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TANNINS AND OTHER PHENOLICS FROM *MYRICA ESCULENTA* BARK

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Key Word Index—*Myrica esculenta*; Myricaceae, epigallocatechin 3-*O*-gallate; epigallocatechin-(4β→8)-epigallocatechin 3-*O*-gallate; 3-*O*-galloylepigallocatechin-(4β→8)-epigallocatechin 3-*O*-gallate; epigallocatechin polymer; castalagin; myricanol; myricanone.

Abstract—An investigation of the bark of *Myrica esculenta* has led to the isolation and identification of gallic acid, myricanol, myricanone, epigallocatechin 3-*O*-gallate, two prodelphinidin dimers epigallocatechin-(4β→8)-epigallocatechin 3-*O*-gallate and 3-*O*-galloylepigallocatechin-(4β→8)-epigallocatechin 3-*O*-gallate and the hydrolysable tannin castalagin. The higher M_r fraction consists exclusively of prodelphinidin units with 2,3-*cis* configuration with average M_r of 5000. The polymer has epigallocatechin 3-*O*-gallate as the terminal unit and a significant proportion of the extender units also bear a galloyl group at C-3.

INTRODUCTION

There are three major species of *Myrica* or the bayberry trees common in south China, particularly in the Provinces of Juangxi, Yunnan and Sichuan but only the hairy bayberry (*Myrica esculenta*) serves as a source of tanning materials for the leather industry. Tannin extracts from the bark of the hairy bayberry tree have been used commercially in China since the early 1970's with present production amounting to several thousand tons annually. The bark yields some 20% of water-soluble tannins which are highly valued because their tanning properties are superior to those of other domestic extracts such as that of larch (*Larix gmelini*) and valonea (*Quercus valonea*) with respect to their rate of penetration into hides and the colour of the finished leather. For reasons of its commercial importance, it is deemed desirable to investigate the tannins and other co-occurring phenolics present in the bark of *Myrica esculenta*.

RESULTS AND DISCUSSION

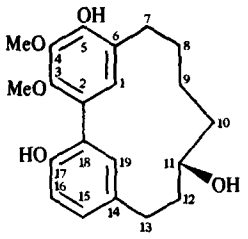
The bark extract of *M. esculenta* consisted of three main fractions, the water-soluble fraction, the ethyl acetate fraction and an insoluble fraction, the last mentioned constituted 1.6% of the dried weight of the bark. The precipitate consisted of primarily two closely related compounds which were readily separated by preparative TLC on silica gel using toluene–ether (1:1) as solvent. The ^{13}C NMR spectrum of the less mobile compound (**1**) employing the GASPE pulse sequence showed the presence of 12 aromatic carbons, only four of which were unsubstituted. The aromatic region of the ^{1}H NMR spectrum confirmed the presence of four aromatic protons, a singlet at δ6.92 and three mutually coupled resonances at δ6.90, 7.03 and 7.20 indicating the presence of only one proton in one phenyl ring and three in the 1,2,4-relative positions in the other aromatic ring. In addition, the observation of 4 oxygenated aromatic carbons, the three lower field resonances at 140.0, 147.5 and 149.8 ppm were consistent with the aromatic ring having the pyrogallol oxidation pattern. Six methylene carbons and an oxygenated methine carbon (68.2 ppm) were also observed and clearly linked together in a chain as evidenced by the absence of a carbon resonance attributable to a point of branching. The presence of two methoxy groups were also indicated in the ^{1}H NMR spectrum at δ3.07 and 3.19 which were corroborated by the carbon chemical shifts at 61.5 and 61.7 ppm, the low field position of the carbon shifts suggested their location to be in the aromatic ring in a di-*ortho* substituted configuration [1–4]. The mass spectrum of the compound showed a strong molecular ion at *m/z* 358 (100%) and the acetylated product at *m/z* 484 (15%) confirming the presence of three hydroxyl groups. These data were consistent with the cyclic biphenyl structure of myricanol (**1**), a constituent of the bark of *Myrica nagi* whose structures was fully elucidated by X-ray analysis [5–7]. Confirmation of the structure was made by further comparison of its optical rotation and infra-red data with those reported for myricanol.

The identification of myricanone (**2**) followed readily from the structure of its parent alcohol (**1**). The EIMS of (**2**) fully supported the ketone structure of myricanone by the appearance of a strong molecular ion two mass unit less than (**1**) at *m/z* 356 (100%). The ^{13}C NMR spectra of both compounds were similar particularly in the aromatic region while the differences in the aliphatic regions could be accounted for by the change from hydroxylated methine carbon to the carbonyl carbon evidenced by the disappearance of the resonance attributable to the hydroxylated carbon and the appearance of the carbonyl signal at 213.5 ppm. Other physical data were also consistent with published data [7] of myricanone.

The ethyl acetate fraction consisted of gallic acid, a hydrolysable tannin (**3**), 3-*O*-galloylepigallocatechin (**4**) and two prodelphinidin dimers (**5**) and (**6**). The hydrolysable tannin (**3**) although not separable from prodelphini-

din oligomers on MCl gel or Sephadex LH20 in ethanol, could be purified on the latter using ethanol–water (1:1) as the eluant. The sample which yielded ellagic acid and a trace amount of glucose on treatment with 5N HCl at 95° was identified as castalagin (**3**) by comparison of its ^{1}H NMR spectrum with published data [8, 9]. This chemical constitution was initially derived from fast atom bombardment mass spectrometry operating in the positive ion mode to give $(M+H)^+$ ion peak at *m/z* 935 consistent with the $C_{41}H_{26}O_{26}$ molecular formula. The ^{13}C NMR spectrum of (**3**) showed the presence of six sugar carbons in the region 65.6–74.2 ppm but no resonance was observed further downfield (90–100 ppm) which could be attributable to a hemiacetal carbon suggesting that the sugar moiety was in the open-chain form. The observation of five carbonyl resonances at 163.9, 165.5, 166.5, 166.7 and 168.9 ppm identifiable with the 5 ester linkages and 3 unsubstituted galloyl carbon resonances at 107.2, 108.7 and 109.2 ppm further support the structure of castalagin.

The structural relationship between 3-*O*-galloylepigallocatechin (**4**) and the prodelphinidins (**5**) and (**6**) were readily apparent from their ^{13}C NMR data (see Table 1). The dimeric constitution of (**5**) and (**6**) was indicated by the comparable intensity of the C-2 or C-3 resonances between the extender and the terminating flavanoid units. The pyrogallol B-ring oxidation pattern of the flavanoid units was characterised by the presence of the chemical shifts in the 107 ppm region attributable to the C-2′ and C-6′ and the analogous carbons on the galloyl ring at about 3.5 pm further downfield. A distinctive feature between these dimers was the relative intensity of these B-ring and galloyl carbon resonances which indicated the presence of only one galloyl group in (**5**) and two in (**6**).



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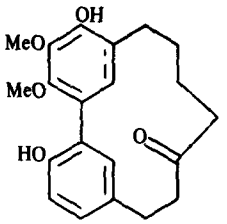

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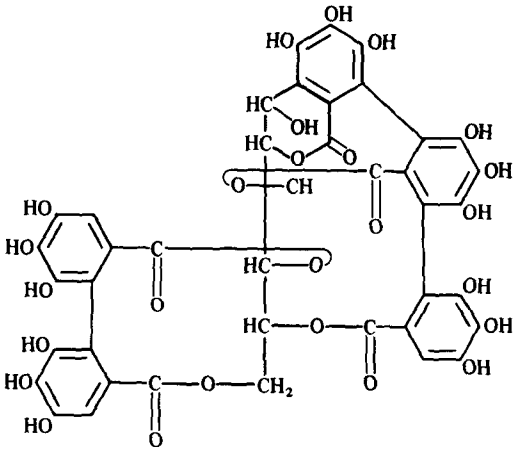

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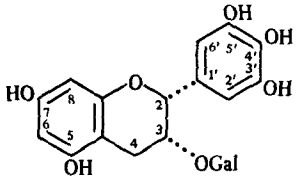

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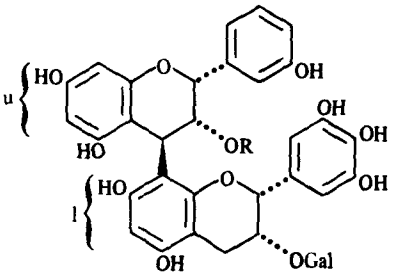


5 R = H

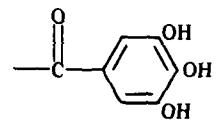
6 R = Gal = 

Table 1. ^{13}C NMR chemical shifts of flavanoids **4–6** in acetone-d_6–H_2O (1:1)

		Flavan moiety					Galloyl moiety			
		C-2	C-3	C-4	C-6	C-8	C-1″	C-2″	C-3″	C-O
4		78.0	70.4	26.4	96.1	97.0	121.2	110.6	110.6	167.5
Dimer (**5**)	upper	77.1	73.2	36.5	96.6	107.9				
	lower	78.9	69.2	26.8	96.0	97.4	121.9	110.5	110.5	166.5
Dimer (**6**)	upper	75.8	74.7	33.6	96.5	107.6	121.6	110.3	110.3	166.2
	lower	78.2	69.3	26.4	96.0	97.3	121.8	110.3	110.3	166.2
Gallic acid							122.0	111.0	111.0	171.2

The upfield positions (75.8–78.2 ppm) of all the C-2 chemical shifts clearly indicated all the flavanoid units to have the 2,3-*cis* configuration [10]. The downfield position of the C-3 chemical shifts compared to unsubstituted flavan-3-ol units defined the location of the galloyl group to be at this point [11–13] and further corroborated by the observation of the consequential upfield shifts of the neighbouring C-3 and C-4 carbons. Thus in the case of the prodelphinidin dimer (**5**), the upfield position (26.8 ppm) of the C-4 lower flavanoid units comparable to that in 3-*O*-galloylepigallocatechin (**4**) indicated that the location of the galloyl group was at the C-3 of the lower flavanoid unit, a case evidenced by the observation of the normal heterocyclic carbon shifts of the proanthocyanidin unit [10]. The chemical constitution of (**5**) was also supported by acid catalysed degradation with phloroglucinol which yielded epigallocatechin-(4β→2) phloroglucinol and 3-*O*-galloylepigallocatechin, the products being identified by comparison with authentic materials on 2D TLC. Similar ^{13}C NMR chemical shift analysis of the heterocyclic carbons of (**6**) confirmed the presence of 3-*O*-galloyl groups in both flavanoid units. Thus (**5**) was identified as epigallocatechin-(4β→8)-epigallocatechnin 3-*O*-gallate and (**6**) as 3-*O*-galloylepigallocatechin-(4β→8)-epigallocatechin 3-*O*-gallate; the C-4 to C-8 interflavanoid linkages were preferred in these compounds as the alternative C-4 to C-6 linkages were less likely due to their more restricted occurrence [14–16].

The water-soluble fraction was purified on Sephadex LH20 and freeze-dried to give a light brown amorphous material. The polymer yielded only delphinidin when heated with 5% HCl in *tert*-butanol. The exclusively pyrogallol B-ring nature of the flavanoid units was also clearly evident in the ^{13}C NMR spectrum (see Fig. 1) of the sample with a strong peak at about 107 ppm and complete absence of other resonances associated with other B-ring oxidation pattern [10]. The presence of the gallate functionality in the polymer was directly indicated by the carbon chemical shifts at about 111 ppm and indirectly by the upfield resonances at about 34 and 26 ppm attributable to the C-4 of the extender and terminal flavanoid units respectively. The presence of the latter two peaks was evidence for the galloyl group to be located in the C-3 position. The likely presence of the resonances attributed to the substituted C-8/C-6 of the A-ring [10] under the pyrogallol B-ring chemical shifts (~107 ppm) prevented a direct measurement of the amount of galloyl present. However, an estimation of the amount of gallate present in the polymer could be made from the relative intensity of the C-4 chemical shifts of the prodelphinidin units (4a and 4b peaks in Fig. 1). This region of the spectrum was re-examined on a Bruker 400 MHz instrument in MeOH-d_4 which gave an improved resolution of the 4a and 4b peaks and suggested that some 25–30 per cent of the extender units possessed a galloyl group at the C-3. This level of gallate was consistent with the ratio of about 3:1 of the yields of the prodelphinidin dimers (**5**) and (**6**) respectively which were isolated. Like the co-occurring lower M_r analogues, the flavanoid units were predominantly of the 2,3-*cis* configuration as indicated by the upfield C-2 resonances in the 77 ppm region and none at lower field [10]. These structural features were also indicated in the IR spectrum of the polymer with absorptions at 800 cm^{-1} characteristic of the 2,3-*cis* configuration, a doublet at 1530 cm^{-1} region reflecting the predominance of the pyrogallol B-ring oxidation [17] and a carbonyl absorption at 1710 cm^{-1} confirming the presence of gallate. The terminal unit was predominantly 3-*O*-galloylepigallocatechin as indicated by the absence of resonances in the 27–29 ppm region [10] (the ^{13}C NMR spectrum re-examined in MeOH-d_4) and the presence of the characteristic upfield C-4 chemical shift at about 26 ppm and further confirmed by degradation with benzylthiol [4].

The VPO measurements of the polymer gave the average number M_r of about 5000 which translated to an average polymer size of about 14 epigallocatechin units with some five to six units bearing a galloyl group.

For many years the commercial bark extracts used in the Chinese tanning industry have been erroneously identified as that of *Myrica rubra*. Only after extensive study of the trees by forestry scientists in Guangxi has the error been recognised and in November 1986 the identification was officially rectified to *Myrica esculenta*. The bark of *M. rubra* has been studied recently by Nonaka and co-workers [13] and as in *M. esculenta*, they found the flavanoids were exclusively of the pyrogallol B-ring type and the prodelphinidin dimers carried galloyl groups which they concluded to have chemotaxonomic significance. The present study on *M. esculenta*, while supporting this taxonomic relationship also reveals structural differences between the prodelphinidins in the two plant species. While in *M. esculenta* the prodelphinidins are exclusively of the 2,3-*cis* configuration, those in *M. rubra* are mixed with a significant proportion of the flavanoid units having the 2,3-*trans* configuration. This stereochemical difference in the prodelphinidins could be employed in further distinguishing between these two closely related species.

EXPERIMENTAL

^{1}H and ^{13}C NMR were determined at 80 and 20 MHz respectively in Me_2CO-d_6–H_2O (1:1) unless otherwise stated.

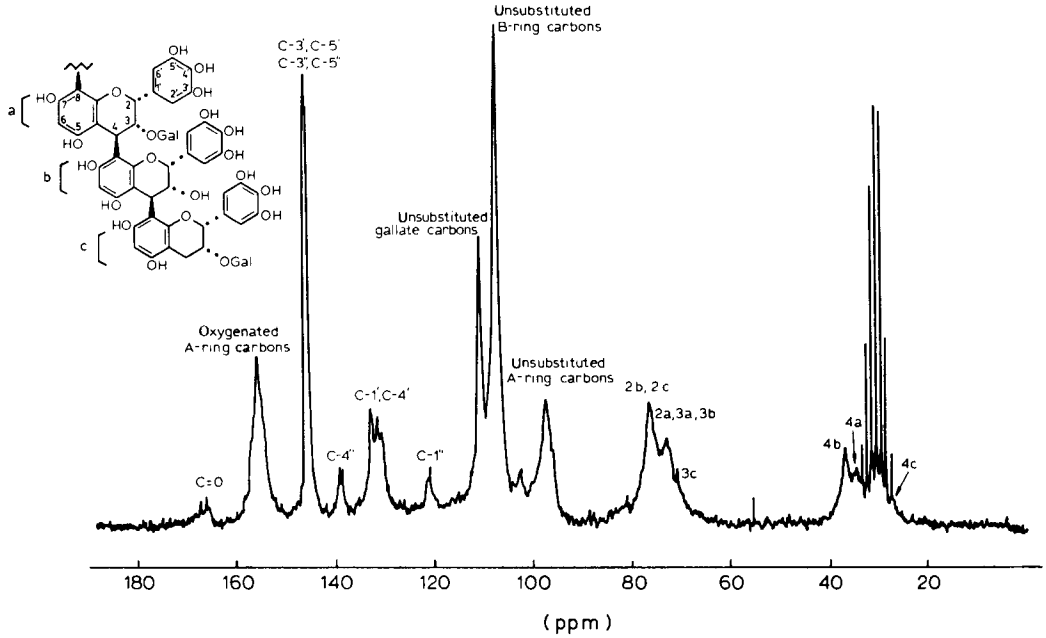


Fig. 1. ^{13}C NMR spectrum of *Myrica esculenta* tannins (in acetone-d_6–H_2O 1:1 v/v)

Electron impact mass spectral/(EIMS) data were obtained on a Kratos MS-30 mass spectrometer while FABMS was run by the Chemistry Department, University of Adelaide, Australia. IR spectra were performed with KBr pellets. R_f measurements were carried out by TLC on Schleicher and Schuell cellulose plates using *t*-BuOH–HOAc–H_2O (3:1:1, solvent A) and HOAc–H_2O (6:94, solvent B) and visualized by spraying with vanillin–HCl or $FeCl_3$–$K_3Fe(CN)_6$ reagents.

Extraction and isolation. Milled bark (640 g) of *Myrica esculenta* was exhaustively extracted with Me_2CO–H_2O (7:3) at room temp. and the combined extracts was concd at 45° under red. pres. The resulting ppt. (fraction 1) was filtered off and the filtrate was exhaustively extracted with EtOAc, the combined extract was evapd to give the EtOAc soluble fraction (fraction 2, 32 g).

The polymer fraction was obtained separately by exhaustively extracting the milled bark with Me_2CO–H_2O (1:1) at room temp. The combined extract was stirred with excess NaCl and the resulting Ac_2O layer was collected and concd at 45° under red. pres. To the residue was added an equal volume of H_2O and the resulting solution (H_2O soluble fraction) washed by partitioning with $CHCl_3$ followed with EtOAc. The washed aqueous extract was diluted with an equal volume of MeOH and treated on a Sephadex LH20 column first washing the column with excess MeOH–H_2O (1:1) before eluting the polymer with Me_2CO–H_2O (3:2).

Prodelphinidin polymer. Obtained as freeze-dried powder (2 g), $[\alpha]_{578}$ +102.7° MeOH–H_2O (1:1); [c 0.3)], Mn̄ 4997 (VPO), λ_{max}275 nm ($E^{1\%}_{cm}$ 156), ν_{max} cm^{-1}: 3100–3600, 1710, 1620, 1535, 1520, 1450, 1345, 1210, 1150, 1040, 830, 800, 770, 738. For ^{13}C NMR data see Fig. 1.

Myricanol (**1**). The ppt. (fraction 1) was subjected to CC on Sephadex LH20 using EtOH as eluant to yield a fraction (9.0 g) containing a mixture of myricanol and myricanone. These two compounds were resolved by prep. TLC on silica gel using toluene–Et_2O (1:1 as eluant, to give myricanol (4.2 g), R_F 0.41; $[\alpha]_D$ −64° ($CHCl_3$; *c* 0.05), (lit [7]-65.6°). MS (*m/z*): 358 (100%), 340 (13), 325 (6), 297 (7), 273 (11), 271 (17), 257 (20), 136 (12). ν_{max} cm^{-1}: 3200–3550, 2940, 2870, 1620, 1590, 1510, 1500, 1460, 1410, 1350, 1280, 1230, 1115, 1080, 1070, 1050, 1040, 1018, 1005, 970, 950, 925, 915, 895, 880, 860, 835, 810, 775, 740, 734. ^{13}C NMR (Me_2CO-d_6, ppm): 23.8 (C-8), 26.4 (C-9), 26.6 (C-10), 27.6 (C-12), 35.5 (C-7), 40.4 (C-13), 61.5, 61.7 (–OMe), 68.2 (C-11), 117.2 (C-16), 123.5 (C-18), 123.9 (C-2), 129.6 (C-19), 130.1 (C-6), 130.4 (C-1), 131.6 (C-14), 134.2 (C-15), 140.4 (C-4), 147.5 (C-5), 149.8 (C-3), 152.4 (C-17). ^{13}C NMR ($CDCl_3$, ppm): 22.8 (C-8), 25.3 (c-9, C-10), 26.7 (C-12), 34.3 (C-7), 39.3 (C-13), 61.3 (2× OMe), 68.3 (C-11), 116.9 (C-16), 123.1 (C-2, C-18), 124.8 (C-6), 129.3 (C-19), 129.7 (C-1), 130.9 (C-14), 132.9 (C-15), 138.8 (C-4), 146.5 (C-5), 148.8 (C-3), 150.8 (C-17). ^{1}H NMR (Me_2CO-d_6, δ): 1.45–2.95 (6×-CH_2), 3.86 (–OMe), 3.89 (–OMe), 3.90 (*m*, –OCH=), 6.79 (*d*, J = 11.0 Hz), 6.83 (*s*), 6.97 (*dd*, J = 2.1 and 11.0 Hz) and 7.17 (*d*, J = 2.1 Hz). Acetylation of myricanol with pyridine–acetic anhydride gave a triacetate, mp 72–78° (lit. [7], mp 70–80°), MS (*m/z*): 484 (15%), 443 (15), 442 (52), 424 (3), 401 (25), 400 (100), 382 (10), 340 (36). 325 (12), 257 (11).

Myricanone (**2**). Separated from myricanol by prep. TLC on silica gel, R_f 0.60 was obtained as a solid (1.2 g) which when dissolved in Ac_2O and left to evap. slowly gave crystalline needles, mp 190–192° (lit. [7] m.p. 194–196°). MS (*m/z*): 356 (100%), 313 (10), 285 (17), 271 (13), 257 (10), 248 (14), 203 (17), 189 (16), 143 (13), 135 (11) and 133 (11). ^{13}C NMR ($CDCl_3$, ppm): 21.8 (C-8), 24.4 (C-9), 26.8 (C-7), 28.8 (C-13), 42.5 (C-10), 46.0 (C-12), 61.3 (–OMe), 61.4 (–OMe), 116.8 (C-16), 123.3 (C-18), 123.1 (B-2), 125.4 (C-6), 128.8 (C-1, C-14, C-19), 132.2 (C-15), 138.7 (C-4), 146.0 (C-5), 147.8 (C-3), 151.6 (C-17), 213 (C=O). ^{1}H NMR ($CDCl_3$, δ): 1.65–1.95 (2×–CH_2–), 2.60–3.0 (4×-CH_2–), 3.77 (–OMe), 3.93 (–OMe), 6.57 (s), 6.72 (d, J = 2.1 Hz), 6.81 (J = 8.3 Hz), 7.02 (*dd*, J = 2.1, 8.3 Hz). ν_{max} cm^{-1}: 3384, 3250, 2943, 1705, 1610, 1510, 1496, 1458, 1409, 1350, 1270, 1226, 1117, 1073, 1047, 986, 950, 823.

The EtOAc soluble fraction was subjected to CC on Sephadex LH 20 using EtOH as eluant to yield gallic acid, 3-*O*-galloylepigallocatechin, a hydrolysable tannin fraction (0.31 g) and a proanthocyanidin fraction (0.60 g).

Gallic acid, (0.70 g) R_f 0.61 (A), 0.35 (B). ^{13}C NMR (Me_2CO-

d_6–H_2O; 1:1 v/v, ppm): 111.0 × 2, 122.0, 138.8, 145.8 × 2, 171.2.

3-O-*Galloylepigallocatechin* (**4**) was obtained as a freeze-dried powder, (0.46 g), $[\alpha]_{598}$ −135.4° (MeOH–H_2O, 1:1; *c* 0.06), R_f 0.72 (A), 0.37 (B). ^{13}C NMR (Me_2CO-d_6–H_2O, 1:1, ppm): 26.4 (C-4), 70.4 (C-3), 78.0 (C-2), 96.1 (C-6), 97.0 (C-8), 99.4 (C-4a), 107.2 (C-2′, C-3′), 110.6 (C-2, C-3 galloyl), 121.2 (C-1, galloyl), 130.7 (C-1′), 133.3 (C-4′), 139.5 (C-4 galloyl), 145.9, 146.2 (C-3, C-5 galloyl and B-ring), 156.6, 156.9, 157.0 (C-5, C-7, C-8a of A-rings), 167.5 (C=O).

Castalagin (**3**) was obtained from the hydrolysable tannin fraction after subjecting the sample to CC on MCI gel and again on LH20 using MeOH–H_2O (1:1) as eluants in both instances and freeze-dried to give a powder (0.15 g), $[\alpha]_{578}$ −116° (MeOH; *c* 0.1), (lit. [9] −134.6°), R_f 0.38 (B), FABMS gave $(M+H)^+$ at *m/z* 935. γ_{max} (cm^{-1}): 3150–3550, 1740, 1620, 1445, 1355, 1315, 1175, 1040. ^{13}C NMR (Me_2CO-d_6, ppm): 65.6, 66.5, 67.8, 69.5, 71.3, 74.2 (C-6, C-3, C-5, C-1, C-4 and C-2 respectively of sugar carbons), 107.9, 108.7 and 109.2 (unsubstituted galloyl carbons), 112.7, 114.3, 114.5, 115.0, 115.9, 116.0 aryl substituted galloyl carbons), 122.7, 125.6, 127.1, 127.9 (remaining non-oxygenated substituted galloyl carbons), 135.0, 136.1, 136.7 (2 ×), 137.7 (oxygenated carbons di-*ortho* to oxygen substitutents in galloyl ring), 143.7–146.9 (remaining oxygenated carbons in galloyl ring), 163.9, 165.5, 166.6, 166.7 and 168.9 (carbonyl carbons). ^{1}H NMR (Me_2CO-d_6, δ): 4.00 (*d*, *J* = 12.9 Hz, H-6′), 5.07 (*m*, H-2, H-6), 5.20 (*d*, *J* = 6.9 Hz, H-3), 5.25 (*dd*, *J* = 6.9 Hz, H-4), 5.67 (*b d*, *J* = 2.2, H-5), 5.71 (*d*, *J* = 4.5 Hz, H-1), 6.64, 6.78 and 6.88 (each *s*, ArH).

Epigallocatechin-(4β→8)-*epigallocatechin*-3-O-*gallate* (**5**) was obtained by subjecting the proanthocyanidin fraction to CC on Sephadex LH 20 using EtOH–H_2O (1:1 as solvent. Compound (5) obtained as freeze-dried material (0.15 g), R_f 0.50 (B), $[\alpha]_{578}$ −124.5° (MeOH–H_2O, 1:1 v/v; *c* 0.05). ν_{max} (cm^{-1}): 3100–3600, 1700, 1620, 1540, 1520, 1455, 1345, 1240, 1150, 1100, 1040, 980, 825, 807, 770, 740. ^{13}C NMR (Me_2CO-d_6, ppm): 26.8 (*l* C-4), 36.5 (*u*C-4), 69.2 (*l*C-3), 73.2 (*u*C-3), 77.1 (*u*C-2), 78.0 (*l*C-2), 96.0 (*l*C-6), 96.6 (*u*C-6), 97.4 (*l*C-8), 99.6 (*l*C-4a), 101.7 (*u*C-4a), 106.7, 107.0 (C-2′, C-6′ of B-ring), 107.9 (*l*C-8), 110.5 (C-2, C-6 of galloyl), 121.9 (C-1 of galloyl), 130.7, 131.7 (C-1′ of B-ring), 132.9 (C-4′ of B-rings), 139.0 (C-4 of galloyl), 145.6–146.2 (C-3, C-5 of both galloyl and B-rings), 154.4–158.0 (C-5, C-7, C-8a of A-rings), 166.5 (C=O. ^{1}H NMR (Me_2CO-d_6, δ): 3.08 (*m*, 1H-4), 4.09 (*m*, *u*H-3), 4.91 (*br s*, *u*H-4), 5.23 (*br s*, *u*H-2, *l*H-2), 5.63 (*m*, *l*H-3), 6.07 (*m*, *u*H-6, *l*H-6, *u*H-8), 6.56 (*s*, lower B-ring protons), 6.76 (*s*, upper B-ring protons), 7.14 (galloyl protons).

3-O-*Galloylepigallocatechin*-(4β→8)*epigallocatechin* 3-O-*gallate* (**6**) was eluted from the Sephadex LH20 column after **5** and freeze-dried to give a powder (0.11 g), R_f 0.35 (B), $[\alpha]_{578}$ −154.9° (MeOH–H_2O, 1:1 v/v; *c* 0.05). ν_{max} cm^{-1}: 3100–3600, 1695, 1620, 1540, 1520, 1455, 1355, 1240, 1150, 1100, 1040, 975, 825, 807, 770, 738. ^{1}H NMR (Me_6CO-d_6, δ): 2.98 (*m*, *l*H-4 × 2), 4.82 (*m*, *u* H-3), 4.98 (*m*, *u* H-4), 5.47–5.57 (*m*, *u* H-2, *l*H-2, *l*H-3), 5.97 (*m*, *u* H-6, *u*H-8), 6.12 (*s*, *l*H-6), 6.51, 6.54 (each *s*, B-ring protons), 6.98, 7.10 (each *s*, galloyl protons). ^{13}C NMR (Me_2CO-d_6, ppm): 26.4 (*l* C-4), 33.6 (*u* C-4), 69.3 (*l*C-3), 74.7 (*u* C-3), 75.8 (*u* C-2), 78.2 (*l*C-2), 96.0 (*l*C-6), 96.5 (*u*C-6), 97.3 (*l*C-8), 99.8 (*l*C-4a), 102.5 (*u*C-4a), 106.9 (unsubstituted B-ring carbons), 107.6 (*u*C-8), 110.3 (unsubstituted galloyl carbons), 121.6, 121.8 (C-1 of galloyl), 130.4, 130.9 (C-1′ of B-ring), 132.8, 133.0 (C-4′ of B-ring), 138.9 (C-4 of galloyl), 145.6–141.3 (C-3, C-5 of both galloyl and B-rings), 154.9–157.6 (C-5, C-7 and C-8a of A-rings), 166.2 (C=O).

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