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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.

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**, $C_{15}H_{14}O_6$, 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 -C*H*OH 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–H_3BO_3 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 $[M-H_2O]^+$, 152 and 139 (base peak) [6]. All the above evidence clearly indicated that **1** is a 3,5,7,2′,5′-pentahydroxyflavan.

The ^{13}C 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 ^{13}C NMR spectrum (Table 1), the relative stereochemistry at C-2 and C-3 of **1** were assigned as (2*R*,3*R*).

Compound **2**, $C_{14}H_{20}O_9$, 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 $(CD_3)_2CO$.
‡ 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 $[M]^+$ 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**, $C_{30}H_{28}O_8$, had similar UV maxima to 2′,4′,4-trihydroxychalcone [9]. The IR spectrum showed an ester absorption band at 1 720 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_2 at δ 4.96, an olefinic proton signal at 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′-tetrasubstituted phenyl moiety [δ 6.51 (1H, *d*, $J = 8.8$ Hz, H-5′) and 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″-dioxygenated or 4″-methoxylated 3″,4″-dioxygenated 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**, $C_{20}H_{20}O_5$, 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″-dioxygenated 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], broussochalcone 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

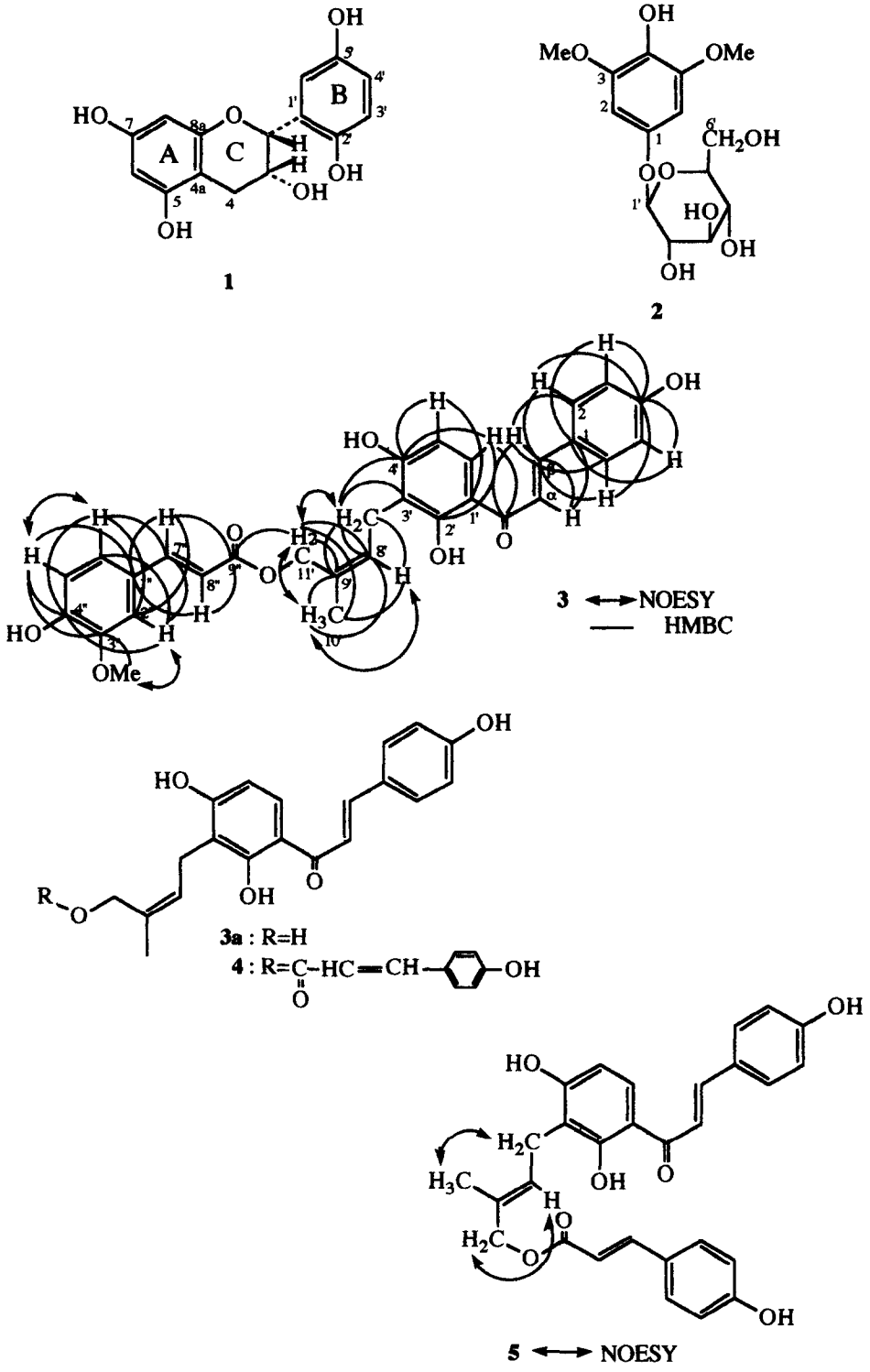

Fig. 1.

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

Compound **4**, $C_{29}H_{26}O_7$, 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 ^{1}H 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 ^{1}H-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**, $C_{29}H_{26}O_7$, gave identical UV, IR and mass spectra to those of **4**. The ^{1}H 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 ^{1}H-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 Hsieng, 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° (*c* 0.05, MeOH). UV λ_{max}^{MeOH} nm (log ε): 220 (4.68), 278 (3.97), 405 (3.54); +NaOMe: 227, 298; +NaOAc–H_3BO_3: unchanged. IR ν_{max}^{KBr} cm^{-1}: 3 400, 1 600. EIMS (direct inlet) 70 eV, *m/z* (rel. int.): 290 $[M]^+$ (17), 152 (37), 139 (100), 123 (41). ^{1}H NMR (pyridine-d_5): see text. ^{13}C NMR (pyridine-d_5): Table 1. HRMS: calc. for $C_{15}H_{14}O_6$, 290.0790; found, 290.0813.

Compound **2**. Powder (pyridine), mp 238°. UV λ_{max}^{MeOH} nm (log ε): 282 (3.89), 402 (3.34). IR ν_{max}^{KBr} cm^{-1}: 3 350, 1 610. EIMS (direct inlet) 70 eV, *m/z* (rel. int.): 332 $[M]^+$ (2), 170 (100), 155 (41). 140 (42), 109 (11). ^{1}H NMR (pyridine-d_5): see text. ^{13}C NMR (pyridine-d_5): δ 56.2 (OMe × 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 $C_{14}H_{20}O_9$, 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 λ_{max}^{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 ν_{max}^{KBr} cm^{-1}: 3 350, 1 720, 1 635. EIMS (direct inlet) 70 eV, *m/z* (rel. int.): 322 $[340-H_2O]^+$ (56), 307 $[322-15]^+$ (20), 203 $[322-120+H]^+$ (42), 194 $[M-322]^+$ (100), 187 $[307-120]^+$ (57), 174 $[322-147-H]^+$ (22), 147 (26), 120 (45), 107 (31). FAB-MS (pos. mode) *m/z*: 517 $[M+1]^+$ (0.4), 307 (8), 289 (5), 155 (28), 154 (100), 136 (87), 120 (17), 107 (31). ^{1}H 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 λ_{max}^{MeOH} nm (log ε): 225 (sh) (4.46), 281 (3.92), 362 (3.87); +NaOMe: 212, 415; +NaOAc: 217, 276 (sh), 405; +$AlCl_3$: unchanged. IR ν_{max}^{KBr} cm^{-1}: 3350, 1630. EIMS (direct inlet) 70 eV, *m/z* (rel. int.): 340 $[M]^+$ (14), 322 $[M-H_2O]^+$ (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). ^{13}C NMR (acetone-d_6): Table 1 HRMS: calc. for $C_{20}H_{20}O_5$, 340.1311; found, 340.1297.

Compound **4**. Yellow needles (MeOH), mp 140°. UV λ_{max}^{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; +$AlCl_3$: unchanged. IR ν_{max}^{KBr} cm^{-1}: 3250, 1720, 1635, 1610. 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). ^{13}C 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 λ_{max}^{MeOH} nm (log ε): 225 (sh) (4.38), 313 (4.29), 365 (4.23); +NaOMe: 212, 360, 430; +NaOAc: 219, 315, 405; +$AlCl_3$: unchanged. IR ν_{max}^{KBr} cm^{-1}: 3300, 1720, 1635, 1610. 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); ^{13}C NMR (acetone-d_6): Table 1.

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