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GALLOYL AND HYDROXYCINNAMOYLGLUCOSES FROM RHUBARB*

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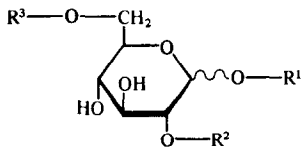
Key Word Index—*Rheum* sp., Polygonaceae; rhubarb; gallotannin, gallic acid, cinnamic acid, *p*-coumaric acid, acylated glucose; chemical evaluation

Abstract—A chemical examination of the commercial rhubarbs, produced in China, North Korea and Japan, has led to the isolation of five hydroxycinnamoyl and galloyl esters with glucose. Their structures were established on the basis of chemical and spectroscopic evidence as 1-*O*-galloyl-6-*O*-cinnamoyl-, 1,2-di-*O*-galloyl-6-*O*-cinnamoyl-, 1,2-di-*O*-galloyl-6-*O*-*p*-coumaroyl-, 1,6-di-*O*-galloyl-2-*O*-*p*-coumaroyl- and 1,2-di-*O*-galloyl-β-D-glucoses

INTRODUCTION

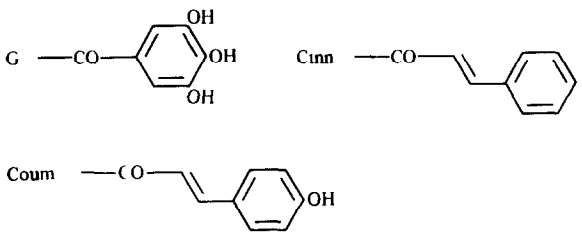
Rhubarb, one of the most important crude drugs in Asiatic regions, is produced from a number of different *Rheum* species, i.e *R. palmatum*, *R tanguticum*, *R. officinale*, etc. Most of these rhubarbs are produced in mainland China, especially in Szechwan and Kanzu provinces, and when exported from Hong Kong they are given various commercial names based on their appearance, qualities or place of production, even if the original plants were identical. Since the growing districts and preparation methods of rhubarbs in China are entirely unknown it is very difficult to determine which *Rheum* species was used from the commercial name. For this reason, we have been investigating phenolic constituents in various commercial rhubarbs as a means of chemically evaluating their qualities. Previously, we reported on the isolation and characterisation of several galloyl and hydroxycinnamoyl esters of glucose from the commercial Chinese rhubarb (Chinese commercial name: Mar-Tie-Da-Huang) [2]. Further chemical examination of other commercial rhubarbs, produced in China, North Korea and Japan, has now resulted in the isolation of five additional hydroxycinnamoyl and galloyl esters of glucose (**1**–**4**, **11**). We now report on the isolation and structure elucidation of these compounds.



	R^1	R^2	R^3
1	G(β)	H	Cinn
1a	H	H	Cinn
2	G(β)	G	Cinn
3	G(β)	G	Coum
3a	H	H	Coum
4	G(β)	Coum	G
4a	H	Coum	H
5	G(β)	Coum	H
6	G(β)	Cinn	H
7	G(β)	Cinn	G
8	G(β)	H	H
9	H	G	H
10	H	H	G
11	G(β)	G	H
12	G(β)	H	G
13	H	G	G
14	G(β)	G	G

RESULTS AND DISCUSSION

The aqueous acetone extract of each rhubarb afforded on chromatography over Sephadex LH-20 a complex mixture of acylated sugars, which was separated by a combination of Sephadex LH-20, MCI-gel CHP 20P, Bondapak C_{18}/Porasil B, Fuji-gel ODS G3 and cellulose chromatographies, to yield compounds **1**, **2**, **6**–**8**, **10**–**14** (from Chinese rhubarb), **4**–**12**, **14** (from North Korean rhubarb) and **2**, **3**, **7**–**12**, **14** (from Japanese rhubarb). Among these compounds, **5**–**10**, **12**–**14** were identified as 1-*O*-galloyl-2-*O*-*p*-coumaroyl-β-D-glucose [2], 1-*O*-glloyl-2-*O*-cinnamoyl-β-D-glucose [2, 3], 1,6-di-*O*-



* Part 68 in the series 'Tannins and Related Compounds'. For part 67 see ref [1]. This paper also forms Part XIII of 'Studies on Rhubarbs (Rhei Rhizoma)'

Table 1 ^{13}C NMR chemical shifts for compounds

		1	1a	2	3
			97 6		
	C-1	95 4		93 5	93 5
			93 4		
			74 6		
	C-2	73 4		75 6	75 9
			74 6		
			77 2		
Glucose moiety	C-3	77 2		73 9	73 9
			74 1		
			71 1		
	C-4	70 7		70 9	71 1
			70 4		
			75 6		
	C-5	75 3		74 8	75 1
			73 3		
	C-6	64 4	64 9	64 2	64 1
	C-1	120 3		119 6	119 8
				120 6	120 8
	C-2	110 0(2C)		110 2(4C)	110 2(4C)
Galloyl moiety					
				145 9(2C)	146 0(2C)
	C-3	146 0(2C)			
				146 0(2C)	146 1(2C)
				139 4	139 3
	C-4	139 6		139 8	139 4
	C-1	135 0	135 1	134 9	
	C-2	129 0(2C)	129 1(2C)	129 0(2C)	
Cinnamoyl	C-3	129 8(2C)	129.8(2C)	129 8(2C)	
moiety	C-4	131 3	131 3	131 4	
	C_α	146 0	145 8	146 2	
	C_β	118 3	118 6	118 2	
	C-1				126 5
	C-2				131 1(2C)
p-Coumaroyl	C-3				116 8(2C)
moiety	C-4				160 8
	C_α				146 3
	C_β				114 8
	–COO–	166 0	167 8	165 6	165 6
		167 7		167 0	167 0
				167 7	168 1

* At 25 05 MHz (δ values) in Me_2CO-d_6 + D_2O

galloyl-2-*O*-cinnamoyl-β-D-glucose [2], 1-*O*-galloyl-β-D-glucose(β-glucogallin) [2, 4], 2-*O*-galloylglucose [5], 6-*O*-galloylglucose [6], 1,6-di-*O*-galloyl-β-D-glucose [6], 2,6-di-*O*-galloylglucose [2] and 1,2,6-tri-*O*-galloyl-β-D-glucose [7], respectively, by comparison of their physical and spectral data with those of authentic samples.

Compounds **1** and **2** gave a positive ferric chloride reaction and showed $[M+H]^+$ ion peaks at *m/z* 463 and 615, respectively in their FDMS The ^1H NMR spectrum of **1** showed signals due to one galloyl group (δ7.19, 2H, *s*), while that of **2** indicated the presence of two galloyl groups (δ7.09 and 7 10, each 2H, *s*). In addition, *trans*-coupled olefinic signals (δ6 54 and 7 68, each 1H, *d*, $J=16$ Hz) and aromatic five-proton multiplets (δ7 3–7 8) appeared in each case, suggesting that both **1** and **2** possess a cinnamoyl group in their molecules Acid hydrolyses of **1** and **2** yielded gallic acid, cinnamic acid and glucose In the case of **1**, the lowfield sugar proton resonances at δ5 76 (1H, *d*, $J=8$ Hz), 4 57 (1H, *dd*, $J=2,12$ Hz) and 4 34 (1H, *dd*, $J=6,12$ Hz), analogous to those of **12**, as well as similar carbon resonances due to the sugar moiety (Table 1), were consistent with a 1,6-diacylglucose structure On the other hand, the ^1H and ^{13}C NMR chemical shifts and coupling patterns of the sugar signals in **2** were in good accord with those of **14**, indicating that the galloyl and cinnamoyl groups are bound to the C-1, C-2 and C-6 positions in the glucose moiety

1, **1a**, **2**, **3**, **3a**, **4**, **11**, **12**, and **14***

3a	**4**	**11**	**12**	**14**
97 6				
	93 7	93 6	95 4	93 4
93.3				
74 1				
	76.1	74 0	73 2	75.7
71 1				
77 2				
	73.5	75.1	77 0	73 7
74 1				
71.1				
	71 1	70 9	70 6	70 8
70 3				
75.6				
	75 5	78 4	75.5	74 8
73 1				
64.6	63 9	61.9	64 3	64 0
	120.3	119.7	120.1	119 3, 120.5
	121 6	120 7	120.9	120.8
	110 0(2C)		110.0(2C)	109 7(4C)
		110 2(4C)		
	110.3(2C)		110.3(2C)	109 9(2C)
		146 0(2C)		
	146 1(4C)		145 8(4C)	145.0(6C)
		146.1(2C)		
	139 6	139 3	139 1	138.8, 139.0
	139 8	139 9	139.5	139 5
126 5	126 8			
131 0(2C)	131 0(2C)			
116.7(2C)	116 7(2C)			
160 7	160 7			
146 1	146 1			
115.7	115.0			
168 4	165 2	165 9	166.3	165 3
	166.7	167 0	167.5	166 6
	166 8			166.9

Tannase hydrolyses of **1** and **2** yielded gallic acid and an identical hydrolysate (**1a**), which showed no galloyl peak in the ^{1}H NMR spectrum and liberated methyl cinnamate and glucose on alkaline methanolysis with 2% sodium methoxide–methanol. The location of the cinnamoyl group in **1a** was determined to be at the C-6 position of the glucose moiety from the lowfield shift (δ64.9) of the C-6 methylene signal in the ^{13}C NMR spectrum The anomeric configurations in **1** and **2** were concluded to be β from the coupling constant value (*d*, J = 8 Hz in each case) of the anomeric proton signals. Consequently, **1** and **2** were established as 1-*O*-galloyl-6-*O*-cinnamoyl-β-D-glucose and 1,2-di-*O*-galloyl-6-*O*-cinnamoyl-β-D-glucose, respectively

Compounds **3** and **4** showed in the FDMS the same $[M+H]^+$ ion peak at *m/z* 631 The ^{1}H NMR spectra of **3** and **4** were quite similar to each other, and also closely correlated with those of **2** and **7**, except for the appearance of A_2B_2-type aromatic signals, suggesting the presence of a *p*-coumaroyl group instead of the cinnamoyl group. Tannase hydrolysis of **3** yielded gallic acid and a hydrolysate (**3a**), which on alkaline methanolysis with 2% sodium methoxide–methanol afforded glucose and methyl *p*-coumaroate. Since in the ^{13}C NMR spectrum of **3a** the carbon resonances due to the sugar moiety were in good agreement with those of **1a**, the location of the *p*-coumaroyl group in **3a** was concluded to be at the C-6 position in the glucose moiety On the other hand, tan-

nase hydrolysis of **4** furnished gallic acid and a hydrolysate (**4a**), which was found to be identical with 2-*O*-*p*-coumaroylglucose [2], obtained previously by similar tannase hydroysis of **5**. The β-configuration in the anomeric center of the glucose moiety was confirmed by the anomeric proton resonances having a large coupling constant ($J=8$ Hz, in each case) Accordingly, **3** and **4** were characterized as 1,2-di-*O*-galloyl-6-*O*-*p*-coumaroyl-β-D-glucose and 1,6-di-*O*-galloyl-2-*O*-*p*-coumaroyl-β-D-glucose, respectively

Compound **11** possesses two galloyl groups as shown by ^{1}H and ^{13}C NMR spectroscopy, and gave gallic acid and glucose on tannase hydrolysis The ^{1}H NMR spectrum of **11** exhibited an anomeric proton signal at extremely lowfield (δ 5.91, *d*, $J=8$ Hz), indicating that one of two galloyl groups is located at the C-1 position It also showed a triplet at relatively lowfield (δ 5 19, 1H, $J=8$ Hz), and this signal could be assigned to the C-2 proton from the fact that it was shown to be coupled with the anomeric proton signal as revealed by spin-decoupling experiments Thus, another galloyl group was concluded to be present at the C-2 position in the glucose moiety The mode of the linkage at the anomeric center was confirmed to be β from the coupling constant value ($J=8$ Hz) of the anomeric proton signal Therefore, **11** was established as 1,2-di-*O*-galloyl-β-D-glucose

Many rhubarbs so far examined have been found to contain gallotannins, in which hydroxycinnamoyl and galloyl groups are randomly located at the C-1, C-2 and C-6 positions in the glucose moiety [2, 6, 7] The North Korean rhubarb examined here, however, seems to be unique in that it contains gallotannins possessing the hydroxycinnamoyl group at the limited C-2 position

EXPERIMENTAL

Details of the instruments and chromatographic conditions used in this work were essentially the same as described in the previous paper [8]

Materials The Chinese rhubarb (Chinese commercial name Chong-Gi-Huang) and the North Korean rhubarb (Korean commercial name Cho-Seon-Dae-Hwang) were purchased from the markets in Hong Kong and Japan, respectively The Japanese rhubarb (Japanese commercial name Hokkai-Dai-Oh) is the one cultivated in Hokkaido, Japan

Extraction and isolation (i) Chinese rhubarb (3 2 kg) was powdered and extracted with 80% aq Me_2CO at room temp The Me_2CO was removed by evapn under red pres to give an aq soln, which was directly subjected to CC over Sephadex LH-20 with H_2O containing increasing amounts of MeOH (1 0–0 1) to afford six fractions (I–VI) Subsequent CC of fraction II over MCI-gel CHP 20P with H_2O containing increasing amounts of MeOH furnished a further five fractions Repeated CC of fraction II-2 over Bondapak C_{18}/Porasil B, Fuji-gel ODS G3 and Sephadex LH-20 with a variety of solvent systems yield compounds **8** (140 mg) and **10** (900 mg) Fraction IV was further chromatographed over MCI-gel CHP 20P[H_2O–MeOH (4 1–0 1)] to give four fractions Repeated CC of fraction IV-1 over Sephadex LH-20[H_2O–MeOH(2 3)], cellulose (2% HOAc) and Fuji-gel ODS G3[H_2O–MeOH (1 0–2 3)] furnished **11** (180 mg), **12** (150 mg) and **13** (460 mg) Fraction IV-3 was rechromatographed over Sephadex LH-20 [H_2O MeOH(1 0 1 4)] to yield **1** (130 mg) and **6** (240 mg) Subsequent CC of fraction V over Sephadex LH-20 with EtOH furnished a further five fractions Repeated CC of V-2 over MCI-gel CHP 20P, Sephadex LH-20 and Fuji-gel ODS G3 with a variety of solvent systems afforded **2** (310 mg) and **7** (390 mg), while a similar CC of V-3 furnished **14** (1 77 g)

(ii) North Korean rhubarb (950 g) was extracted and fractionated as described above to give seven fractions (I–VII) Fraction II consisted mainly of **8**, and was recryst. from H_2O to give 5 8 g of pure sample The mother liquor was rechromatographed over Sephadex LH-20 and Bondapak C_{18}/Porasil B with H_2O to furnish **9** (134 mg) and **10** (235 mg) Further CC of fraction IV over MCI-gel CHP 20P[H_2O–MeOH(1 0–0 1)] afforded four fractions Repeated CC of fraction IV-2 over Sephadex LH-20, cellulose and MCI-gel CHP 20P with a variety of solvent systems yielded **11** (732 mg) and **12** (100 mg) Fraction IV-3 consisted of a large amount of stilbene gallates which were separated by cryst from H_2O, and the mother liquor was chromatographed over Sephadex LH-20[EtOH and H_2O MeOH(2 3)] to give **5** (1 08 g). Fraction IV-4 consisted mainly of **6**, and recryst from H_2O furnished the pure sample (1 19 g) Fraction V was subseqeuntly chromatographed over Sephadex LH-20 with EtOH to give five fractions Repeated CC of fraction V-4 over MCI-gel CHP 20P, Sephadex LH-20 and Bondapak C_{18}/Porasil B with a variety of solvent systems yielded **4** (72 mg) and **7** (501 mg) Fraction V-5 was further chromatographed over MCI-gel CHP 20P[H_2O–MeOH(4 1–0 1)] and recryst from H_2O furnished **14** (200 mg)

(iii) Japanese rhubarb (1 1 kg) was extracted and fractionated as above to afford seven fractions (I–VII) Fraction II consisted mainly of **8**, and recryst from H_2O furnished 2 9 g of the pure sample The mother liquor, consisting of a mixture of monogalloylglucoses, was repeatedly chromatographed over Sephadex LH-20 and Bondapak C_{18}/Porasil B with H_2O to give **10** (100 mg) and **9** (32 mg) Further CC of fraction IV over Sephadex LH-20(EtOH) afforded four fractions Fraction IV-3 was chromatographed repeatedly over cellulose (2% HOAc), MCI-gel CHP 20P[H_2O–MeOH(1 0–3 2)] and Fuji-gel ODS G3[H_2O–MeOH(1 0–0 1)] to yield **12** (185 mg) and **11** (438 mg) Subsequent CC of fraction V over Sephadex LH-20 with EtOH furnished three fractions Fraction V-1 was chromatographed repeatedly over MCI-gel CHP 20P and Sephadex LH-20 with a variety of solvent systems to afford **2** (773 mg), **3** (194 mg) and **7** (149 mg) Repeated CC of fraction IV-2 over MCI-gel CHP 20P[H_2O–MeOH(1 0–1 4)] and Sephadex LH-20[H_2O–MeOH(2 3)] gave **14** (62 mg)

General procedure for enzymatic hydrolysis A soln of each sample (30–60 mg) in H_2O(8–15 ml) was treated with tannase at room temp for 20 min The reaction mixture was concd under red pres to dryness, and the residue treated with EtOH The EtOH-soluble portion was subjected to CC over Sephadex LH-20 Elution with EtOH afforded the hydrolysate and gallic acid

1-*O*-*Galloyl*-6-*O*-*cinnamoyl*-β-D-*glucose* (**1**) An off-white amorphous powder, $[\alpha]_D^{27}+3\,3°$ (Me_2CO, *c* 0 64) FDMS *m/z* 485 $[M+Na]^+$, 463 $[M+H]^+$, 170, 148 ^{1}H NMR (Me_2CO-d_6) δ 3 2–3 9 (4H, *m*, H-2, 3, 4, 5), 4 34 (1H, *dd*, $J=6$, 12 Hz, H-6), 4 57 (1H, *dd*, $J=2$, 12 Hz, H-6), 5 76 (1H, *d*, $J=8$ Hz, anomeric-H), 6.54, 7 68 (each 1H, *d*, $J=16$ Hz, olefinic-H), 7 19 (2H, *s*, galloyl-H), 7 3–7 8 (5H, *m*, aromatic-H) (Found C, 54 90, H, 5 21 $C_{22}H_{22}O_{11}\,H_2O$ requires C, 55 00, H, 5 04%)

Acid hydrolyses of **1** *and* **2** A soln of each sample (5 mg) in 5% aq H_2SO_4 (1 ml) was heated in a water bath for 4 hr The reaction mixture was neutralized with $BaCO_3$, filtered and concd under red pres The residue was directly analysed by TLC to detect gallic acid [silica gel, C_6H_6–HCO_2Et–HCO_2H (5 4 1), R_f 0 23], cinnamic acid [silica gel, C_6H_6–HCO_2Et–HCO_2H(5 4 1), R_f 0 80] and glucose [cellulose, *n*-BuOH–pyridine–H_2O (6 4 3), R_f 0 43]

6-*O*-*Cinnamoylglucose* (**1a**) Colourless needles (H_2O), mp 157–158°, $[\alpha]_D^{27}+25\,8°$ (MeOH *c* 0 33), ^{1}H NMR(Me_2CO-

d_6+D_2O): δ3.1–3.9 (4H, *m*, H-2, 3, 4, 5), 4.48 (1H, *dd*, *J*=5, 12 Hz, H-6), 4.54 (1H, *dd*, *J*=2, 12 Hz, H-6), 4.68 (1H, *d*, *J*=8 Hz, anomeric-H), 6.58, 7.72 (each 1H, *d*, *J*=16 Hz, olefinic-H), 7.4–7.8(5H, *m*, aromatic-H) (Found C, 58.03; H, 5.90 $C_{15}H_{18}O_7$ requires C, 58.06, H, 5.85%).

Alkaline hydrolysis of **1a** A soln of **1a** (15 mg) in 2% NaOMe–MeOH (7 ml) was left standing at room temp for 2 hr The reaction mixture was neutralized with Amberlite IR-120B (H^+ form), and products separated by CC over MCI-gel CHP 20P[H_2O–MeOH (2 3–0 1)], to give glucose and methyl cinnamate (2 mg) as colourless needles (*n*-hexane–benzene), mp 32–33°, [silica gel; C_6H_6, R_f 0.38]

1,2-*Di*-O-*galloyl*-6-*cinnamoyl*-β-D-*glucose* (**2**) An off-white amorphous powder, $[\alpha]_D^{20}$ −76.9° (Me_2CO, *c* 0.75), FDMS *m/z* 615 $[M+H]^+$, 170, 148 ^{1}H NMR (Me_2CO-d_6) δ3.5–4.1 (3H, *m*, H-3, 4, 5), 4.41 (1H, *dd*, *J*=6, 12 Hz, H-6), 4.62 (1H, *dd*, *J*=2, 12 Hz, H-6), 5.47 (1H, *t*, *J*=8 Hz, H-2), 6.00 (1H, *d*, *J*=8 Hz, anomeric-H), 6.58, 7.70 (each 1H, *d*, *J*=16 Hz, olefinic-H), 7.09, 7.10 (each 2H, *s*, galloyl-H), 7.3–7.8 (5H, *m*, aromatic-H) (Found C, 56.22, H, 4.72 $C_{29}H_{26}O_{15}$ 1/2H_2O requires C, 55.86, H, 4.36%)

1,2-*Di*-O-*galloyl*-6-O-p-*coumaroyl*-β-D-*glucose* (**3**) An off-white amorphous powder, $[\alpha]_D^{21}$ −68.7° (Me_2CO, *c* 0.95) FDMS *m/z* 631 $[M+H]^+$, 170, 164. ^{1}H NMR (Me_2CO-d_6) δ3.6–4.1 (3H, *m*, H-3, 4, 5), 4.39 (1H, *dd*, *J*=6, 12 Hz, H-6), 4.60 (1H, *dd*, *J*=2, 12 Hz, H-6), 5.28 (1H, *t*, *J*=8 Hz, H-2), 5.97 (1H, *d*, *J*=8 Hz, anomeric-H), 6.37, 7.65 (each 1H, *d*, *J*=16 Hz, olefinic-H), 6.89 (2H, *d*, *J*=8 Hz, p-coumaroyl H-2, 6); 7.11 (4H, *s*, galloyl-Hx2), 7.66 (2H, *d*, *J*=8 Hz, *p*-coumaroyl H-3, 5) (Found. C, 50.64, H, 4.71 $C_{29}H_{26}O_{16}$ 3H_2O requires. C, 50.88, H, 4.71%)

6-O-p-*Coumaroylglucose* (**3a**) Colourless needles (H_2O), mp 184–186°, $[\alpha]_D^{24}$ +30.1° (MeOH, *c* 0.72) FDMS *m/z* 326 $[M]^+$ ^{1}H NMR (Me_2CO-d_6+D_2O) δ3.2–4.6 (6H, *m*, H-2, 3, 4, 5, 6), 4.58 (2/3H, *d*, *J*=8 Hz, H-1), 5.16 (1/3H, *d*, *J*=4 Hz, H-1), 6.40, 7.66 (each 1H, *d*, *J*=16 Hz, olefinic-H), 6.91 (2H, *d*, *J*=8 Hz, *p*-coumaroyl H-3, 5), 7.56 (2H, *d*, *J*=8 Hz, *p*-coumaroyl H-2, 6) (Found C, 54.80, H, 5.61 $C_{15}H_{18}O_8$ requires C, 55.21, H, 5.56%)

Alkaline hydrolysis of **3a** A soln of **3a** (10 mg) in 2% NaOMe–MeOH (5 ml) was left standing at room temp for 2 hr Work-up as for **1a** furnished glucose and methyl *p*-coumaroate (2 mg) as colourless needles, mp 142–143°.

1,6-*Di*-O-*galloyl*-2-O-p-*coumaroyl*-β-D-*glucose* (**4**) Colourless needles (H_2O), mp 179–181°, $[\alpha]_D^{28}$ −112.8° (Me_2CO, *c* 0.53) FDMS *m/z* 631 $[M+H]^+$, 460 $[M+H-galloyl]^+$, 170, 164 ^{1}H NMR (Me_2CO-d_6) δ 3.6–4.0 (3H, *m*, H-3, 4, 5), 4.44 (1H, *dd*, *J*=4, 12 Hz, H-6), 4.58 (1H, *dd*, *J*=2, 12 Hz, H-6), 5.19 (1H, *t*, *J*=8 Hz, H-2), 5.92 (1H, *d*, *J*=8 Hz, anomeric-H), 6.32, 7.64 (each 1H, *d*, *J*=16 Hz, olefinic-H), 6.86 (2H, *d*, *J*=8 Hz, *p*-coumaroyl H-2, 6), 7.10, 7.15 (each 2H, *s*, galloyl-H), 7.52 (2H, *d*, *J*=8 Hz, *p*-coumaroyl H-3, 5) (Found C, 50.18, H, 4.63 $C_{29}H_{26}O_{16}$ 7/2H_2O requires· C, 50.22, H, 4.80%)

2-O-p-*Coumaroylglucose* (**4a**) Colourless needless (H_2O), mp 204–206°, $[\alpha]_D^{27}$ +32.8° (MeOH, *c* 0.3) ^{1}H NMR (Me_2CO-d_6+D_2O) δ3.4–4.0 (5H, *m*, H-3, 4, 5, 6), 4.62–4.88 (2H, *m*, H-1, 2), 6.38, 7.66 (each 1H, *d*, *J*=16 Hz, olefinic-H), 6.90 (2H, *d*, *J*=8 Hz, *p*-coumaroyl H-3, 5), 7.55 (2H, *d*, *J*=8 Hz, *p*-coumaroyl H-2, 6).

1,2-*Di*-O-*galloyl*-β-D-*glucose* (**11**) Colourless needles (H_2O), mp 169–170°, $[\alpha]_D^{17}$ −79.1° (Me_2CO, *c* 0.64) FDMS *m/z* 484 $[M]^+$, 314 $[M-galloyl]^+$, 170 ^{1}H NMR (Me_2CO-d_6) δ3.5–4.0 (5H, *m*, H-3, 4, 5, 6), 5.19 (1H, *t*, *J*=8 Hz, H-2), 6.91 (1H, *d*, *J*=8 Hz, anomeric-H), 7.07 (4H, *s*, galloyl-H) (Found. C, 46.50, H, 4.58 $C_{20}H_{20}O_{14}$ 2H_2O requires C, 46.16, H, 4.65%)

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