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PHENOLIC GLUCOSIDE GALLATES FROM *QUERCUS MONGOLICA* AND *Q. ACUTISSIMA**

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Key Word Index—*Quercus mongolica*; *Q. acutissima*; Fagaceae; phenolic glucoside gallates; D-*threo*-guaiacylglycerol; L-*threo*-guaiacylglycerol; 3-methoxy-4-hydroxyphenol; gentisic acid; 3,5-dimethoxy-4-hydroxyphenol; *cis*-coniferyl alcohol.

Abstract—Six phenolic glucoside gallates: D-*threo*-guaiacylglycerol 8-*O*-, L-*threo*-guaiacylglycerol 8-*O*-, 3-methoxy-4-hydroxyphenol 1-*O*-, gentisic acid 5-*O*-, 3,5-dimethoxy-4-hydroxyphenol 1-*O*- and *cis*-coniferyl alcohol 4-*O*-β-D-(6′-*O*-galloyl)glucopyranosides were isolated from *Quercus mongolica* and *Q. acutissima*.

INTRODUCTION

Although fagaceous plants are regarded as rich sources of varying polyphenolic compounds including hydrolysable and condensed tannins [1–8], little is known about the lower molecular weight phenolics [7, 8]. In continuing our systematic chemical studies of polyphenolic constituents in fagaceous plants, we have now isolated and characterized six new phenolic glucoside gallates (**1**–**6**), together with 3,4,5-trimethoxyphenol 1-*O*-β-D-(6′-*O*-galloyl)glucopyranoside (**7**) [8], from acorns of *Quercus mongolica* and the bark of *Q. acutissima*.

RESULTS AND DISCUSSION

The aqueous acetone extract of the fresh acorns of *Quercus mongolica* as subjected to a combination of Sephadex LH-20 and MCI-gel CHP-20P chromatography using various solvent systems to afford compounds **1**–**3** and **6**. Extraction of the fresh bark of *Q. acutissima* with aqueous acetone, followed by a similar chromatographic separation, gave compounds **3**–**5** and **7**. Compound **7** was found to be identical with 3,4,5-trimethoxyphenol 1-*O*-β-D-(6′-*O*-galloyl)glucopyranoside [8] by comparison of its physical and spectral data with those of an authentic sample.

Compound **1** showed a prominent $(M-H)^-$ ion peak at *m/z* 527 in negative FABMS and the ^1H and ^{13}C NMR spectra indicated the presence of a galloyl group [δ7.18 (2H, *s*); δ110.0 (2C), 121.0, 139.1, 145.9 (2C), 167.4] and a sugar moiety. On enzymatic hydrolysis with tannase **1** gave gallic acid and a hydrolysate (**1a**), whose ^1H NMR spectrum showed signals due to three aromatic protons [δ6.76 (1H, *d*, *J* = 8 Hz), 6.86 (1H, *br d*, *J* = 8 Hz), 7.04 (1H, *br s*)] and a methoxyl group [δ3.83 (3H, s)]. Compound **1a**, when incubated with crude hesperidinase, yielded glucose and an aglycone (**1b**), which was identified as D-guaiacylglycerol [9] by comparison of the physical and spectral data with those of an authentic sample. Furthermore, **1b** was concluded to be a *threo*-isomer on the basis of a large coupling constant (8 Hz) [10] of the lowfield benzylic proton (H-7) signal (δ5.96) in the ^1H NMR spectrum of the tetraacetate (**1c**) of **1b**. Examination of the ^1H and ^{13}C NMR spectra of **1** suggested that the galloyl group was located at the C-6 position of the glucose moiety [δ4.33 (1H, *dd*, *J* = 12, 6 Hz, H-6′), 4.70 (1H, *dd*, *J* = 12, 2 Hz, H-6′); δ64.4 (C-6′)]. The location of the glucose moiety was determined as follows. Methylation of **1** with CH_2N_2 gave the tetramethyl ether (**1d**), FDMS *m/z*: 584 $[M]^+$, indicating that the glucose residue was not linked to the phenolic hydroxyl group of the C-4 position, but to C-7, C-8 or C-9 position (alcoholic hydroxyl). The ^1H NMR spectrum of the nonaacetate (**1e**) of **1** revealed the H-7 signal shifted downfield at δ5.97 (1H, *d*, *J* = 5 Hz), showing that the glucose moiety was not linked to this position. On the other hand, the ^{13}C NMR spectrum of **1a** showed a lowfield methine signal (δ87.5) ascribable to C-8, indicating clearly the location of the glucose moiety at this position (C-8). The configuration of the anomeric carbon was determined to be β on the basis of the *J* value (8 Hz) of the anomeric proton signal (δ4.64 or 4.68) in the ^1H NMR spectrum of **1**. Consequently **1** was characterized as D-*threo*-guaiacylglycerol 8-*O*-β-D-(6′-*O*-galloyl)glucopyranoside.

Compound **2**, negative FABMS *m/z*: 527 $[M-H]^-$ showed ^1H and ^{13}C NMR spectra similar to those of **1**. Enzymatic hydrolysis of **2** with tannase yielded gallic acid and a hydrolysate (**2a**), which on subsequent enzymatic hydrolysis with crude hesperidinase gave glucose and L-guaiacylglycerol (**2b**). The ^1H NMR spectrum of the tetraacetate (**2c**) of **2b** showed a large coupling constant (8 Hz) of the H-7 signal (δ5.96), indicating **2b** to be a *threo*-isomer. The galloyl group was determined to be located at the C-6 position of the glucose moiety by lowfield shifts of the corresponding signals [δ4.26 (1H, *dd*, *J* = 12, 6 Hz, H-6′), 4.74 (1H, *dd*, *J* = 12, 2 Hz, H-6′); δ64.5 (C-6′)] in the ^1H and ^{13}C NMR spectra of **2**. The ^1H NMR spectrum of

*Part 54 in the series "Tannins and Related Compounds". For Part 53 see Ishimaru, K., Nonaka, G. and Nishioka, I., *Phytochemistry* **26**, 1167.

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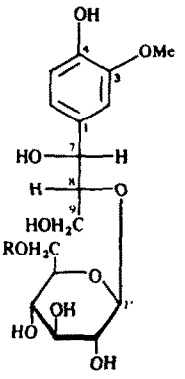
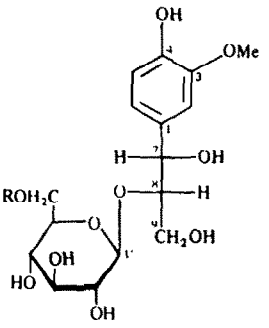


1 R = galloyl
1a R = H



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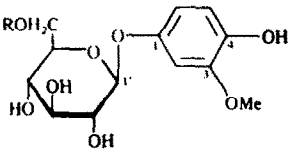

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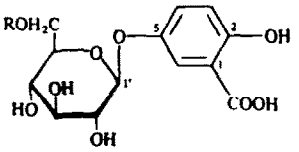
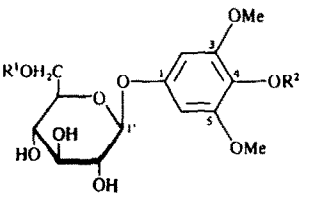
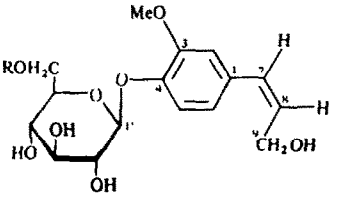
3a R = H



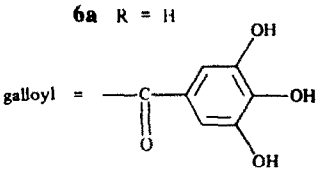
4 R = galloyl
4a R = H



5 R^1 = galloyl, R^2 = H
7 R^1 = galloyl, R^2 = Me



6 R = galloyl
6a R = H



the nonaacetate (**2d**) (FDMS *m/z*: 906 $[M]^+$) of **2** showed the lowfield H-7 signal [δ5.84 (1H, *d*, J = 8 Hz)], while the ^{13}C NMR spectrum of **2a** showed a lowfield methine signal (δ87.9) ascribable to C-8. From these spectral data the location of the glucose moiety was established to be at the C-8 position. The configuration of the anomeric centre was concluded to be β based on the J value (8 Hz) of the H-1′ signal (δ4.60 or 4.68) in the ^{1}H NMR spectrum of **2**. Consequently **2** was characterized as L-*threo*-guaiacylglycerol 8-*O*-β-D-(6′-*O*-galloyl)glucopyranoside.

The ^{1}H NMR spectrum of **3** suggested the presence of a galloyl group [δ7.19 (2H, *s*)] and an aromatic ring with one methoxyl group [δ3.72 (3H, *s*, OMe), 6.60 (1H, *br d*, J = 8 Hz), 6.68 (1H, *br s*), 6.74 (1H, *d*, J = 8 Hz)]. This was also supported by ^{13}C NMR spectroscopy (Table 1). On enzymatic hydrolysis with tannase **3** gave gallic acid and a hydrolysate (**3a**), which on subsequent enzymatic hydrolysis with crude hesperidinase, afforded glucose and a crystalline aglycone (**3b**). Compound **3b** was identified as 3-methoxy-4-hydroxyphenol by direct comparison of the physical and spectral data with those of an authentic sample prepared from vanillin by the Dakin reaction. The location of the glucose moiety was determined by analysis of the ^{1}H NMR spectrum of the pentaacetate (**3c**) of **3a**; the aromatic signal attributed to H-5 was shifted downfield [δ6.92 (1H, *d*, J = 8 Hz)] by acetylation as compared with that in **3a** [δ6.76 (1H, *d*, J = 8 Hz)], thus indicating that the sugar was not located at the neighbouring C-4 phenolic hydroxyl group, but was situated at the C-1 position. Furthermore, the galloyl group was concluded to be located at the C-6 position of the glucose moiety by examination of the ^{1}H and ^{13}C NMR spectra of **3** [δ4.38 (1H, *dd*, J = 12, 6 Hz, H-6′), 4.70 (1H, *dd*, J = 12, 2 Hz, H-6′). δ64.6 (C-6′)]. The β-configuration of the anomeric centre was determined on the basis of the coupling constant (8 Hz) of the H-1′ signal (δ4.90) in the ^{1}H NMR spectrum of **3**. Thus, compound **3** was characterized as 3-methoxy-4-hydroxyphenol 1-*O*-β-D-(6′-*O*-galloyl)glucopyranoside.

Compound **4** was shown to contain a galloyl group by ^{1}H NMR spectroscopy [δ7.20 (2H, *s*)]. On enzymatic hydrolysis with tannase, **4** gave gallic acid and a hydrolysate (**4a**), which on acid hydrolysis with 1 N H_2SO_4 yielded glucose and gentisic acid (**4b**). The location of the glucose moiety was determined by an NOE experiment on the dimethyl ether (**4c**) of **4a**. On irradiation of the methoxyl signal at δ3.77, 20% NOE was observed at the H-3 signal [δ7.08 (1H, *d*, J = 8 Hz)], indicating that the methoxyl group was located at the C-2 position and the glucose at the C-5 position. The galloyl group was concluded to be located at the C-6 position of the glucose moiety by analysis of the ^{1}H and ^{13}C NMR spectra of **4** [δ4.40 (1H, *dd*, J = 12, 6 Hz, H-6′), 4.66 (1H, *dd*, J = 12, 2 Hz, H-6′)]. The β-configuration of the anomeric carbon was established on the basis of the J value (8 Hz) of the H-1′ signal (δ4.96) in the ^{1}H NMR spectrum of **4**.

Table 1. ^{13}C NMR spectral data of 1–6 and their derivatives at 25.05 MHz (δ values)

	1*	1a*	1b*	2*	2a*	2b†	3*	3a*	4†	5*	6*	6a*
Aglycone												
C-1	132.4	132.8	134.3	132.9	133.1	134.9	151.9	151.9	113.3	151.5	132.2	132.4
C-2	111.6	111.7	111.3	111.4	111.6	111.2	102.7	102.8	157.2	96.4	113.7	113.8
C-3	148.0	148.2	148.1	148.2	148.3	148.0	148.4	148.6	118.6	148.6	146.3	146.6
C-4	146.5	146.9	146.3	146.7	146.8	146.7	142.3	142.3	126.2	131.9	149.1	149.5
C-5	115.5	115.5	115.1	115.5	115.5	115.2	115.7	115.7	150.8	148.6	116.0	116.6
C-6	120.6	120.7	120.6	120.5	120.6	120.3	109.2	109.5	118.9	96.4	122.5	122.6
C-7	73.8	74.2	76.9	74.2	74.4	77.2					132.2	132.4
C-8	87.4	87.5	74.6	88.1	87.9	74.8					129.6	129.8
C-9	61.8	62.2	63.5	62.4	62.5	63.9					59.5	59.4
OMe	56.2	56.3	56.2	56.2	56.3	56.2	56.2	56.3		56.6(×2)	56.3	56.4
COOH									172.3			
Glucose												
C-1′	104.1	104.1		104.8	104.7		103.3	103.5	103.0	102.8	101.4	101.9
C-2′	74.6	74.8		74.6	74.8		74.2	74.2	74.4	74.3	74.1	74.2
C-3′	76.9	77.7		76.9	77.4		77.1	77.2	77.3	77.2	76.9	77.5
C-4′	71.0	71.0		71.0	70.8		71.1	70.7	71.0	71.0	71.1	70.7
C-5′	75.0	77.4		75.1	77.3		74.6	77.1	74.9	74.9	74.8	77.1
C-6′	64.4	62.2		64.5	62.1		64.6	62.0	64.5	64.8	64.6	62.1
Galloyl												
	110.0			109.9			110.0		109.9	109.9	110.0	
	121.0			121.0			121.1		121.3	121.2	121.0	
	139.1			139.1			139.0		139.0	138.9	139.1	
	145.9			145.9			145.9		146.0	146.0	146.0	
	167.4			167.3			167.3		167.1	167.2	167.3	

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

Consequently, **4** was characterized as gentisic acid 5-*O*-*β*-D-(6′-*O*-galloyl)glucopyranoside.

The ^1H and ^{13}C NMR spectra of **5** showed the presence of a galloyl group [δ7.14 (2H, *s*)], a sugar moiety (δ64.8, 71.0, 74.3, 74.9, 77.2, 102.8), an aromatic ring with a symmetrical substitution pattern [δ96.4 (2C), 131.9, 148.6 (2C), 151.5] and two methoxyl groups [δ3.70 (6H, *s*, OMe × 2)]. From these spectral data **5** was likely to be a 3,5-dimethoxy-4-hydroxyphenol glucoside gallate. Methylation of **5** with Me_2SO_4–K_2CO_3 gave the tetramethyl ether (**5a**), which was found to be identical with **7**. Based upon the results described above **5** was concluded to be 3,5-dimethoxy-4-hydroxyphenol 1-*O*-*β*-D-(6′-*O*-galloyl)glucopyranoside.

Compound **6** FDMS *m/z*: 494 $[M]^+$, exhibited a galloyl peak [δ7.16 (2H, *s*)] and carbohydrate signals in the ^1H NMR spectrum. On enzymatic hydrolysis with tannase **6** gave gallic acid and a hydrolysate (**6a**), which on subsequent enzymatic hydrolysis with crude hesperidinase yielded glucose and an aglycone (**6b**). The ^1H NMR spectrum of **6b** exhibited signals due to three aromatic protons [δ6.72 (1H, *dd*, J = 8, 2 Hz), 6.76 (1H, *d*, J = 2 Hz), 6.82 (1H, *d*, J = 8 Hz)], a methoxyl group [δ3.84 (3H, *s*)], methylene protons [δ4.35 (2H, *br d*)] and two olefinic protons (δ5.70 and 6.38) with a small coupling constant (12 Hz) indicative of the *cis*-orientation of the double bond. From these spectral data **6b** was concluded to be *cis*-coniferyl alcohol. The location of the glucose moiety was presumed to be at the C-4 position since **6a** gave a negative ferric chloride reaction, in contrast to the dark purple colour of **6b** with this reagent. The galloyl group was found to be linked to the C-6 position of the glucose by analysis of the ^1H and ^{13}C NMR spectra of **6** [δ4.38 (1H, *dd*, J = 12, 8 Hz, H-6′), 4.62 (1H, *dd*, J = 12, 2 Hz, H-6′); δ64.6 (C-6′)]. The *β*-configuration of the anomeric centre was established on the basis of the J value (8 Hz) of the H-1′ signal (δ5.02) in the ^1H NMR spectrum of **6**. Thus, **6** was characterized as *cis*-coniferyl alcohol 4-*O*-*β*-D-(6′-*O*-galloyl)glucopyranoside.

EXPERIMENTAL

Mps are uncorr. ^1H and ^{13}C NMR spectra were measured at 100 and 25.05 MHz, respectively, with TMS as int. standard. TLC was conducted on silica gel and Avicel SF cellulose, and spots were visualized by spraying $FeCl_3$ (for phenolics) and aniline hydrogen phthalate (for sugars) reagents. Plant material was collected at Fukuoka and Oita prefectures, Japan. Voucher specimens are deposited at Herbarium, Faculty of Pharmaceutical Sciences, Kyushu University.

Extraction and isolation. (a) From the acorn of *Quercus mongolica* Fisch. ex Turcz: fresh acorns (12.3 kg) of *Q. mongolica* were mashed and extracted × 5 at room temp. with 80% aq. Me_2CO. The combined extracts, after concn under red. pres. to *ca* 3 l., were subjected to Sephadex LH-20 CC using H_2O with increasing amounts of MeOH to afford 6 fractions; fraction 1 (6.1 g), 2 (*ca* 130 g), 3 (2.9 g), 4 (*ca* 315 g), 5 (20 g) and 6 (29 g). Fraction 2 was rechromatographed over MCI-gel CHP-20P [H_2O–MeOH (1:0–1:9)] and Sephadex LH-20 (EtOH, 60% aq. MeOH) to give **1** (320 mg) and **2** (290 mg). Fraction 4 was chromatographed over Sephadex LH-20 (60% aq. MeOH, EtOH) and MCI-gel CHP-20P (H_2O–MeOH) to afford 3

(98 mg) and 6 (110 mg). (b) From the bark of *Q. acutissima Carruth.* fresh bark (6.1 kg) of *Q. acutissima* was chopped into small pieces and extracted ×4 at room temp. with 80% aq. Me_2CO. The combined extracts were concd under red. pres., and the ppt was filtered off. The filtrate (*ca* 1.5 l.) was subjected to CC over Sephadex LH-20 using H_2O–EtOH (1:0–0:1) to give 3 fractions. Subsequent separation of fraction 1 on Sephadex LH-20 using H_2O–EtOH afforded 3 fractions: fractions 1-1 (130 mg), 1-2 (6.1 g) and 1-3 (3.2 g) and 1-3 (3.2 g). Fraction 1-2 was purified by repeated chromatography using a variety of solvent systems (EtOH, H_2O–MeOH, etc.) to give 4 (230 mg) and 7 (73 mg). Fraction 2 was further separated by Sephadex LH-20 CC using H_2O–EtOH into 5 fractions (fractions 2-1–2-5). Fraction2-1 was rechromatographed over Sephadex LH-20 using 60% MeOH and over MCI-gel CHP-20P using H_2O–MeOH (1:0–3:7) to give 3 (90 mg) and 5 (61 mg).

General procedure for enzymatic hydrolysis. (a) With tannase: a soln of the sample (100–200 mg) in H_2O (6 ml) was treated with tannase at room temp. for 3 hr. The reaction mixture was filtered, the filtrate concd to dryness and the residue subjected to Sephadex LH-20 CC using EtOH to furnish gallic acid and a hydrolysate. (b) With crude hesperidinase: an aqueous soln (6 ml) of the sample (100–200 mg) was incubated at 37° with crude hesperidinase for 5 hr. The solution was concd to dryness, the residue treated with MeOH, and insoluble materials filtered off. The conc. filtrate was applied to Sephadex LH-20 CC (EtOH, 60% MeOH) to give the sugar and an aglycone.

General procedure for acetylation. The sample (30–50 mg) was dissolved in a mixture of Ac_2O (1 ml) and pyridine (0.5 ml). After 12 hr, the reaction mixture was poured into ice H_2O, and the resulting oil extracted with EtOAc. The EtOAc layer was washed with 3% HCl, 3% Na_2CO_3 and H_2O, dried (Na_2SO_4) and concd to dryness. The residue was purified by CC over silica gel with C_6H_6–Me_2CO (9:1).

General procedure for methylation. (a) With CH_2N_2: a soln of the sample (30–50 mg) in MeOH (5 ml) was treated with CH_2N_2 at room temp. for 1 hr. The solvent was evaporated off and the residue separated by silica gel CC. (b) With Me_2SO_4 and K_2CO_3: a mixture of the sample (50–100 mg), Me_2SO_4 (0.5 ml) and K_2CO_3 (1 g) in dry Me_2CO (15 ml) was refluxed for 3 hr with stirring. After removal of inorganic salts, the filtrate was concd to a syrup which was purified by silica gel CC.

D-threo-*Guaiacylglycerol* 8-O-*β*-D-(6′-O-*galloyl*)*glucopyranoside* (**1**). Needles, mp 143–145°, $[\alpha]_D^{17}$ −47.5° (MeOH; *c* 0.5). ^{1}H NMR (Me_2CO-d_6 + D_2O): *δ* 3.74 (3H, *s*, OMe), 4.33 (1H, *dd*, *J* = 12, 6 Hz, H-6′), 4.64, 4.68 (each 1H, *d*, *J* = 8 Hz, anomeric H and H-7), 4.70 (1H, *dd*, *J* = 12, 2 Hz, H-6′), 6.72 (1H, *d*, *J* = 8 Hz, H-5), 6.82 (1H, *br d*, *J* = 8 Hz, H-6), 6.96 (1H, *br s*, H-2), 7.18 (2H, *s*, galloyl H). ^{13}C NMR: see Table 1. (Found: C, 49.67; H, 5.54. $C_{23}O_{14}H_{28}$. 3/2 H_2O requires: C, 49.73; H, 5.63%.) Negative FABMS *m/z* (rel. int.): 527 $[M-H]^-$ (19).

D-threo-*Guaiacylglycerol* 8-O-*β*-D-*glucopyranoside* (**1a**). An amorphous powder, $[\alpha]_D^{17}$ −47.1° (MeOH; *c* 0.6). ^{1}H NMR (Me_2CO-d_6 + D_2O): *δ* 3.83 (3H, *s*, OMe), 4.58, 4.60 (each 1H, *d*, *J* = 8 Hz, anomeric H and H-7), 6.76 (1H, *d*, *J* = 8 Hz, H-5), 6.86 (1H, *br d*, *J* = 8 Hz, H-6), 7.04 (1H, *br s*, H-2). ^{13}C NMR: see Table 1. (Found: C, 50.26; H, 6.88. $C_{16}O_{10}H_{14}\cdot 1/2\ H_2O$ requires: C, 49.87; H, 6.54%.)

D-threo-*Guaiacylglycerol* (**1b**). Needles, mp 126–127°, $[\alpha]_D^{22}$ −21.0° (EtOH; *c* 0.8). ^{1}H NMR (Me_2CO-d_6 + D_2O): *δ* 3.3–3.8 (3H, *m*, H-8 and -9), 3.84 (3H, *s*, OMe), 4.58 (1H, *d*, *J* = 7 Hz, H-7), 6.76 (1H, *d*, *J* = 8 Hz, H-5), 6.86 (1H, *br d*, *J* = 8 Hz, H-6), 7.02 (1H, *br s*, H-2). ^{13}C NMR: see Table 1. (Found: C, 55.92; H, 6.64. $C_{10}O_5H_{14}$ requires: C, 56.06; H, 6.59%.)

D-threo-*Guaiacylglycerol tetraacetate* (**1c**). An amorphous powder, $[\alpha]_D^{19}$ −16.0° (Me_2CO; *c* 0.6). ^{1}H NMR ($CDCl_3$): *δ* 2.04, 2.06, 2.08, 2.30 (each 3H, *s*, OAc × 4), 3.82 (1H, *dd*, *J* = 12, 6 Hz, H-9), 3.83 (3H, *s*, OMe), 4.26 (1H, *dd*, *J* = 12, 4 Hz, H-9), 5.3–5.5 (1H, *m*, H-8), 5.96 (1H, *d*, *J* = 8 Hz, H-7), 6.9–7.1 (3H, *m*, H-2, -5 and -6). ^{13}C NMR ($CDCl_3$): *δ* 20.7, 20.9 (OAc), 56.0 (OMe), 62.1 (C-9), 72.3 (C-8), 73.4 (C-7), 111.3 (C-2), 119.8 (C-6), 123.1 (C-5), 134.7 (C-1), 140.2 (C-4), 151.3 (C-3), 168.7, 169.7, 170.0, 170.4 (C=O). (Found: C, 56.65; H, 6.01. $C_{18}O_9H_{22}$ requires: C, 56.54; H, 5 80%.)

D-threo-*Guaiacylglycerol* 8-O-*β*-D-(6′-O-*galloyl*)*glucopyranoside tetramethyl ether* (**1d**). An amorphous powder, $[\alpha]_D^{27}$ −26.8° (MeOH; *c* 0.7). ^{1}H NMR (Me_2CO-d_6 + D_2O): *δ* 3.72, 3.76, 3.78 (15 H in total, *s*, OMe × 5), 4.30 (1H, *dd*, *J* = 12, 8 Hz, H-6′), 4.64, 4.70 (each 1H, *d*, *J* = 8 Hz, anomeric H and H-7), 4.88 (1H, *dd*, *J* = 12, 2 Hz, H-6′), 6.8–6.9 (2H, *m*, H-5 and -6), 7.00 (1H, *br s*, H-2), 7.38 (2H, *s*, galloyl H). (Found: C, 54.39; H, 6.55. $C_{27}O_{14}H_{36}$. 1/2 H_2O requires: C, 54.63; H, 6.28%.) FDMS *m/z* (rel. int.): 584 $[M]^+$ (100).

D-threo-*Guaiacylglycerol* 8-O-*β*-D-(6′-O-*galloyl*)*glucopyranoside nonaacetate* (**1e**). A white powder, mp 193–196°, $[\alpha]_D^{17}$ −7.8° (Me_2CO; *c* 1.3). ^{1}H NMR ($CDCl_3$ + D_2O): *δ* 2.00, 2.04, 2.05 (15H in total, *s*, OAc × 5), 2.28, 2.30 (12H in total, *s*, OAc × 4), 3.80 (3H, *s*, OMe), 5.97 (1H, *d*, *J* = 5 Hz, H-7), 6.8–7.1 (3H, *m*, H-2, -5 and -6), 7.76 (2H, *s*, galloyl H). ^{13}C NMR ($CDCl_3$ + D_2O): *δ* 20.1, 20.5, 20.8 (OAc), 55.9 (OMe), 63.3 (C-6′ and -9), 68.9, 71.5, 71.9, 72.8 (C-2′, -3′,-4′ and -5′), 73.5 (C-7), 78.8 (C-8), 100.7 (C-1′), 111.7 (C-2), 119.2 (C-6), 122.7 (C-5), 134.6 (C-1), 139.8 (C-4), 150.9 (C-3), 122.3, 127.7, 143.6, 163.9 (galloyl). (Found: C, 54.19; H, 5.02. $C_{41}O_{23}H_{46}$ requires: C, 54.30; H, 5.11%.) FDMS *m/z* (rel. int.): 906 $[M]^+$ (100). EIMS *m/z* (rel. int.): 864 $[M-Ac]^+$ (37), 567 (29), 279 (75).

L-threo-*Guaiacylglycerol* 8-O-*β*-D-(6′-O-*galloyl*)*glucopyranoside* (**2**). An amorphous powder, $[\alpha]_D^{17}$ −21.5° (MeOH; *c* 0.7). ^{1}H NMR (Me_2CO-d_6 + D_2O): *δ* 3.80 (3H, *s*, OMe), 4.26 (1H, *dd*, *J* = 12, 6 Hz, H-6′), 4.60, 4.68 (each 1H, *d*, *J* = 8 Hz, anomeric H and H-7), 4.74 (1H, *dd*, *J* = 12, 2 Hz, H-6′), 6.76 (1H, *d*, *J* = 8 Hz, H-5), 6.86 (1H, *br d*, *J* = 8 Hz, H-6), 7.04 (1H, *br s*, H-2), 7.14 (2H, *s*, galloyl H). ^{13}C NMR: see Table 1. (Found: C, 49.67; H, 5.48. $C_{23}O_{14}H_{28}$. 3/2 H_2O requires: C, 49.73; H, 5.63%.) Negative FABMS *m/z* (rel. int.): 527 $[M-H]^-$ (25).

L-threo-*Guaiacylglycerol* 8-O-*β*-D-*glucopyranoside* (**2a**). An amorphous powder, $[\alpha]_D^{17}$ +12.5° (MeOH; *c* 0.4). ^{1}H NMR (Me_2CO-d_6 + D_2O: *δ* 3.84 (3H, *s*, OMe), 4.56, 4.65 (each 1H, *d*, *J* = 8 Hz, anomeric H and H-7), 6.76 (1H, *d*, *J* = 8 Hz, H-5), 6.86 (1H, *br d*, *J* = 8 Hz, H-6), 7.06 (1H, *br s*, H-2). ^{13}C NMR: see Table 1. (Found: C, 50.20; H, 6.81. $C_{16}O_{10}H_{14}$. 1/2 H_2O requires: C, 49.87; H, 6.54%.)

L-threo-*Guaiacylglycerol* (**2b**). Prisms, mp 132–133°, $[\alpha]_D^{16}$ +23.0° (EtOH; c 0.6). ^{1}H NMR (Me_2CO-d_6): *δ* 3.2–3.8 (3H, *m*, H-8 and -9), 3.82 (3H, *s*, OMe), 4.56 (1H, *d*, *J* = 6 Hz, H-7), 6.72 (1H, *d*, *J* = 8 Hz, H-5), 6.84 (1H, *br d*, *J* = 8 Hz, H-6), 7.00 (1H, *br s*, H-2). ^{13}C NMR: see Table 1. (Found: C, 55.70; H, 6.79. $C_{10}O_5H_{14}$ requires: C, 56.06; H, 6.59%.)

L-threo-*Guaiacylglycerol tetraacetate* (**2c**). An amorphous powder, $[\alpha]_D^{19}$ +16.1° (Me_2CO: *c* 0.6). ^{1}H NMR ($CDCl_3$): *δ* 2.04, 2.06, 2.08, 2.30 (each 3H, *s*, OAc × 4), 3.82 (1H, *dd*, *J* = 12, 6 Hz, H-9), 3.83 (3H, *s*, OMe), 4.26 (1H, *dd*, *J* = 12, 4 Hz, H-9), 5.3–5.5 (1H, *m*, H-8), 5.96 (1H, *d*, *J* = 8 Hz, H-7), 6.9–7.1 (3H, *m*, H-2, -5 and -6). ^{13}C NMR ($CDCl_3$): *δ* 20.7, 20.8, 20.9 (OAc), 56.0 (OMe), 62.1 (C-9), 72.3 (C-8), 73.4 (C-7), 111.3 (C-2), 119.7 (C-6), 121.3 (C-5), 134.7 (C-1), 140.2 (C-4), 151.3 (C-3), 168.8, 169.7, 170.1, 170.4 (C=O). (Found: C, 56.49; H, 6.05. $C_{18}O_9H_{22}$ requires: C, 56.54; H, 5.80%.)

L-threo-*Guaiacylglycerol* 8-O-*β*-D-(6′-O-*galloyl*)*glucopyranoside nonaacetate* (**2d**). $[\alpha]_D^{17}$ +2.2° (Me_2CO; *c* 0.9). ^{1}H NMR ($CDCl_3$): *δ* 1.96, 2.00, 2.04, 2.12, 2.16 (15H in total, *s*, OAc × 5), 2.28, 2.30, 2.31 (12H in total, *s*, OAc × 4), 3.80 (3H, *s*,

OMe), 5.84 (1H, *d*, $J = 8$ Hz, H-7), 6.8–7.1 (3H, *m*, H-2, -5 and -6), 7.80 (2H, *s*, galloyl H). ^{13}C NMR ($CDCl_3$): δ20.1, 20.5, 21.1 (OAc), 56.0 (OMe), 63.4 (C-6′ and -9), 68.8, 71.3, 72.0, 72.8 (C-2′, -3′, -4′ and -5′), 75.5 (C-7), 78.6 (C-8), 101.0 (C-1′), 111.4 (C-2), 119.6 (C-6), 123.0 (C-5), 134.8 (C-1), 140.1 (C-4), 151.2 (C-3), 122.3, 127.5, 143.6, 163.9 (galloyl). (Found: C, 54.64; H, 5.51. $C_{41}O_{23}H_{46}$ requires: C, 54.30; H, 5.11%.) FDMS *m/z* (rel. int.): 906 $[M]^+$ (100). EIMS *m/z* (rel. int.): 864 $[M-Ac]^+$ (24), 567 (39), 279 (100).

L-threo-*Guaiacylglycerol* 8-O-β-D-(6′-O-*galloyl*)*glucopyranoside tetramethyl ether* (**2e**). An amorphous powder, $[\alpha]_D^{27}$ −6.7° (MeOH; *c* 0.5). ^{1}H NMR (Me_2CO-d_6 + D_2O): δ3.76, 3.78, 3.80, 3.82 (15H in total, *s*, OMe × 5), 4.26 (1H, *dd*, J = 12, 6 Hz, H-6′), 4.64, 4.68 (each 1H, *d*, $J = 8$ Hz, anomeric H and H-7), 4.86 (1H, *dd*, J = 12, 2 Hz, H-6′), 6.8–6.9 (2H, *m*, H-5 and -6), 7.06 (1H, *br s*, H-2), 7.36 (2H, *s*, galloyl H). (Found: C, 53.99; H, 6.44. $C_{27}O_{14}H_{36}$. H_2O requires: C, 53.81; H, 6.36%.) FDMS *m/z* (rel. int.): 584 $[M]^+$ (100).

3-*Methoxy-4-hydroxyphenol* 1-O-β-D-(6′-O-*galloyl*)*glucopyranoside* (**3**). An amorphous powder, $[\alpha]_D^{25}$ −31.3° (Me_2CO; *c* 0.5). ^{1}H NMR (Me_2CO-d_6): δ3.72 (3H, *s*, OMe), 4.38 (1H, *dd*, J = 12, 6 Hz, H-6′), 4.70 (1H, *dd*, J = 12, 2Hz, H-6′), 4.90 (1H, *d*, J = 8 Hz, anomeric H), 6.60 (1H, *br d*, $J = 8$ Hz, H-6), 6.68 (1H, *br s*, H-2), 6.74 (1H, *d*, $J = 8$ Hz, H-5), 7.19 (2H, *s*, galloyl H). ^{13}C NMR: see Table 1. (Found: C, 51.13; H, 5.02. $C_{20}O_{12}H_{22}$. H_2O requires: C, 50.85; H, 5.12%.)

3-*Methoxy-4-hydroxyphenol* 1-O-β-D-*glucopyranoside* (**3a**). Needles, mp 208–210°, $[\alpha]_D^{16}$ −53.3° (MeOH; *c* 0.6). ^{1}H NMR (Me_2CO-d_6 + D_2O): δ3.81 (3H, *s*, OMe), 4.84 (1H, *d*, $J = 8$ Hz, anomeric H), 6.58 (1H, *dd*, $J = 8$, 3 Hz, H-6), 6.76 (1H, *d*, J = 8 Hz, H-5), 6.81 (1H, *d*, $J = 3$ Hz, H-2). ^{13}C NMR: see Table 1. (Found: C, 50.61; H, 6.02. $C_{13}O_8H_{18}$. 1/2 H_2O requires: C, 50.15; H, 6.15%.)

3-*Methoxy-4-hydroxyphenol* (**3b**). Prisms, mp 75–76°. ^{1}H NMR (Me_2CO-d_6): δ3.76 (3H, *s*, OMe), 6.26 (1H, *dd*, $J = 8$, 3 Hz, H-6), 6.46 (1H, *d*, $J = 3$ Hz, H-2), 6.64 (1H, *d*, $J = 8$ Hz, H-5).

Preparation of 3-*methoxy-4-hydroxyphenol.* 6% H_2O_2 (1 ml) was added slowly to a mixture of vanillin (50 mg) and 1 N NaOH (3 ml) with stirring. After 15 hr, the reaction mixture was neutralized with HOAc, and extracted with EtOAc. The EtOAc layer, after concn, was applied to silica gel CC with C_6H_6–Me_2CO (7:1) to yield 3-methoxy-4-hydroxyphenol (15 mg).

3-*Methoxy-4-hydroxyphenol* 1-O-β-D-*glucopyranoside pentaacetate* (**3c**). An amorphous powder, $[\alpha]_D^{25}$ −17.1° (Me_2CO; *c* 1.5). ^{1}H NMR ($CDCl_3$): δ2.02, 2.04, 2.06 (12H in total, *s*, OAc × 4), 2.24 (3H, *s*, OAc), 3.78 (3H, *s*, OMe), 3.7–4.0 (1H, *m*, H-5′), 4.0–4.4 (2H, *m*, H-6′), 5.0–5.4 (4H, *m*, anomeric H, H-2′, -3′ and -4′), 6.50 (1H, *dd*, $J = 8$, 3 Hz, H-6), 6.62 (1H, *d*, $J = 3$ Hz, H-2), 6.92 (1H, *d*, $J = 8$ Hz, H-5). ^{13}C NMR ($CDCl_3$): δ20.6 (OAc), 56.0 (OMe), 62.0 (C-6′), 68.3, 71.1, 72.1, 72.7 (C-2′, -3′, -4′ and -5′), 99.3 (C-1′), 103.2 (C-2), 107.6 (C-6), 122.9 (C-5), 132.2 (C-4), 151.8 (C-3), 155.4 (C-1), 169.2, 170.0, 170.2, 170.5 (C=O). (Found: C, 54.43; H, 5.83. $C_{23}O_{13}H_{28}$ requires: C, 53.93; H, 5.51%.)

Gentisic acid 5-O-β-D-(6′-O-*galloyl*)*glucopyranoside* (**4**). Needles, mp 238–240°, $[\alpha]_D^{20}$ −56.5° (Me_2CO; *c* 0.7). ^{1}H NMR (Me_2CO-d_6): δ4.40 (1H, *dd*, J = 12, 6 Hz, H-6′), 4.66 (1H, *dd*, J = 12, 2 Hz, H-6′), 4.96 (1H, *d*, $J = 8$ Hz, anomeric H), 6.85 (1H, *d*, $J = 8$ Hz, H-3), 7.20 (2H, *s*, galloyl H), 7.38 (1H, *dd*, $J = 8$, 2 Hz, H-4), 7.57 (1H, *d*, $J = 2$ Hz, H-6). ^{13}C NMR: see Table 1. (Found: C, 50.14; H, 4.48. $C_{20}O_{13}H_{20}$. 1/2 H_2O requires: C, 50.32; H, 4.22%.)

Gentisic acid 5-O-β-D-*glucopyranoside* (**4a**). An amorphous powder, ^{1}H NMR (Me_2CO-d_6 + D_2O): δ4.90 (1H, *d*, $J = 8$ Hz, anomeric H), 6.88 (1H, *d*, $J = 8$ Hz, H-3), 7.34 (1H, *dd*, $J = 8$, 2 Hz, H-4), 7.58 (1H, *d*, $J = 2$ Hz, H-6). Acid hydrolysis of **4a** (40 mg) in 1 N H_2SO_4 (5 ml) for 2 hr after Sephadex LH-20 CC (H_2O-EtOH) afforded glucose and gentisic acid (**4b**), tan needles, mp 204–205°. ^{1}H NMR (Me_2CO-d_6): δ6.80 (1H, *d*, $J = 8$ Hz, H-3), 7.06 (1H, *dd*, $J = 8$, 2 Hz, H-4), 7.32 (1H, *d*, $J = 2$ Hz, H-6). IR ν_{max}^{KBr} cm^{-1}: 3200 (OH), 1900, 1660, 1640, 1620.

Gentisic acid 5-O-β-D-*glucopyranoside dimethyl ether* (**4c**). An amorphous powder, $[\alpha]_D^{25}$ −35.6° ($CHCl_3$: MeOH 7:3; *c* 0.5). ^{1}H NMR (DMSO-d_6): δ3.39 (3H, *s*, COOMe), 3.77 (3H, *s*, OMe), 4.75 (1H, *d*, $J = 8$ Hz, anomeric H), 7.08 (1H, *d*, $J = 8$ Hz, H-3), 7.26 (1H, *dd*, $J = 8$, 2 Hz, H-4), 7.32 (1H, *br s*, H-6). (Found: C, 44.46; H, 6.48. $C_{15}O_9H_{20}$. 7/2 H_2O requires; C, 44.22; H, 6.68%.)

3,5-*Dimethoxy-4-hydroxyphenol* 1-O-β-D-(6′-O-*galloyl*)*glucopyranoside* (**5**). Needles, mp 150–151°, $[\alpha]_D^{25}$ −42.2° (Me_2CO; *c* 0.6). ^{1}H NMR (Me_2CO-d_6 + D_2O): δ3.70 (6H, *s*, OMe × 2), 4.40 (1H, *dd*, J = 12, 6 Hz, H-6′), 4.65 (1H, *dd*, J = 12, 2 Hz, H-6′), 4.92 (1H, *d*, $J = 8$ Hz, anomeric H), 6.44 (2H, *s*, H-2 and -6), 7.14 (2H, *s*, galloyl H). ^{13}C NMR: see Table 1. (Found: C, 50.48; H, 5.14. $C_{21}O_{13}H_{24}$. H_2O requires: C, 50.20; H, 5.22%.) Acid hydrolysis of **5** (3 mg) with 2 N H_2SO_4 (0.5 ml) heated at 90° for 2 hr afforded gallic acid and glucose.

3,5-*Dimethoxy-4-hydroxyphenol* 1-O-β-D-(6′-O-*galloyl*)*glucopyranoside tetramethyl ether* (**5a**). An amorphous powder, $[\alpha]_D^{25}$ −77.4° ($CHCl_3$; *c* 0.4). ^{1}H NMR ($CDCl_3$): δ3.60 (6H, *s*, OMe × 2), 3.68 (3H, *s*, OMe), 3.80 (6H, *s*, OMe × 2), 3.86 (3H, *s*, OMe), 4.2–4.8 (2H, *m*, H-6′), 4.86 (1H, *d*, $J = 8$ Hz, anomeric H), 6.28 (2H, *s*, H-2 and -6), 7.20 (2H, *s*, galloyl H). (Found: C, 54.97; H, 6.17. $C_{25}O_{13}H_{32}$. 1/2 H_2O requires: C, 54.64; H, 6.05%.)

cis-*Coniferyl alcohol* 4-O-β-D-(6′-O-*galloyl*)*glucopyranoside* (**6**). Needles, mp 195–196°, $[\alpha]_D^{24}$ −38.3° (MeOH; *c* 0.7). ^{1}H NMR (Me_2CO-d_6 + D_2O): δ3.84 (3H, *s*, OMe), 4.35 (2H, *br d*, $J = 6$ Hz, H-9), 4.38 (1H, *dd*, $J = 12$, 8 Hz, H-6′), 4.62 (1H, *dd*, J = 12, 2 Hz, H-6′), 5.02 (1H, *d*, $J = 8$ Hz, anomeric H), 5.76 (1H, *dt*, $J = 12$, 6 Hz, H-8), 6.38 (1H, *br d*, $J = 12$ Hz, H-7), 6.68 (1H, *dd*, $J = 8$, 2 Hz, H-6), 6.87 (1H, *d*, $J = 2$ Hz, H-2), 7.15 (1H, *d*, J = 8 Hz, H-5), 7.16 (2H, *s*, galloyl H). ^{13}C NMR: see Table 1. (Found: C, 53.48; H, 5.52. $C_{23}O_{12}H_{26}$. H_2O requires: C, 53.90; H, 5.51%.) FDMS *m/z* (rel. int.): 494 $[M]^+$ (100).

cis-*Coniferyl alcohol* 4-O-β-D-*glucopyranoside* (**6a**). Needles, mp 140–141°, $[\alpha]_D^{27}$ −55.3° (MeOH; *c* 0.3). ^{1}H NMR (Me_2CO-d_6 + D_2O): δ3.84 (3H, *s*, OMe), 4.35 (2H, *br d*, $J = 6$ Hz, H-9), 4.96 (1H, *d*, $J = 8$ Hz, anomeric H), 5.80 (1H, *dt*, $J = 12$, 6 Hz, H-8), 6.42 (1H, *br d*, $J = 12$ Hz, H-7), 6.78 (1H, *dd*, $J = 8$, 2 Hz, H-6), 6.90 (1H, *d*, $J = 2$ Hz, H-2), 7.15 (1H, *d*, $J = 8$ Hz, H-5). ^{13}C NMR: see Table 1. (Found: C, 54.47; H, 6.39. $C_{16}O_8H_{22}$. 1/2 H_2O requires: C, 54.70; H, 6.60%.)

cis-*Coniferyl alcohol* (**6b**). An amorphous powder, ^{1}H NMR (Me_2CO-d_6): δ3.84 (3H, *s*, OMe), 4.35 (2H, *br d*, $J = 6$ Hz, H-9), 5.70 (1H, *dt*, $J = 12$, 6 Hz, H-8), 6.38 (1H, *br d*, $J = 12$ Hz, H-7), 6.72 (1H, *dd*, $J = 8$, 2 Hz, H-6), 6.76 (1H, *d*, $J = 2$ Hz, H-2), 6.82 (1H, *d*, $J = 8$ Hz, H-5). ^{13}C NMR (Me_2CO-d_6): δ56.2 (OMe), 59.7 (C-9), 113.4 (C-2), 115.6 (C-5), 122.9 (C-6), 130.2 (C-8), 131.6 (C-1 and -7), 146.8 (C-3), 148.1 (C-4). (Found: C, 63.02; H, 7.20. $C_{10}O_3H_{12}$. 1/2 H_2O requires: C, 63.48; H, 6.93%.)

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