

PHENOLICS FROM *HYPERICUM GEMINIFLORUM*

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Key Word Index—*Hypericum geminiflorum*; Guttiferae; chalcone; heartwood; roots; 3,5,7,2',5'-pentahydroxy-flavan; 3,5-dimethoxy-4-hydroxy-1-*O*- β -D-glucoside; 3'-[γ -hydroxymethyl-(*Z*)- γ -methylallyl]-2',4',4-trihydroxychalcone 11'-*O*-ferulate; 3'-[γ -hydroxymethyl-(*Z*)- γ -methylallyl]-2',4',4-trihydroxychalcone 11'-*O*-coumarate; 3'-[γ -hydroxymethyl-(*E*)- γ -methylallyl]-2',4',4-trihydroxychalcone 11'-*O*-coumarate.

Abstract—Five new constituents were isolated from the heartwood and roots of *Hypericum geminiflorum*. The structures were characterized as (2*R*,3*R*)-3,5,7,2',5'-pentahydroxyflavan, 3,5-dimethoxy-4-hydroxy-1-*O*- β -D-glucoside, 3'-[γ -hydroxymethyl-(*Z*)- γ -methylallyl]-2',4',4-trihydroxychalcone 11'-*O*-ferulate, named gemichalcone A, 3'-[γ -hydroxymethyl-(*Z*)- γ -methylallyl]-2',4',4-trihydroxychalcone 11'-*O*-coumarate, named gemichalcone B, and 3'-[γ -hydroxymethyl-(*E*)- γ -methylallyl]-2',4',4-trihydroxychalcone 11'-*O*-coumarate, named isogemichalcone B. Copyright © 1997 Elsevier Science Ltd

INTRODUCTION

Studies on the constituents of *Hypericum* species have been reported [1]. However, no work has been done on the constituents of *H. geminiflorum* and as part of a study of the bioactive principles of Formosan plants, its constituents were studied. Five new constituents, (2*R*,3*R*)-3,5,7,2',5'-pentahydroxyflavan (**1**), 3,5-dimethoxy-4-hydroxy-1-*O*- β -D-glucoside (**2**), gemichalcone A (**3**), gemichalcone B (**4**) and isogemichalcone B (**5**), and eight known compounds, 2,6-dimethoxy-*p*-benzoquinone, β -sitosterol, betulinic acid, 1,5-dihydroxy-6-methoxyxanthone, β -sitosterol-3-*O*- β -D-glucoside, cycloartocarpin [2], cudraflavone A [3] and isobavachalcone [4], were isolated and characterized from the roots of this species. In this paper, we report on the structure characterization of these five new compounds.

RESULTS AND DISCUSSIONS

Compound **1**, C₁₅H₁₄O₆, showed UV absorption maxima characteristic of flavans [5]. The present of a bathochromic shift with NaOMe in the UV spectrum suggested that it was a 7-hydroxylated flavan [5]. Its IR spectrum showed the present of absorptions at 3400 cm⁻¹ (OH) and 1600 cm⁻¹ (C=C) but had no absorptions for any type of carbonyl groups. The ¹H

NMR spectrum of **1** indicated three benzylic proton signals at δ 3.41 (1H, *dd*, *J* = 16.0, 4.4 Hz, H-4), 3.55 (1H, *dd*, *J* = 16.0, 3.2 Hz, H-4) and 5.37 (1H, *brs*, H-2), a -CHOH signal at δ 4.72 (*brs*, H-3), a *meta*-coupled proton system at δ 6.67 (*d*, *J* = 2.0 Hz, H-6) and 6.70 (*d*, *J* = 2.0 Hz, H-8) and three aromatic proton signals at δ 7.27 (*d*, *J* = 8.0 Hz), 7.34 (*dd*, *J* = 8.0, 1.6 Hz) and 7.92 (*d*, *J* = 1.6 Hz) [5, 6]. Because of the absence of a bathochromic shift with NaOAc-H₃BO₃ in the UV spectrum, the above three aromatic proton signals at δ 7.27, 7.34 and 7.92 were assigned to H-3', H-4' and H-6', respectively. The EI-mass spectrum of **1** showed a [M]⁺ at *m/z* 290 and significant peaks at *m/z* 272 [M-H₂O]⁺, 152 and 139 (base peak) [6]. All the above evidence clearly indicated that **1** is a 3,5,7,2',5'-pentahydroxyflavan.

The ¹³C NMR spectrum of **1** (Table 1) was assigned by ¹H-decoupled spectra, DEPT pulse sequence and comparison of chemical shifts with those of corresponding data for (-)-epicatechin and 2',5'-dimethoxyflavone [7]. Based on the similar coupling effect between H-4, H-3 and H-2 to those of corresponding protons of 3,5,7,3',5'-pentahydroxyflavan [5] in the ¹H NMR spectrum and identical chemical shifts of C-2, C-3, C-4 and C-1' to those of corresponding carbons of (-)-epicatechin in ¹³C NMR spectrum (Table 1), the relative stereochemistry at C-2 and C-3 of **1** were assigned as (2*R*,3*R*).

Compound **2**, C₁₄H₂₀O₉, showed hydroxyl (3350 cm⁻¹) and aromatic (1610 cm⁻¹) absorptions in its IR spectrum. The UV spectrum showed maximum

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Table 1. ^{13}C NMR spectral data of compounds **1** and **3–5**

C	1*	C	3†‡	3a†	4†‡	5†‡	C	3†‡	3a†	4†‡	5†‡
2	80.0	1	128.2	128.2	128.2	127.7	7'	22.8	22.7	22.7	22.7
3	66.9	2	132.4	132.4	132.4	132.4	8'	129.1	125.8	129.0	128.3
4	29.6	3	117.4	117.5	117.4	117.4	9'	131.7	136.5	131.8	131.9
4a	100.2	4	161.7	161.7	161.7	161.7	10'	22.3	22.8	22.3	14.9
5	158.6	5	117.4	117.5	117.4	117.4	11'	64.2	62.5	64.2	70.9
6	96.6	6	132.4	132.4	132.4	132.4	1''	128.2		127.2	127.7
7	158.6	α	119.0	119.0	119.0	119.1	2''	112.0		131.6	131.6
8	95.8	β	145.7	145.7	145.7	145.7	3''	149.4		117.3	117.3
8a	157.6	CO	193.7	193.7	193.7	193.7	4''	150.7		161.2	161.2
1'	132.1	1'	115.7	115.8	115.7	115.8	5''	116.7		117.3	117.3
2'	146.7	2'	165.7	165.7	165.7	165.9	6''	124.6		131.6	131.6
3'	116.3	3'	115.0	114.9	115.1	115.1	7''	146.3		146.0	146.0
4'	119.3	4'	163.5	163.7	163.4	163.6	8''	116.6		116.3	116.3
5'	146.8	5'	108.8	109.2	108.7	108.7	9''	168.3		168.3	170.2
6'	116.0	6'	131.2	131.2	131.2	131.2	OMe	56.3			

Numbers of directly attached protons to individual carbons verified by DEPT pulse sequence.

* Measured in pyridine- d_5 .

† Measured in $(\text{CD}_3)_2\text{CO}$.

‡ Signals obtained by ^1H - ^1H COSY, HMQC, HMBC and NOESY techniques.

absorption at 282, 402 and 446 (sh) nm. The ^1H NMR spectrum of **2** indicated two methoxyl signals at δ 3.41 (s), an anomeric proton signal at δ 5.37 (d, $J = 7.6$ Hz), two aromatic proton signals at δ 6.92 (s, H-2 and H-6) and a phenolic hydroxyl signal at δ 10.3. The ^{13}C NMR spectrum (see Experimental) showed two methoxyl signals at δ 56.3 and signals due to β -glucopyranose (δ 103.8, 75.1, 71.6, 79.0 and 62.6). Based on the above evidence, **2** was concluded to be 3,5-dimethoxy-4-hydroxy-1-*O*- β -D-glucoside or 3,5-dimethoxy-1-hydroxy-4-*O*- β -glucoside [8]. Acidic hydrolysis yielded glucose as detected by TLC.

Alkaline hydrolysis of permethylated **2** yielded **2a**, identified by UV, IR, mass spectral, NMR and comparison of mmp and spectral data with those of authentic 3,4,5-trimethoxyphenol. Based on the above evidence, **2** was characterized as 3,5-dimethoxy-1-hydroxy-4-*O*- β -D-glucoside (**2**). The EI-mass spectrum of **2** show a $[\text{M}]^+$ at m/z 332 and significant peaks at m/z 170, 155, 140 and 109. It also supported the characterization of **2** as 3,5-dimethoxy-1-hydroxy-4-*O*- β -D-glucoside (**2**).

Compound **3**, $\text{C}_{30}\text{H}_{28}\text{O}_8$, had similar UV maxima to 2',4',4'-trihydroxychalcone [9]. The IR spectrum showed an ester absorption band at 1720 cm^{-1} . The ^1H NMR spectrum of **3** showed a vinyl methyl at δ 1.74 (s), a methylene signal at δ 3.49 (d, $J = 7.2$ Hz), a singlet of OCH_3 at δ 4.96, an olefinic proton signal at δ 5.59 (t, $J = 7.2$ Hz) [10], a methoxyl group at δ 3.91, a 1,4-disubstituted phenyl moiety [δ 6.93 (2H, dd, $J = 8.5, 2.0$ Hz, H-3 and H-5) and δ 7.73 (2H, dd, $J = 8.5, 2.0$ Hz, H-2 and H-6)], a 1',2',3',4'-tetra-substituted phenyl moiety [δ 6.51 (1H, d, $J = 8.8$ Hz, H-5') and δ 8.00 (1H, d, $J = 8.8$ Hz, H-6')], α and β proton signals in a chalcone skeleton [δ 7.75 (1H, d, $J = 15.6$ Hz, H- α) and δ 7.84 (1H, d, $J = 15.6$ Hz, H- β)] [11], ABX-type signals at δ 6.87 (1H, d, $J = 8.4$

Hz, H-5''), δ 7.16 (1H, dd, $J = 8.4, 2.0$ Hz, H-6'') and δ 7.36 (1H, d, $J = 2.0$ Hz, H-2''), a cinnamoyl moiety by the presence of doublets at δ 6.43 (H-8'') and δ 7.62 (H-7'') ($J = 15.9$ Hz) [12], and a hydrogen-bonded hydroxyl group [δ 14.07 (1H, s, C-2'-OH)]. Based on the above evidence and the absence of a bathochromic shift induced by AlCl_3 , **3** was concluded to be a 3''-methylated 3'',4''-dioxxygenated or 4''-methoxylated 3'',4''-dioxxygenated cinnamoyl ester of a 3-substituted 2',4',4'-trihydroxychalcone.

Alkaline hydrolysis of **3** afforded ferulic acid, identified by comparison of mmp and spectral data with those of authentic ferulic acid and **3a**. Compound **3a**, $\text{C}_{20}\text{H}_{20}\text{O}_5$, showed similar UV maxima and bathochromic shifts induced by NaOAc, NaOMe, and AlCl_3 to **3** in its UV spectrum. The IR spectrum indicated hydroxyl and chelated carbonyl group absorptions at 3350 and 1630 cm^{-1} but the absence of an ester absorption band. The ^1H NMR spectrum of **3a** indicated the presence of a γ -hydroxymethyl, γ -methylallyl moiety [10] and a 2',4',4'-trihydroxychalcone moiety but the absence of a 3'',4''-dioxxygenated cinnamoyl moiety. Based on the above evidence and the absence of a bathochromic shift induced by AlCl_3 in the UV spectrum, **3a** was characterized as 3'-[γ -hydroxymethyl-(Z)- γ -methylallyl]-2',4',4'-trihydroxychalcone (**3a**). The ^{13}C NMR spectrum (Table 1) was assigned by ^1H -decoupling spectra, DEPT pulse sequence and comparison of chemical shifts with those of corresponding data for norachalcone A [13], broussoschalcone B [11], cabenegrin A-I [10] and the literature [14]. The ^{13}C NMR spectrum and mass spectrum of **3a** also supported its structural assignment. The chemical shift values of C-11' and H-11' of **3** were both downfield in comparison with those of the corresponding signals for **3a** (Table 1 and Experimental). This indicated that the cinnamoyl

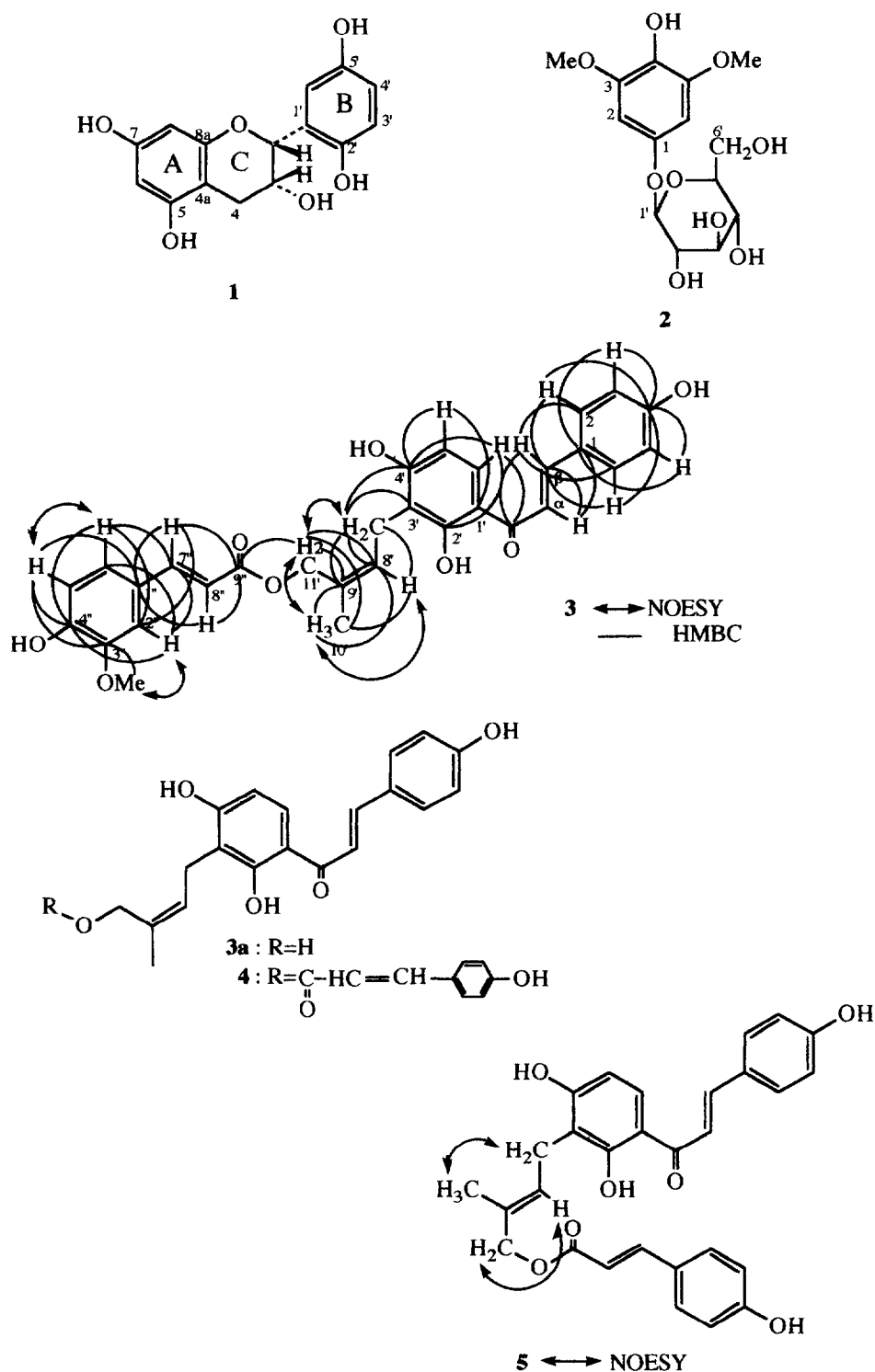


Fig. 1.

moiety was linked to C-11'-OH. In addition to the above evidence, the NOESY spectrum showed intense interactions between H-2'' and OMe. Therefore, gemichalcone A (3) was characterized as 3. The ^{13}C NMR spectrum of 3 (Table 1) was assigned by ^1H -decoupled

spectra, DEPT pulse sequence, ^1H - ^1H COSY, HMQC, NOESY, HMBC and comparison with corresponding data for 3a and in the literature [12].

Compound 4, $\text{C}_{29}\text{H}_{26}\text{O}_7$, had similar UV and IR spectra to those of 3, suggesting that 4 was also an

ester of a 2',4',4-trihydroxychalcone derivative. The ^1H NMR spectrum showed identical proton signals to those of corresponding signals for **3** except for presence of an additional 1'',4''-disubstituted phenyl moiety, δ 6.90 (2H, *dd*, $J = 8.8, 2.4$ Hz, H-3'' and H-5'') and δ 7.57 (2H, *dd*, $J = 8.8, 2.4$ Hz, H-2'' and H-6'') and the absence of the ABX-type proton signals. Based on the above evidence and the absence of a bathochromic shift induced by AlCl_3 , **4** was concluded to be a 4''-monooxygenated cinnamoyl ester of a 3-substituted 2',4',4-trihydroxychalcone.

Alkaline hydrolysis of **4** afforded coumaric acid (*p*-hydroxycinnamic acid) and **3a**, identified by comparison of mmp and spectral data with those of authentic samples, respectively. The chemical shift values of C-11' and H-11' in **4** were also downfield in comparison with the corresponding signals for **3a** (Table 1 and Experimental). This indicated that the cinnamoyl moiety was linked to C-11'-OH. Therefore, gemichalcone **B** (**4**) was characterized as **4**. The ^{13}C NMR spectrum of **4** was assigned by ^1H -decoupled spectra, DEPT pulse sequence, 2D spectra and comparison with those of corresponding data for **3**. The characterization of **4** was also supported by its ^{13}C NMR spectrum, mass spectrum and 2D spectra.

Compound **5**, $\text{C}_{29}\text{H}_{26}\text{O}_7$, gave identical UV, IR and mass spectra to those of **4**. The ^1H NMR spectrum showed identical proton signals to those of corresponding signals for **4**, except for the chemical shift values of H-8' and H-10', and H-11' which were shifted downfield and highfield, respectively, compared with the corresponding signals for **4**. In addition to the above evidence, the NOESY spectrum showed intense interactions between H-7' and H-10', and H-8' and H-11'. Therefore, isogemichalcone **B** (**5**) was characterized as **5**. The ^{13}C NMR spectrum was assigned by ^1H -decoupling spectra, DEPT pulse sequence, 2D spectra and literature [10] and comparison with the corresponding data for **4**. The ^{13}C NMR spectrum of **5** showed identical chemical shifts to those of the corresponding carbon signals for **4**, except for the chemical shifts of C-10' and C-11', which were highfield and lowfield, respectively, compared with **4**. This clearly indicated that the vinyl methyl of **3**, **3a** and **4**, and **5** were assigned to (*Z*)-Me and (*E*)-Me, attached to C-8', respectively [14].

EXPERIMENTAL

Plant material, extraction and isolation. Plants of *H. geminiflorum* Hemsl. were collected at Ping Tung Hsiang, Taiwan, during November 1993 and a voucher specimen is deposited in the authors' laboratory. Heartwood (aerial part, 13 kg) and roots (3 kg) were chipped and extracted with MeOH and Me_2CO , successively. The MeOH extract was subjected to chromatography on a silica gel column. Elution with CHCl_3 -EtOAc (9:1) yielded 2,6-dimethoxy-*p*-benzoquinone and 1,5-dihydroxy-6-methoxyxanthone, elution with CHCl_3 -EtOAc-MeOH (8.5:0.5:1) yielded

β -sitosterol and 3,5,7,2',5'-pentahydroxyflavan (**1**) and elution with CHCl_3 -MeOH (9:1) yielded β -sitosterol-3-*O*- β -D-glucoside and 3,5-dimethoxy-4-hydroxy-1-*O*- β -D-glucoside (**2**). The Me_2CO extract was also subjected to chromatography on a silica gel column. Elution with CHCl_3 yielded betulinic acid, elution with hexane- CHCl_3 -EtOAc (4.5:1:1) yielded fr. A, elution with CHCl_3 -MeOH (9:1) yielded isobavachalcone [**4**], elution with hexane- CHCl_3 - Me_2CO -MeOH (1:8:1:0.2) yielded gemichalcone **A** (**3**) and elution with hexane- CHCl_3 - Me_2CO -MeOH (1:7.3:1.5:0.2) yielded frs **B** and **C**. Frs **A**-**C** were further subjected to chromatography on Sephadex LH-20. Elution of fr. A with MeOH yielded cycloartocarpin [**2**] and cudraflavone **A** [**3**], elution of fr. B with MeOH yielded gemichalcone **B** (**4**) and elution of fr. C with MeOH yielded isogemichalcone **B** (**5**) and β -sitosterol-3-*O*- β -D-glucoside. Characterization of known compounds was achieved by spectral methods.

Compound 1. Red needles (Me_2CO), mp 224° . $[\alpha]_D^{23} -54^\circ$ (c 0.05, MeOH). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 220 (4.68), 278 (3.97), 405 (3.54); + NaOMe: 227, 298; + NaOAc- H_3BO_3 : unchanged. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3400, 1600. EIMS (direct inlet) 70 eV, m/z (rel. int.): 290 $[\text{M}]^+$ (17), 152 (37), 139 (100), 123 (41). ^1H NMR (pyridine- d_5): see text. ^{13}C NMR (pyridine- d_5): Table 1. HRMS: calc. for $\text{C}_{15}\text{H}_{14}\text{O}_6$, 290.0790; found, 290.0813.

Compound 2. Powder (pyridine), mp 238° . UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 282 (3.89), 402 (3.34). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3350, 1610. EIMS (direct inlet) 70 eV, m/z (rel. int.): 332 $[\text{M}]^+$ (2), 170 (100), 155 (41), 140 (42), 109 (11). ^1H NMR (pyridine- d_5): see text. ^{13}C NMR (pyridine- d_5): δ 56.2 (OMe $\times 2$), 62.6 (C-6'), 71.6 (C-4'), 75.1 (C-2'), 78.7 (C-3'), 79.0 (C-5'), 96.6 (C-2 and C-6), 103.8 (C-1'), 132.8 (C-4), 149.3 (C-3 and C-5). HRMS: calc. for $\text{C}_{14}\text{H}_{20}\text{O}_9$, 322.1107; found, 322.1095. Acid hydrolysis (2 N HCl-MeOH) of **2** yielded glucose identified by PC, R_f 0.21 (*n*-BuOH-HOAc- H_2O , 4:1:2).

3,4,5-Trimethoxyphenol 2a. Compound **2** (20 mg) in dry Me_2CO (10 ml) was refluxed over dry K_2CO_3 (0.5 g) with dry Me_2SO_4 (5 ml) for 6 hr. The product was refluxed with 5% KOH in MeOH (10 ml) and yielded **2a**, 146–148°. Mmp, IR, NMR and MS identical to authentic compound.

Compound 3. Yellow needles (MeOH), mp 106° . UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 225 (sh) (4.52), 344 (4.56), 360 (sh) (4.52); + NaOMe: 207, 405; + NaOAc: 220, 344, 400; + AlCl_3 : unchanged. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3350, 1720, 1635. EIMS (direct inlet) 70 eV, m/z (rel. int.): 322 $[\text{340}-\text{H}_2\text{O}]^+$ (56), 307 $[\text{322}-15]^+$ (20), 203 $[\text{322}-120+\text{H}]^+$ (42), 194 $[\text{M}-322]^+$ (100), 187 $[\text{307}-120]^+$ (57), 174 $[\text{322}-147-\text{H}]^+$ (22), 147 (26), 120 (45), 107 (31). FAB-MS (pos. mode) m/z : 517 $[\text{M}+1]^+$ (0.4), 307 (8), 289 (5), 155 (28), 154 (100), 136 (87), 120 (17), 107 (31). ^1H NMR (acetone- d_6): see text. ^{13}C NMR (acetone- d_6): Table 1.

Compound 3a and ferulic acid. **3** (20 mg) was sapon-

ified as described for **2** to yield **3a** and ferulic acid, mp 166–167° (mmp, IR, NMR and MS identical to authentic ferulic acid). Compound **3a**. Yellow needles (MeOH), mp 146°. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 225 (sh) (4.46), 281 (3.92), 362 (3.87); + NaOMe: 212, 415; + NaOAc: 217, 276 (sh), 405; + AlCl₃: unchanged. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3 350, 1 630. EIMS (direct inlet) 70 eV, m/z (rel. int.): 340 [M]⁺ (14), 322 [M - H₂O]⁺ (40), 307 (37), 203 (60), 147 (45), 119 (37), 107 (34). ¹H NMR (acetone-*d*₆): δ 1.73 (3H, *s*, C10'-Me), 3.46 (2H, *d*, *J* = 7.2 Hz, H-7'), 4.23 (2H, *s*, H-11'), 5.36 (1H, *t*, *J* = 7.2 Hz, H-8'), 6.51 (1H, *d*, *J* = 8.8 Hz, H-5'), 6.93 (2H, *d*, *J* = 8.4 Hz, H-3 and H-5), 7.74 (2H, *d*, *J* = 8.4 Hz, H-2 and H-6), 7.76 (1H, *d*, *J* = 15.6 Hz, H- α), 7.84 (1H, *d*, *J* = 15.6 Hz, H- β), 8.0 (1H, *d*, *J* = 8.8 Hz, H-6'), 14.13 (1H, *s*, C2'-OH). ¹³C NMR (acetone-*d*₆): Table 1 HRMS: calc. for C₂₀H₂₀O₅, 340.1311; found, 340.1297.

Compound 4. Yellow needles (MeOH), mp 140°. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 212 (4.52), 221 (sh) (4.45), 317 (4.56), 362 (4.43); + NaOMe: 210, 236 (sh), 363, 430; + NaOAc: 221, 315, 398; + AlCl₃: unchanged. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3 250, 1 720, 1 635, 1 610. EIMS (direct inlet) 70 eV, m/z (rel. int.): 322 (52), 307 (16), 203 (43), 187 (55), 174 (22), 164 (9), 147 (24), 120 (100), 119 (34), 107 (16). FAB-MS (pos. mode) m/z : 487 [M + 1]⁻ (0.5), 391 (5), 307 (0.1), 289 (0.2), 155 (28), 154 (100), 136 (84), 120 (16), 107 (29). ¹H NMR (acetone-*d*₆): δ 1.63 (3H, *s*, C10'-Me), 3.38 (2H, *d*, *J* = 7.6 Hz, H-7'), 4.84 (2H, *s*, H-11'), 5.45 (1H, *m*, H-8'), 6.27 (1H, *d*, *J* = 15.9 Hz, H-8''), 6.43 (1H, *d*, *J* = 8.9 Hz, H-5'), 6.80 (2H, *dd*, *J* = 8.7, 2.4 Hz, H-3 and H-5), 6.90 (2H, *dd*, *J* = 8.6, 2.0 Hz, H-3'' and H-5''), 7.51 (1H, *d*, *J* = 15.9 Hz, H-7''), 7.57 (2H, *dd*, *J* = 8.6, 2.0 Hz, H-2'' and H-6''), 7.60 (2H, *dd*, *J* = 8.7, 2.4 Hz, H-2 and H-6), 7.62 (1H, *d*, *J* = 15.3 Hz, H- α), 7.71 (1H, *d*, *J* = 15.3 Hz, H- β), 7.78 (1H, *d*, *J* = 8.9 Hz, H-6'), 14.01 (1H, *s*, C2'-OH). ¹³C NMR (acetone-*d*₆): Table 1. Compound **4** (20 mg) was saponified as described for **2** to yield **3a** and *p*-coumaric acid, mp 210–211° (mmp, IR, NMR and MS identical to those of authentic *p*-coumaric acid).

Compound 5. Yellow granules (MeOH), mp 176°. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 225 (sh) (4.38), 313 (4.29), 365 (4.23); + NaOMe: 212, 360, 430; + NaOAc: 219, 315, 405; + AlCl₃: unchanged. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3 300, 1 720, 1 635, 1 610. EIMS (direct inlet) 70 eV, m/z (rel. int.): 322 (94), 307 (26), 203 (73), 187 (80), 147 (36), 120

(100), 119 (44), 107 (30). FAB-MS (pos. mode) m/z : 509 [M + Na]⁺ (0.7), 154 (19), 137 (27), 69 (100). ¹H NMR (acetone-*d*₆): δ 1.88 (3H, *s*, C10'-Me), 3.47 (2H, *d*, *J* = 7.2 Hz, H-7'), 4.55 (2H, *s*, H-11'), 5.68 (1H, *m*, H-8'), 6.36 (1H, *d*, *J* = 16.0 Hz, H-8''), 6.55 (1H, *d*, *J* = 8.8 Hz, H-5'), 6.88 (2H, *dd*, *J* = 8.4, 2.0 Hz, H-3'' and H-5''), 6.93 (2H, *dd*, *J* = 8.4, 2.0 Hz, H-3 and H-5), 7.55 (2H, *dd*, *J* = 8.4, 2.0 Hz, H-2'' and H-6''), 7.59 (1H, *d*, *J* = 16.0 Hz, H-8'), 7.74 (2H, *dd*, *J* = 8.4, 2.0 Hz, H-2 and H-6), 7.80 (1H, *d*, *J* = 16.0 Hz, H- α), 7.84 (1H, *d*, *J* = 16.0 Hz, H- β), 8.00 (1H, *d*, *J* = 8.8 Hz, H-6'), 14.07 (1H, *s*, C2'-OH); ¹³C NMR (acetone-*d*₆): Table 1.

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