H-6 and H-8), 6.68–6.93 (total 3H, H-2′, H-5′ and H-6′).

(+)-*Gallocatechin* (**8**). Colourless granules (H_2O), mp 186–188°, $[\alpha]_D^{24}$ +1.4° (Me_2CO; *c* 1.0). ^1H NMR (Me_2CO-d_6): δ2.52 (1H, *dd*, *J* = 8, 16 Hz, H-4), 2.90 (1H, *dd*, *J* = 6, 16 Hz, H-4), 4.00 (1H, *m*, H-3), 4.54 (1H, *d*, *J* = 6 Hz, H-2), 5.89, 6.03 (each 1H, *d*, *J* = 2 Hz, H-6 and H-8), 6.47 (2H, *s*, H-2′ and H-6′).

(−)-*Epicatechin* 3-O-*gallate* (**9**). An amorphous powder, $[\alpha]_D^{24}$ −177.5° (Me_2CO; *c* 1.6). ^1H NMR (Me_2CO-d_6): δ2.88 (1H, *dd*, *J* = 3, 18 Hz, H-4), 3.10 (1H, *dd*, *J* = 4, 18 Hz, H-4), 5.12 (1H, *br s*, H-2), 5.50 (1H, *m*, H-3), 6.04, 6.08 (each 1H, *d*, *J* = 2 Hz, H-6 and H-8), 6.75 (1H, *d*, *J* = 8 Hz, H-5′), 6.90 (1H, *dd*, *J* = 2, 8 Hz, H-6′), 7.03 (2H, *s*, galloyl H).

(−)-*Epigallocatechin* 3-O-*gallate* (**10**). Colourless needles (H_2O), mp 245–247°, $[\alpha]_D^{23}$ −183.7° (Me_2CO; *c* 1.0). ^1H NMR (Me_2CO-d_6): δ2.90 (1H, *dd*, *J* = 3, 18 Hz, H-4), 3.10 (1H, *dd*, *J* = 4, 18 Hz, H-4), 5.07 (1H, *br s*, H-2), 5.55 (1H, *m*, H-3), 6.05 (2H, *br s*, H-6 and H-8), 6.63 (2H, *s*, H-2′ and H-6′), 7.03 (2H, *s*, galloyl H).

Prodelphinidin B-3 (**11**). An amorphous powder, $[\alpha]_D^{24}$ −205.6° (Me_2CO; *c* 1.0). ^1H NMR (Me_2CO-d_6 + D_2O): δ2.57 (1H, *dd*, *J* = 8, 16 Hz, H-4′), 2.93 (1H, *dd*, *J* = 6, 16 Hz, H-4′), 5.77–6.39 (total 4H, H-6, H-8, H-6′ and H-8′), 6.57, 6.60 (each 2H, *s*, B-ring H and B′-ring H).

Prodelphinidin B-2 3′-O-*gallate* (**12**). An amorphous powder, $[\alpha]_D^{20}$ −52.7° (Me_2CO; *c* 0.6). ^1H NMR (Me_2CO-d_6): δ2.74–3.26 (2H, *m*, H-4′), 4.02 (1H, *m*, H-3), 4.84 (1H, *br s*, H-4), 5.15 (2H, *br s*, H-2 and H-2′), 5.58 (1H, *m*, H-3′), 5.97–6.09 (total 3H, H-6, H-8 and H-6′), 6.50, 6.70 (each 2H, *s*, B-ring H and B′-ring H), 7.09 (2H, *s*, galloyl H).

Prodelphinidin B-4 3′-O-*gallate* (**13**). An amorphous powder, $[\alpha]_D^{23}$ −262.2° (Me_2CO; *c* 1.2). ^1H NMR (Me_2CO-d_6): δ2.81–3.21 (2H, *m*, H-4′), 5.88–6.29 (total 3H, H-6, H-8 and H-6′), 6.41, 6.63, 6.76, 7.02 (total 4H, B-ring H and B′-ring H), 7.08 (2H, *s*, galloyl H).

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