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MYRICATIN, A GALLOYL FLAVANONOL SULFATE AND PRODELPHINIDIN GALLATES FROM *MYRICA RUBRA**

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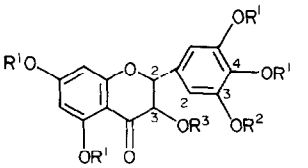
Key Word Index—*Myrica rubra*, Myricaceae, myricatin, galloyl flavanonol sulfate, prodelphinidin gallates, tannins

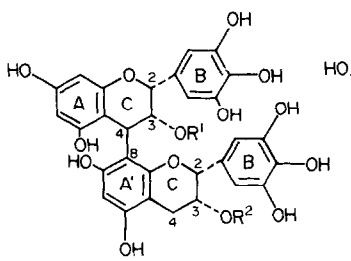
Abstract—An investigation of the bark of *Myrica rubra* has led to the isolation and characterization of myricatin (a galloyl flavanonol sulfate) and four new galloyl prodelphinidin dimers, together with gallic acid, (±)-gallocatechin and 3-*O*-galloyl-(−)-epicatechin Evidence for the structures of these compounds was obtained from analyses of ^1H and ^{13}C NMR spectra, and from hydrolytic studies

INTRODUCTION

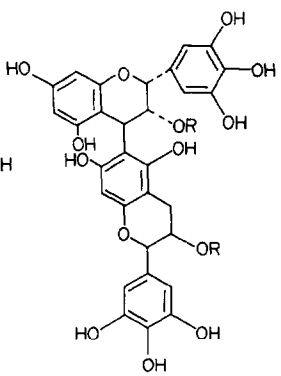
Myrica rubra commonly distributed in the southern parts of Japan, is well-known as a rich source of tannin, along with flavonoids such as myricetin and myricitrin [1] with a 5,7,3′,4′,5′-phenolic substitution pattern Its bark has been used in Japan and China as an astringent and an antidiarrheic and also as a dyeing and tanning agent As part of chemical studies on tannins in crude drugs, we have undertaken the analysis of the ethyl acetate soluble portion of the bark extract This has resulted in the isolation of a flavanonol sulfate named myricatin (**1**) and four new galloyl prodelphinidin dimers (**2**–**5**), together with gallic acid (**6**), (±)-gallocatechin (**7**) and 3-*O*-galloyl-(−)-epigallocatechin (**8**), and the assignments of the structures **1**–**8** for these compounds



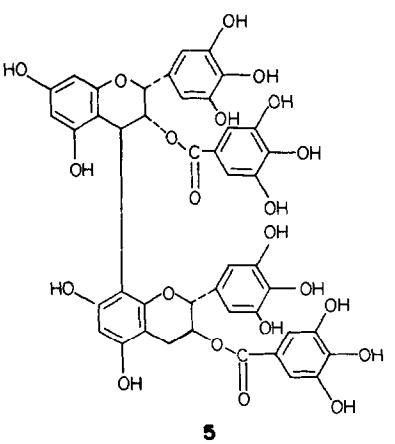
1 $R^1=H$, $R^2=SO_3K$, $R^3=$Galloyl
1a $R^1=R^2=H$, $R^3=$Galloyl
1b $R^1=R^2=$Me, $R^3=$Trimethylgalloyl
1c $R^1=H$, $R^2=SO_3K$, $R^3=H$



2 $R^1=R^2=$Galloyl
2a $R^1=R^2=H$
3 $R^1=H$, $R^2=$Galloyl



4 R = Galloyl
4a R = H



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*Part 6 in the series "Tannins and Related Compounds" For Part 5 see Nishizawa, M, Yamagishi, T, Nonaka, G and Nishioka, I *J Chem Soc Perkin Trans* 1 (submitted)

RESULTS AND DISCUSSION

The aqueous acetone extract of the fresh bark afforded, upon concentration of the solution, a yellow crystalline mass consisting of flavonols Partition of the filtrate with ethyl acetate followed by chromatography of the ethyl acetate soluble portion over Sephadex LH-20 and LH-60 eluting with varying solvent systems, viz ethanol, ethanol–water, methanol–water and ethanol–acetone–water [2], yielded myricatin (**1**) and prodelphinidin dimers (**2**–**5**) In addition, the known compounds **6**–**8** were isolated and their structures were confirmed by comparisons of the physical and spectral data with those reported in the literature

Myricatin (**1**) showed an intense blue colouration with ferric chloride reagent on TLC The molecular formula, $C_{22}H_{16}O_{16}SK$, was assigned to this compound on the basis of elemental analysis The occurrence of the potassium atom was deduced from quantification of the ashes obtained by combustion analysis The ^{1}H NMR spectrum exhibited AB-type double doublet signals at δ5 47 (J = 12 Hz) and 5 87 (J = 12 Hz) due to the C-2 and C-3 protons of a flavonoid skeleton, together with a two-proton singlet signal at δ6 04 which was assigned to the C-6 and C-8 protons Two *meta*-coupled doublets at δ6 94 (J = 2 Hz) and 7 00 (J = 2 Hz) arising from a flavonoid B-ring, suggested that this ring has an unsymmetrical 3′,4′,5′-trisubstitution pattern These ^{1}H NMR spectral observations were also supported by the ^{13}C resonances listed in Table 1 Of these the C-4 carbonyl signal at δ192 5, along with the signals at δ73 4 and 81 9 due to the C-3 and C-2, respectively, were typical for flavanonols The presence of a galloyl group was evident from a two-proton singlet at δ6 94 in the ^{1}H NMR spectrum and also the corresponding carbon signals in the ^{13}C NMR spectrum (Table 1) These spectral data coupled with the result of elemental analysis suggested that the 12 oxygen atoms out of 15 were located in the flavanonol and galloyl moieties, and that the remaining three oxygens might form a sulfate function Treatment of **1** with a mixture of pyridine–dioxane (1 1) [3] afforded a desulfated product (**1a**), which displayed in the ^{1}H NMR spectrum a two-proton singlet due to the B-ring protons at δ6 66, thus suggesting that this ring in **1a** possesses a symmetrical 3′,4′,5′-trisubstitution pattern Furthermore, methylation of **1** with dimethyl sulfate and potassium carbonate in dry acetone furnished an octamethyl ether (**1b**) showing M^+ at m/z 584 in the mass spectrum The ^{1}H NMR spectrum

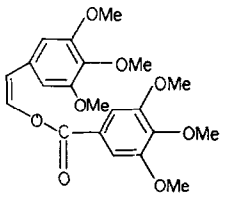
Table 1 ^{13}C NMR spectral data of compounds **1**, **1b**, **3** and **4***

		1	**1b**	**3**	**4**
	C-2	81 9	81 1	76 8	73 0
	C-3	73 4	73 9	73 0	73 0
	C-4	192 5	184 3	36 5	34 4
	C-4a	101 4	104 3	99 3†	99 8
	C-5, C-7, C-8a	163 2	162 2	154 2‡	155 0†
		164 2	163 8	155 3‡	155 5†
		165 6	164 5	155 7‡	156 6†
	C-6	97 2	93 5	95 5	95 0‡
	C-8	96 1	93 5	96 0	96 1‡
B-ring	C-1′	127 1	130 8	132 8	132 7
B-ring	C-2′, C-6′	111 3	104 3	106 2§	106 3
B-ring		114 9			
B-ring	C-3′, C-5′	147 2	153 0	146 0	145 7§
B-ring	C-4′	141 0	138 5	130 2‖	130 0‖
	C-2	—	—	77 8	77 8
	C-3	—	—	69 0	69 7
	C-4	—	—	—¶	—¶
	C-4a	—	—	101 2†	99 8
	C-5, C-7, C-8a	—	—	157 2‡	157 4‡
				157 7‡	158 1†
	C-6	—	—	96 9	106 9
	C-8	—	—	107 5	96 8‡
Lower unit	C-1′	—	—	132 8	132 7
Lower unit B′-ring	C-2′, C-6′	—	—	106 5§	106 3
Lower unit B′-ring	C-3′, C-5′	—	—	146 0	145 7§
Lower unit B′-ring	C-4′	—	—	131 3‖	130 1‖
	C-1	119 9	124 1	121 3	121 1
					121 1
Galloyl	C-2, C-6	109 9	107 0	110 1	109 7
Galloyl	C-3, C-5	145 6	152 5	145 5	145 5§
Galloyl	C-4	138 9	142 5	138 9	139 2
Galloyl	–COO–	168 0	166 2	166 0	166 3
	–OMe		55 6, 56 0, 60 6		

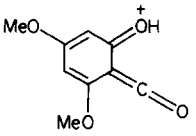
*Recorded in Me_2CO-d_6 + D_2O at 25 05 MHz

†,‡,§,‖ Values with the same sign, may be reversed in the vertical column

¶ Overlapped with solvent signal



m/z 404



m/z 181

of **1b** exhibited, like that of **1a**, a two-proton singlet for C-2′ and C-6′ protons at δ6 73 The ^{13}C NMR spectrum (Table 1) was also in good agreement with the proposed structure (**1b**) for this methylate On the basis of these results, it was concluded that the sulfate group was located at the C-3′ hydroxyl group on the B-ring The location of the galloyl group was determined to be at the C-3 position in the C-ring by comparison of the ^{1}H NMR spectrum of **1** with that of the degalloylated product (**1c**) formed by enzymatic hydrolysis of **1** Namely, the C-2 and C-3 proton signals in **1c** (C-2 δ4 88, *d*, J = 12 Hz, C-3 δ4 48, *d*, J = 12 Hz) were observed at higher field than those of **1**, while other signals remained almost unchanged The appearance of fragment peaks at *m/z* 404 and 181 in the mass spectrum of **1b**, which were formed by a retro-Diels-Alder type cleavage, has also supported this conclusion In order to establish the absolute stereochemistry of the C-2 position, CD spectral comparison of **1c** with that of flavanonols of known configuration was attempted Compound **1b** showed a negative Cotton effect at 286 mμ and a positive one at *ca* 320–330 mμ due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition, respectively, analogous to flavanonols reported to have a 2*R*-configuration [4] Since C-2 and C-3 hydrogens were *trans*-oriented, as revealed by the ^{1}H NMR coupling constant (J = 12 Hz), the absolute configuration at both C-2 and C-3 positions could be determined to be *R* Based on these results myricatin was assigned the structure **1**

A prodelphinidin dimer (**2**) was, apart from the flavones, a major constituent of *M rubra*, and was obtained as a pale brown amorphous powder The ^{1}H NMR spectrum showed two galloyl signals at δ6 96 and 7 07, two two-proton singlets at δ6 50 and 6 53 arising from the flavan B-ring, and three signals at δ5 94 (1H, *d*, J = 2 Hz), 6 00 (1H, *d*, J = 2 Hz) and 6 14 (1H, *s*) due to the C-6 and C-8 protons In the aliphatic region, five signals derived from the C-ring protons were observed at lower field, protons for C-2 at δ5 56 (*s*), C-2′ and C-3′ at δ5 40–5 56 (overlapped), C-3 at δ4 96 (*m*), and C-4 at δ4 78 (*d*, J = 3 Hz) The C-4′ methylene signals appeared at δ2 98 as a two-proton multiplet These ^{1}H NMR characteristics were, except for the two aromatic singlets at δ6 50 and 6 53, closely related to those of 3,3′-di-*O*-galloyl procyanidin B-2 reported previously [5, 6] Enzymatic hydrolysis of **2** with tannase yielded gallic acid and prodelphinidin B-2 (**2a**) The structure of **2a** was confirmed by the ^{1}H NMR spectrum which displayed close similarities in the aliphatic region to that of procyanidin B-2 [7] From these facts, **2** was characterized as 3,3′-di-*O*-galloyl prodelphinidin B-2

The second prodelphinidin (**3**) contained one galloyl group as shown by the ^{1}H NMR spectrum (δ7 04) Although the ^{1}H NMR spectrum closely resembles that of **2**, a broad singlet at δ4 01 due to a methine proton attached to a hydroxy-bearing carbon atom was shifted upfield Compound **3** gave gallic acid and prodelphinidin B-2 (**2a**) on hydrolysis with tannase, thus indicating **3** to be a monogallate of prodelphinidin B-2 The position of the galloyl group was determined as follows The ^{13}C NMR spectrum showed an upfield shift of C-3 (δ73 0) and a lowfield shift of C-2 (δ76 8) as compared with those of procyanidin B-2 (C-3 δ74 8, C-2 δ75 5), while other aliphatic carbon signals were not shifted Moreover, chemical shift of a broad multiplet at δ5 62 due to the C-3′ methine proton was analogous to that of **2** These observations allowed the galloyl group to be located on the C-3′ hydroxyl group

The third prodelphinidin dimer (**4**) was shown to be a structural isomer of **2** having the same functional groups by ^{1}H and ^{13}C NMR analyses Hydrolysis of **4** with tannase gave gallic acid and a dimer (**4a**) Compound **4a** exhibited, in the ^{1}H NMR spectrum, similar aliphatic resonances to procyanidin B-5 [7] which is a C-4–C-6 linked epicatechin dimer Since in the ^{1}H NMR spectrum of **4** the signals due to C-3 and C-3′ protons were shifted downfield, two galloyl groups could be placed on these positions Based on these results the structure of **4** was established as 3,3′-di-*O*-galloyl prodelphinidin B-5 The differentiation between C-4–C-8′ and C-4–C-6′ linked procyanidins by comparison of the respective C-2′ proton chemical shift was described previously [8] In the case of **4**, as well as prodelphinidin B-5, the C-2′ proton signal appeared at comparatively higher field than that of the corresponding C-4–C-8′ linked counterpart These results were consistent with those obtained for procyanidins

The fourth prodelphinidin (**5**) gave a ^{1}H NMR spectrum analogous to the dimer **2**, besides a doublet at δ4 84 (J = 8 Hz) and a two-proton multiplet at 2 60–3 20, with large coupling constants due to the C-2′ and C-4′ protons, respectively, indicating the presence of a gallocatechin moiety (C-2 and C-3 *trans*) in the lower unit The mode of linkage between the two units was deduced from the chemical shift of the C-2′ proton which was affected by the upper unit, resulting in the upfield shift (cf the C-2 proton signal in 3-*O*-galloyl-(−)-catechin which appeared at δ 5 08 [6]) This may imply that the two units are linked through a C-4–C-8′ bond

It has been recognized that in plant tissues prodelphinidins are usually associated with procyanidins, forming a complex mixture of tannins [9–11] However, proanthocyanidins so far obtained from *M rubra* exceptionally contain only one flavan unit of 5,7,3′,4′,5′-pentahydroxy substitution The occurrence of galloyl proanthocyanidins is limited in the plant kingdom, e g in rhubarb [5], roots of *Polygonum multiflorum* [6], grapes [12] and persimmons [13], although proanthocyanidins are widely distributed It is, therefore, of chemotaxonomic significance from these points of view to have isolated prodelphinidin dimers all having galloyl groups Furthermore, this is the first time that a galloyl flavanonol with a sulfate group has been reported

EXPERIMENTAL

Mps are uncorr ^{1}H and ^{13}C NMR spectra were measured at 100 and 25 05 MHz, respectively, in Me_2CO-d_6 + D_2O unless otherwise stated Chemical shifts are given in δ(ppm), scale relative to TMS MS were recorded using a direct inlet system at 70 eV TLC was carried out on Si gel and spots were visu-

alized by spraying with either $FeCl_3$ or anisaldehyde–H_2SO_4 reagent

Extraction and isolation Freshly collected bark (6 kg) of *M rubra* Sieb et Zucc, was extracted at room temp with 80% aq Me_2CO The Me_2CO was removed by evaporation under red pres (*ca* 40°) The resulting aq soln deposited a yellow crystalline mass which was shown by TLC to be a mixture of flavones After removal of the ppt, the filtrate was extracted with EtOAc The EtOAc extract (88 g) was chromatographed over Sephadex LH-20 eluting with EtOH containing increasing amounts of H_2O to yield five fractions Crystallization of fraction 1 (5 2 g) afforded gallic acid (**6**) (0 83 g) Fraction 2 (13 4 g) was separated by Si gel using EtOAc–C_6H_6 (1 1–2 1) to give a further crop of gallic acid (0 87 g) and (±)-gallocatechin (**7**) (0 62 g) Polyamide chromatography of fraction 3 (7 8 g) using a H_2O–MeOH system afforded 3-*O*-galloyl-(−)-epigallocatechin (**8**) (4 0 g) Fraction 4 (8 2 g) was repeatedly chromatographed over Sephadex LH-20 eluting with 80% aq MeOH giving myricatin (**1**) (0 38 g) and the prodelphinidins **2** (1 65 g) and **3** (0 07 g) Prodelphinidins **4** (0 41 g) and **5** (0 03 g) were isolated pure from fraction 5 by chromatography over Sephadex LH-60 (80% aq MeOH) and LH-20 (EtOH–Me_2CO–H_2O)

Myricatin (**1**) Pale yellow needles (H_2O), mp 235–237°, $[\alpha]_D^{17}$ + 78 2° (Me_2CO, *c* 0 87) ^{1}H NMR δ5 47 (1H, *d*, *J* = 12 Hz, H-2), 5 87 (1H, *d*, *J* = 12 Hz, H-3), 6 04 (2H, *s*, H-6, and H-8), 6 94 (2H, *s*, galloyl H), 6 94 (1H, *d*, *J* = 2 Hz, H-6′), 7 00 (1H, *d*, *J* = 2Hz, H-2′) ^{13}C NMR see Table 1 (Found C, 41 14, H, 3 37, S, 5 10 $C_{22}H_{16}O_{15}SK$ requires C, 40 93, H, 3 43, S, 5 42%)

Desulfation of **1** Compound **1** (80 mg) in pyridine–dioxane (1 1) (4 ml) was refluxed for 1 hr Evaporation of solvent under red pres afforded a brown residue which was purified by Sephadex LH-20 chromatography using EtOH to yield a yellow amorphous powder (**1a**), $[\alpha]_D^{20}$ + 80 7° (Me_2CO, *c* 1 7) ^{1}H NMR δ5 46 (1H, *d*, *J* = 12 Hz, H-2), 5 96 (1H, *d*, *J* = 12 Hz, H-3), 6 03 (2H, *s*, H-6 and H-8), 6 66 (2H, *s*, H-2′ and H-6′), 7 06 (2H, *s*, galloyl H)

Enzymatic hydrolysis of **1** Compound **1** (100 mg) in aq soln was incubated with tannase at 37° for 30 min The solvent was concd and the residue treated with EtOH The EtOH soluble portion was subjected to CC over Sephadex LH-20 Elution with EtOH afforded gallic acid and a hydrolysate (**1c**), colourless needles (H_2O), mp 241–245°, $[\alpha]_D^{19}$ + 6 1° (MeOH, *c* 0 13) ^{1}H NMR (CD_3OD) δ4 48 (1H, *d*, *J* = 12 Hz, H-3), 4 88 (1H, *d*, *J* = 12 Hz, H-2), 5 88 (1H, *d*, *J* = 2 Hz, H-6), 5 91 (1H, *d*, *J* = 2 Hz, H-8), 6 82 (1H, *d*, *J* = 2 Hz, H-6′), 7 02 (1H, *d*, *J* = 2 Hz, H-2′) CD (MeOH) $[\theta]_{286} - 2\,8 \times 10^5$, $[\theta]_{311}$ 0, $[\theta]_{325} + 5 \times 10^4$

Methylation of **1** Compound **1** (80 mg) was methylated for 3 hr with Me_2SO_4 (0 7 ml) and K_2CO_3 (1 ml) in dry Me_2CO (8 ml) After filtration of the inorganic ppt, the soln was concd to a syrup which was purified by CC over Si gel Elution with C_6H_6–Me_2CO (5 1) furnished the octamethyl ether (**1b**), colourless needles (MeOH), mp 102–104°, $[\alpha]_D^{18}$ + 51 0° ($CHCl_3$, *c* 0 4) ^{1}H NMR ($CDCl_3$) δ3 80–3 84 (8 × OMe), 5 46 (1H, *d*, *J* = 12 Hz, H-2), 5 89 (1H, *d*, *J* = 12 Hz, H-3), 6 15 (1H, *d*, *J* = 2 Hz, H-6), 6 20 (1H, *d*, *J* = 2 Hz, H-8), 6 73 (2H, *s*, H-2′), 7 19 (2H, *s*, galloyl H) ^{13}C NMR see Table 1 MS *m/z* (rel int) 584 $[M]^+$ (4), 556 $[M-CO]^+$ (3), 404 (3), 376 (16), 374 (20), 212(20), 195 (100), 181 (66)

3,3′-*Di*-*O*-*galloyl prodelphinidin B*-2 (**2**) An off-white amorphous powder, $[\alpha]_D^{25}$ − 60 9° (Me_2CO, *c* 0 87) ^{1}H NMR δ2 98 (2H, *m*, H-4′), 4 78 (1H, *d*, *J* = 3 Hz, H-4), 4 96 (1H, *m*, H-3′), 5 40–5 56 (2H, *m*, H-3 and H-2′), 5 56 (1H, *s*, H-2), 6 00 (1H, *d*, *J* = 2 Hz, H-6), 6 14 (1H, *d*, *J* = 2 Hz, H-8), 6 11 (1H, *s*, H-6′), 6 50 (2H, *s*, B-ring H), 6 53 (2H, *s*, B-ring H), 6 96, 7 07 (each 2H, *s*, galloyl H) Hydrolysis of **2** with tannase in a similar manner to that described above yielded prodelphinidin B-2 (**2a**) and gallic acid **2a** an off-white amorphous powder, $[\alpha]_D^{18}$ + 35 3° (Me_2CO, *c* 0 55) ^{1}H NMR δ2 84 (2H, *m*, H-4′), 3 97 (1H, *br s*, H-3), 4 29 (1H, *br s*, H-3′), 4 71 (1H, *d*, *J* = 3 Hz, H-4), 4 89 (1H, *s*, H-2), 5 01 (1H, *s*, H-2′), 5 95, 6 03 (3H in total, H-6, H-8 and H-6′), 6 47 (2H, *s*, B-ring H), 6 64 (2H, *s*, B′-ring H)

3′-*O*-*Galloyl prodelphinidin B*-2 (**3**) An off-white amorphous powder, $[\alpha]_D^{18}$ + 73 2° (MeOH, *c* 0 93) ^{1}H NMR δ3 02 (2H, *m*, H-4′), 4 01 (1H, *br s*, H-3), 4 84 (1H, *d*, *J* = 3 Hz, H-4), 5 14 (2H, *s*, H-2 and H-2′), 5 62 (1H, *br s*, H-3′), 5 92 (1H, *s*, H-6′), 5 99 (2H, *s*, H-6 and H-8), 6 48 (2H, *s*, B-ring H), 6 66 (2H, *s*, B′-ring H), 7 04 (2H, *s*, galloyl H) ^{13}C NMR see Table 1

3,3′-*Di*-*O*-*galloyl prodelphinidin B*-5 (**4**) An off-white amorphous powder, $[\alpha]_D^{18}$ + 57 4° (Me_2CO, *c* 1 01) ^{1}H NMR δ3 00 (2H, *m*, H-4′), 4 60 (1H, *br s*, H-4), 5 05 (1H, *s*, H-2′), 5 33 (1H, *s*, H-2), 5 58 (1H, *s*, H-3′), 6 00 (1H, *d*, *J* = 2 Hz, H-6), 6 12 (1H, *d*, *J* = 2 Hz, H-8), 6 16 (1H, *s*, H-8′), 6 53, 6 64 (each 2H, *s*, B-, B′-ring H), 7 04 (4H, *s*, 2 × galloyl H) ^{13}C NMR see Table 1 Treatment of **4** with tannase followed by chromatography over Sephadex LH-20 using EtOH afforded gallic acid and prodelphinidin B-5 (**4a**) **4a** an off-white amorphous powder, $[\alpha]_D^{14}$ + 112 0° (Me_2CO, *c* 0 56) ^{1}H NMR δ2 68 (2H, *m*, H-4), 4 02 (1H, *br s*, H-3), 4 12 (1H, *s*, H-3′), 4 58 (1H, *d*, *J* = 3 Hz, H-4), 4 75 (1H, *s*, H-2), 4 85 (1H, *s*, H-2′), 6 02–6 05 (3H, *m*, H-6, H-8 and H-8′), 6 44, 6 56 (each 2H, *s*, B-, B′-ring H)

3,3′-*Di*-*O*-*galloyl prodelphinidin B*-1 (**5**) An off-white amorphous powder, $[\alpha]_D^{14}$ + 26 6° (Me_2CO, *c* 0 25) ^{1}H NMR δ2 6–3 2 (2H, *m*, H-4′), 4 84 (1H, *d*, *J* = 8 Hz, H-2′), 4 96 (1H, *br s*, H-4), 5 3–5 5 (3H in total, *m*, H-2, H-3 and H-3′), 5 94 (1H, *d*, *J* = 2 Hz, H-6), 6 00 (1H, *d*, *J* = 2 Hz, H-8), 6 09 (1H, *s*, H-6′), 6 56, 6 63 (each 2H, *s*, B-, B′-ring H), 6 59, 6 99 (each 2H, *s*, galloyl H)

Gallic acid (**6**) Colourless needles (H_2O), mp 245–248°, IR ν_{max}^{KBr} cm^{-1} 3250 (OH), 1700 (COOH)

(±)-*Gallocatechin* (**7**) Colourless needles (H_2O), mp 190–193°, $[\alpha]_D^{18}$ 0° (Me_2CO, *c* 1 05) IR ν_{max}^{KBr} cm^{-1} 3360 (OH), 1625 (aromatic)

3-*O*-*Galloyl*-(−)-*epicatechin* (**8**) Colourless needles (H_2O), mp 223°, $[\alpha]_D^{18}$ − 186 1° (MeOH, *c* 1 15) ^{1}H NMR δ2 96 (2H, *d*-like, *J* = 4 Hz, H-4), 5 07 (1H, *s*, H-2), 5 56 (1H, *t*-like, *J* = 4 Hz, H-3), 6 03 (1H, *d*, *J* = 2 Hz, H-6), 6 06 (1H, *d*, *J* = 2 Hz, H-8), 6 63 (2H, *s*, H-2′), 7 02 (2H, *s*, galloyl H)

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