New Salicylic Acid and Isoflavone Derivatives from *Flemingia paniculata*

M. Mukhlesur Rahman,[†] Satyajit D. Sarker,[‡] Maureen Byres,[‡] and Alexander I. Gray*,[†]

Phytochemistry Research Laboratory, Department of Pharmaceutical Sciences, University of Strathclyde, SIBS Building, 27 Taylor Street, Glasgow G4 0NR, Scotland, U.K., and Phytopharmaceutical Research Laboratory, School of Pharmacy, The Robert Gordon University, Schoolhill, Aberdeen AB10 1FR, Scotland, U.K.

A new salicylic acid derivative, 2-carboxy-3-(2-hydroxypropanyl)phenol (**1**), and four new isoflavones, 5,7,4′-trihydroxy-8-(1,1-dimethylprop-2-enyl)isoflavone (**2**), 5,7,2′,4′-tetrahydroxy-8-(1,1-dimethylprop-2-enyl)-isoflavone (**3**), 5,2′,4′-trihydroxy-4′′,4′′,5′′(ξ)-trimethyl-4′′,5′′-dihydrofurano-(7,6,2′′,3′′)isoflavone (**4**), and 5,2′,4′-trihydroxy-7-(3-methylbut-2-enyloxy)isoflavone (**5**), were isolated from the stem bark of *Flemingia paniculata*. The structures of these compounds were established unambiguously by spectroscopic data interpretation. The biogenetic pathways to **1** and **2**−**4** have been postulated.

Flemingia paniculata Wall. (Leguminosae), an erect shrub attaining a height of 4−6 feet, is distributed widely in Bangladesh, India, Nepal, and other tropical countries.[1] While this species has never been investigated before, the genus *Flemingia* is known to produce chalcones,[2] isoflavonoids,[3,4] and flavanone[5] and flavonol glycosides.[6] As part of our recently initiated research project focusing on phytochemical investigation on Bangladeshi plants of the family Leguminosae, we now report on the isolation of a new salicylic acid derivative (**1**) and four new isoflavones (**2**−**5**) together with six known compounds from the stem bark of *F. paniculata.*

Results and Discussion

The stem bark of *F. paniculata* was extracted sequentially with petroleum ether (bp 60−80 °C), chloroform, and methanol. Vacuum-liquid chromatography (VLC) fractionation of the petroleum ether extract followed by preparative thin-layer chromatography yielded compounds **1**, β-sitosterol, and sitosterone. The molecular formula of **1** was established as $C_{10}H_{12}O_4$ from the molecular ion peak as *m/z* 196.0729 in the HREIMS. The mass spectrum showed the base peak at *m/z* 178 corresponding to the $[M - H_2O]^+$ ion, indicating the presence of a hydroxyl group in the molecule. The ^1H NMR spectrum of **1** (Table 1) showed three aromatic protons as an ABC system at δ 6.90 (br d, *J* = 8.4 Hz), 7.42 (dd, *J* = 8.4, 7.5 Hz), and 6.70 (dd, *J* = 7.5, 0.9 Hz), indicative of a trisubstituted benzene ring. The presence of a 2H doublet (δ 2.94, *J* = 7.6 Hz), a deshielded 1H multiplet (δ 4.74), and a 3H doublet (δ 1.55, *J* = 6.4 Hz) indicated the presence of a 2-hydroxypropanyl substituent on the benzene ring. The COSY spectrum showed the expected couplings among these protons. The presence of a 2-hydroxypropanyl substituent was supported further by the *J*-modulated ^{13}C NMR spectrum (Table 1), which exhibited signals for a methyl (δ 21.0, C-3′), a methylene (δ 34.9, C-1′), and an oxymethine (δ 76.3, C-2′) group. A sharp singlet at δ 11.04 in the ^1H NMR spectrum could be for either an aldehyde or a H-bonded hydroxyl group. However, the ^{13}C NMR data showed an oxygen-bearing quaternary carbon at δ 162.5 (C-1) rather than an aldehydic methine ($\sim\delta$ 190). The *J*-modulated ^{13}C NMR spectrum also supported the presence of one H-bonded carbox-

1
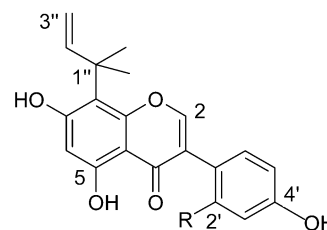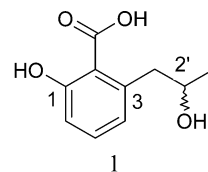
2 R = H

3 R = OH

4

5
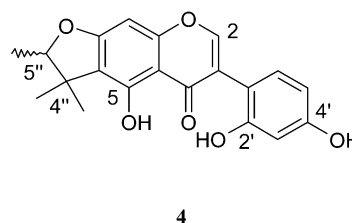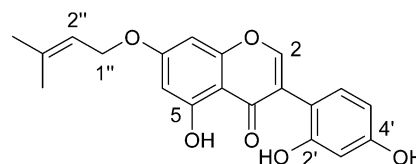
ylic acid unit (δ 170.2), three aromatic methine carbons (δ 116.5, 118.1, and 136.3), and a quaternary carbon at δ 139.6. Unambiguous assignments of all ^1H and ^{13}C signals were achieved using a combination of HC-COBI-dec and HMBC experiments (Table 1). In the HMBC spectrum, H-1′ showed a ^2J correlation to C-3 (δ 139.6) and ^3J connectivities to C-2 (δ 108.0) and C-4 (δ 118.1), confirming the

Table 1. ¹H (400 MHz), ¹³C (100 MHz), and HMBC (400 MHz) NMR Data of **1** in CDCl₃ (*J* in Hz, in parentheses)

position	δ_H	δ_C	HMBC ^2J	HMBC ^3J
1		162.5		
2		108.0		
3		139.6		
4	6.90 d (8.4)	118.1		C-2, C-6
5	7.42 dd (8.4, 7.6)	136.3		C-1, C-3
6	6.70 dd (7.6, 0.9)	116.5		C-2, C-4
1′	2.94 d (7.6)	34.9	C-2′, C-3	C-2, C-4, C-3′
2′	4.74 m	76.3		
3′	1.55 d (6.4)	21.0	C-2′	C-1′
HO-1	11.04 (s)		C-1	C-2, C-6
COOH		170.2		

attachment of the 2-hydroxypropanyl substituent at C-3 of the aromatic ring. The H-bonded hydroxyl proton showed correlations, ^2J to the oxygen-bearing aromatic quaternary (δ 162.5, C-1) and ^3J to the C-6 methine (δ 116.5) and the C-2 quaternary carbon (δ 108.0), which confirmed its attachment at C-1. The H-5 resonance was connected by the ^3J correlation to C-1 and C-3, while both the H-4 and H-6 signal showed a ^3J connectivity to the C-2 quaternary carbon (δ 108.0). The lower chemical shift of C-2 (α to carbonyl) and the presence of the H-bonded hydroxyl at C-1 confirmed the C-2 substituent to be the carboxylic acid. Thus, this compound was identified as 2-carboxy-3-(2-hydroxypropanyl)phenol (**1**, named flemingipanic acid), which is a new natural product. The two known compounds were identified as β-sitosterol and sitosterone by co-TLC with authentic samples as well as direct comparison of their ¹H NMR data with the literature.[7,8]

VLC fractionation of the chloroform extract followed by gel filtration over Sephadex LH-20 and preparative HPLC led to the isolation of compounds **2**−**5** and 3-hydroxy-4-methoxycinnamaldehyde, which was identified by comparing its spectral data with those of an authentic sample.[9] The molecular formula of **2** was established as $C_{20}H_{18}O_5$

from the molecular ion peak at *m/z* 338.1145 in the HREIMS. The ¹H NMR spectrum (Table 2) revealed the presence of a C-5 hydrogen-bonded hydroxyl at δ 14.06 and a downfield singlet at δ 8.24 for H-2, typical of an isoflavone nucleus. The spectrum also showed signals (δ 7.80, dt, *J* = 8.4, 1.9 Hz, and δ 7.33, dt, *J* = 8.4, 1.9 Hz) for a *para*-disubstituted benzene ring (ring B), together with a singlet at δ 6.78 for H-6 or H-8 of ring A. The signals at δ 5.19 (1H, d, *J* = 17.4 Hz), 5.09 (1H, d, *J* = 10.6 Hz), 6.62 (1H, dd, *J* = 17.4, 10.6 Hz), and 1.92 (6H, s) were indicative of a 1,1-dimethylprop-2-enyl side chain in the molecule. The *J*-modulated ¹³C NMR spectrum (Table 2) showed signals at δ 182.4, 153.2, 151.0, and 108.4, respectively, for a carbonyl, an oxymethine, an olefinic methine, and a vinyl methylene, together with signals for nine quaternary carbons (four being oxygenated) and five methines. The assignment of all ¹H and ¹³C NMR resonances as well as the confirmation of the attachment of the 1,1-dimethylprop-2-enyl side chain at C-8 was achieved by a combination of HC-COBI-dec and HMBC experiments (Table 2). In the HMBC experiment, H-2 showed correlations, ^2J to the quaternary at δ 123.3 (C-3) and ^3J to the carbonyl carbon at δ 182.4 (C-4) and oxygen-bearing quaternary at δ 157.2 (C-9). The proton of the C-5 hydroxyl group showed a ^2J correlation to the C-5 quaternary carbon (δ 161.9) and a ^3J correlation to the methine carbon at δ 101.3 (C-6) to which the aromatic singlet (δ 6.78) showed direct coupling. Thus, this signal at δ 6.78 must be for the H-6, which exhibited ^2J connectivities with the oxygen-bearing quaternary carbons at δ 161.9 (C-5) and 165.0 (C-7) and ^3J correlations to the quaternary carbons at δ 112.5 (C-8) and 106.7 (C-10). The methyl protons of the 1,1-dimethylprop-2-enyl side chain showed long-range (^3J) coupling with the C-8 quaternary carbon, which confirmed the attachment of the side chain at C-8. In ring B, both direct and long-range (^3J) correlations were shown by H-2′/H-6′ and H-3′/H-5′ with methine carbons at δ 131.3 (C-2′/6′) and 116.7 (C-3′/5′), respectively. The ^3J correlations from H-2′/H-6′

Table 2. ¹H, ¹³C, and HMBC NMR Data of **2** and **3** in C₅D₅N (*J* in Hz, in parentheses)

position	δ_H **2**	δ_H **3**	δ_C **2**	δ_C **3**	HMBC **2** ^2J	HMBC **2** ^3J	HMBC **3** ^2J	HMBC **3** ^3J
2	8.24 s	8.41 s	153.2	155.4	C-3	C-4, C-9	C-3	C-4, C-9
3			123.3	121.5				
4			182.4	182.7				
5			161.9	161.7				
6	6.78 s	6.75 s	101.3	101.4	C-5, C-7	C-8, C-10	C-5, C-7	C-8, C-10
7			165.0	164.9				
8			112.5	112.4				
9			157.2	157.2				
10			106.7	106.9				
1′			122.8	110.6				
2′	7.80 dt (8.4, 1.9)		131.3	158.7		C-3, C-4′		
3′	7.33 dt (8.4, 1.9)	7.01 d (2.2)	116.7	105.0		C-1′, C-5′	C-2′, C-4′	C-1′, C-5′
4′			159.6	161.1				
5′	7.33 dt (8.4, 1.9)	6.96 dd (8.4, 2.2) 7.63 d	116.7	108.2		C-1′, C-4′	C-4′	C-1′, C-3′
6′	7.80 dt (8.4, 1.9)	7.63 d (8.4)	131.3	133.6		C-3, C-4′		C-3, C-2′, C-4′
1″			41.9	41.9				
2″	6.62 dd (17.4, 10.6)	6.57 dd (17.4, 10.6)	151.0	151.0		Me-1″		Me-1″
3″	5.19 d (17.4) 5.09 d (10.6)	5.15 d (17.4) 5.05 d (10.6)	108.4	108.3	C-2″	C-1″	C-2″	C-1″
HO-5	14.06 brs	14.08 brs			C-5	C-6, C-10	C-5	C-6
Me-1″	1.92 s (2×Me)	1.87 s (2×Me)	26.0	30.0	C-1″	C-8, C-2″, Me-1″	C-1″	C-8, C-2″, Me-1″

Table 3. ^{1}H, ^{13}C, and HMBC NMR Data of **4** in C_5D_5N (*J* in Hz, in parentheses)

position	δ_H	δ_C	HMBC ^2J	^3J
2	8.34 s	155.6	C-3	C-4, C-9
3		122.2		
4		182.4		
5		165.6		
6		113.2		
7		164.4		
8	6.54 s	95.2	C-7	C-6, C-10
9		153.9		
10		107.2		
1′		110.4		
2′		158.7		
3′	7.09 d (2.3)	104.9	C-2′, C-4′	C-1′, C-5′
4′		161.1		
5′	6.95 dd (8.3, 2.3)	108.2	C-4′	C-1′, C-3′
6′	7.62 d (8.3)	133.8		C-3, C-2′, C-4′
4″		44.3		
5″	4.45 q (6.5)	91.3		Me-4″
HO-5	14.01 br s			
Me-4″	1.16 s	21.7	C-4″	C-6, C-5″, Me-4″
	1.39 s	25.9		
Me-5″	1.31 d (6.5)	14.7	C-5″	C-4″

Table 4. ^{1}H, ^{13}C, and HMBC NMR Data of **5** in C_5D_5N (*J* in Hz, in parentheses)

position	δ_H	δ_C	HMBC ^2J	^3J
2	8.20 s	156.3	C-3	C-4, C-9
3		122.4		
4		182.3		
5		163.6		
6	6.69 d (2.2)	99.5	C-5, C-7	C-8, C-10
7		165.4		
8	6.63 d (2.2)	93.8	C-7, C-9	C-6, C-10
9		158.7		
10		107.2		
1′		110.4		
2′		158.6		
3′	7.08 d (2.3)	104.8	C-2′, C-4′	C-1′, C-5′
4′		161.2		
5′	6.94 dd (8.3, 2.3)	108.2	C-4′	C-1′, C-3′
6′	7.60 d (8.3)	133.7		C-3, C-2′, C-4′
1″	4.66 d (6.7)	66.3	C-2″	C-7, C-3″
2″	5.54 t (6.7)	120.0		
3″		139.0		
HO-5	13.65 br s			
Me-3″	1.66 s	18.5	C-4″	C-2″
	1.70 s	26.0	C-3″	

to C-3 (δ 123.3) and C-4′ (δ 159.6) and from H-3′/5′ to C-1′ (δ 122.8) were observed in the HMBC spectrum. In the side chain, ^3J correlations from H-3″ to C-1″ (δ 41.9) and from H-2″ to Me-1″ (δ 26.0) were also observed. Thus the compound was identified unequivocally as 5,7,4′-trihydroxy-8-(1,1-dimethylprop-2-enyl)isoflavone (**2**), which is a new isoflavone.

The HREIMS of **3** showed a molecular ion peak at *m/z* 354.1098, corresponding to $C_{20}H_{18}O_6$, 16 amu more than **2**. The ^{1}H and ^{13}C NMR spectra (Table 2) of **3** were similar to those of **2** with the exception that signals (δH 7.01, 6.96, and 7.63, respectively, for H-3′, H-5′, and H-6′; δC 110.6, 158.7, 105.0, 161.1, 108.2, 133.6, respectively, for C-1′ to C-6′) for a 1,2,4-trisubstituted benzene ring (instead of *para*-disubstituted as in **2**) were present with hydroxyl substituents at C-2′ and C-4′. Like **2**, the HMBC experiment (Table 2) showed the same sort of correlations in ring A, ring C, and the side chain, and confirmed the placement of the 1,1-dimethylprop-2-enyl side chain at C-8. Thus, the compound was identified unambiguously as 5,7,2′,4′-tetrahydroxy-8-(1,1-dimethylprop-2-enyl)isoflavone (**3**), which is also new.

Compound **4** had the same molecular formula as **3** with the molecular ion peak at *m/z* 354.1103 in the HREIMS. Like **3**, the ^{1}H NMR spectrum (Table 3) of **4** showed signals at δ 14.01 (br s) for a H-bonded hydroxyl (at C-5) and δ 8.34 for H-2 characteristic of an isoflavone nucleus. The compound differed from **3** in not showing the vinyl protons of a 1,1-dimethylallyl group. Instead, the spectrum showed signals for an oxymethine (δ 4.45, q, *J* = 6.5 Hz) and three methyls (δ 1.31, d, *J* = 6.5 Hz; δ 1.16, s and 1.31, s). The *J*-modulated ^{13}C NMR spectrum (Table 3) showed a total of 20 carbons including a carbonyl (182.4), three methyls, five methines, and the remainder as quaternary carbons. The HMBC experiment (Table 3) played a key role in the assignments of protons and carbons as well as the placement of the dihydrofuran ring in the molecule. In ring B and ring C, the HMBC experiment showed the same types of correlations as were observed for **3**. The ring A aromatic singlet (δ 6.54) showed long-range connectivities with the oxygen-bearing quaternary carbons at δ 164.4 (C-7) and 153.9 (C-9). The latter carbon also correlated (^3J) with H-2, confirming its identity as C-9. Thus, the ring A aromatic proton must be at H-8, which had a strong correlation with

the quaternary carbons at δ 107.2 (C-10) and 113.2 (C-6). The C-6 carbon was also correlated to the methyl singlets (δ 1.16 and 1.31) by ^3J correlations. In the side chain, all three methyls coupled to the quaternary carbon C-4″ (δ 44.3). The H-5″ signal was connected to C-4″ methyls by ^3J correlations. These methyl protons also correlated (^3J) back to C-5″ (δ 91.3). The stereochemistry of the chiral center in position 5″ is, as yet, unknown. On the basis of this spectral evidence, the compound was identified conclusively as 5,2′,4′-trihydroxy-4″,4″,5″(ξ)-trimethyl-4″,5″-dihydrofurano-(7,6,2″,3″)isoflavone (**4**), a new dihydrofuranoisoflavone.

Compound **5** was obtained as a minor component in a mixture (1:2) with **2** by preparative HPLC. However, the ^{1}H and ^{13}C NMR spectra of the mixture were clear enough to distinguish signals originating from the minor compound **5** from those of **2**. The 2D NMR spectra (mainly COSY-90 and HMBC) were useful to assign all ^{1}H and ^{13}C NMR signals for **5**. Many of the ^{1}H and ^{13}C NMR signals (Table 4) were almost identical with those of 2′-hydroxygenistein except for the attachment of a prenyloxy (3-methylbut-2-enyloxy) side chain. The position of the attachment of the prenyloxy was determined by HMBC (Table 4), in which the prenyl oxymethylene (H-1″) correlated to C-7 of the isoflavone nucleus, which had further connectivities with H-6 and H-8. Accordingly, the compound was identified as 5,2′,4′-trihydroxy-7-(3-methylbut-2-enyloxy)isoflavone (**5**), a new prenyloxyisoflavone.

In addition, fractionation of the methanol extract followed by preparative HPLC yielded three known isoflavones, which were identified as genistein,[10,11] 2′-hydroxygenistein,[11,12] and genistein 7-*O*-β-D-glucoside by direct comparison of their physical and spectroscopic data with the respective literature data.

Isolation of an isoflavone with a 1,1-dimethylprop-2-enyl unit connected through C-6 was reported before only from *Moghania macrophylla*.[11] Isoflavones with dihydrofurano substituents have not been reported previously.

This series of hemiterpenoid-substituted isoflavones forms an interesting group of compounds that are biogenetically related to each other. The biosynthesis of **2** and **3** (Figure S1, Supporting Information) may arise from **5** via a Claisen-type rearrangement.[13,14] Alternatively, nucleophilic attack of the carbocation formed from DMAPP

on C-8 of an isoflavone is another possible route (a) to the biosynthesis of compounds **5** and **6** (Figure S1, Supporting Information). Acid-catalyzed cyclization of an isoflavone with 1,1-dimethylallyl group at C-6 is one possible route (b) of the biosynthesis of **4** (Figure S1, Supporting Information).[15]

The putative precursor for the biosynthesis of compound **1** is a polyketo ester that is formed from five acetate units (one acetyl co-A as starter plus four malonyl co-A as chain extension units).[16] The next step is the reduction of a carbonyl group to an alcohol by NADPH. This is followed by dehydration and subsequent aldol condensation to achieve a cyclic system. Enolization, hydrolysis of the latter cyclic compound, and reduction of the side chain carbonyl to alcohol by NADPH would form compound **1** (Figure S2, Supporting Information).

Experimental Section

General Experimental Procedures. Optical rotations were measured on a Perkin-Elmer polarimeter 341. UV spectra were obtained on a Unicam UV 4-100 UV/vis spectrophotometer in MeOH. IR spectra were recorded as dry film on a Mattson Galaxy 5000 FT-IR spectrometer. NMR spectra (both 1D and 2D) were obtained on a Bruker AMX-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer, using the residual solvent peaks as internal standard. J-modulated ^{13}C spectra were acquired with a relaxation time (d_1) of 6 s. HMBC spectra were optimized for a long-range J_{H-C} of 7 Hz ($d_6 = 0.07$ s), and the NOESY experiment was carried out with a mixing time of 0.6 s. HREIMS were recorded on a JEOL JMS-AX505HA double-focusing instrument at 70 eV. Vacuum-liquid chromatography (VLC) was carried out using Merck Si gel 60 H. The methanol extract was prefractionated using a Waters Sep-Pak cartridge (vac 35 cm^3, C$_{18}$, 10 g) under vacuum. Gel filtration was performed using Sephadex LH-20 (Sigma). The DIONEX preparative HPLC system coupled with photodiode detector (serial No. DIONEX UVD 240S) using a Phenomenex LUNA C$_{18}$ preparative column (250 × 21.2 mm; particle size 10 μm) was employed with a flow rate of 20 mL/min. The analytical JASCO HPLC gradient system (LG 1580-02) coupled with UV detector (model No. JASCO-UV 1575), utilizing a Discovery C$_{18}$ analytical column (250 × 4.6 mm; particle size 5 μm), was operated at a flow rate of 1 mL/min. Preparative TLC was carried out using Merck Si gel 60 PF$_{254}$ on glass plates (20 cm × 20 cm) at a thickness of 0.5 mm. TLC was conducted on normal-phase Merck Si gel 60 PF$_{254}$. Spots on TLC and preparative TLC plates were visualized under UV light (254 and 366 nm) and sprayed with 1% vanillin−H$_2$SO$_4$ followed by heating at 110 °C for 5−10 min.

Plant Material. The stem bark of *Flemingia paniculata* was collected from Modhupur Forest, Tangail, Bangladesh, in March 2000. The plant was identified by Dr. Toby Pennington, Royal Botanical Garden, Edinburgh, Scotland, where a voucher specimen (MMR-004/RBGE) has been deposited.

Extraction and Isolation. The dried, ground plant material (250 g) was sequentially extracted with petroleum ether (bp 60−80 °C), CHCl$_3$, and methanol in a Soxhlet apparatus. VLC fractionation of the petroleum ether extract (1.5 g) on Si gel was performed using the mobile phase petroleum ether, EtOAc, and MeOH in order of increasing polarity. The fraction eluting with 10% EtOAc in petroleum ether was further subjected to preparative TLC (15% EtOAc in petroleum ether) to yield **1** (3.2 mg) and β-sitosterol (12.2 mg). Recrystallization of the fraction eluted with 20% EtOAc in petroleum ether yielded sitosterone (14 mg).

The CHCl$_3$ extract (3.8 g) was fractionated by VLC over Si gel 60H using petroleum ether−EtOAc and EtOAc−MeOH mixtures of increasing polarity. The eluates were combined on the basis of TLC analysis. The VLC fraction eluting with 10% EtOAc in petroleum ether was further subjected to preparative TLC (15% EtOAc in petroleum ether) to yield **1**

(14 mg). The VLC fraction eluting with 25% EtOAc in petroleum ether was further subjected to gel filtration over Sephadex LH-20. Concentration of the eluate from the Sephadex column (100% CHCl$_3$−10% MeOH in CHCl$_3$) gave 3-hydroxy-4-methoxycinnamaldehyde (3.4 mg). The eluate (20−40% MeOH in CHCl$_3$) of the same Sephadex column was further subjected to preparative HPLC (developed with 70% MeOH in H$_2$O, isocratic, flow rate 20 mL/min) and yielded 5.4 mg of **3** and 5 mg as a mixture (2:1) of **2** and **5**, whereas compounds **2** (5 mg) and **3** (6.2 mg) were obtained from the same Sephadex column (50% MeOH in CHCl$_3$) followed by preparative TLC over Si gel PF$_{254}$ (15% EtOAc in toluene). Compound **3** (5.2 mg) was also isolated from the VLC fraction eluting with 30% EtOAc in petroleum ether followed by Sephadex column (20−50% MeOH in CHCl$_3$) and preparative HPLC (eluted with 70% MeOH in H$_2$O, isocratic, flow rate 20 mL/min). Sep-Pak fractions (40−60% MeOH in H$_2$O) of the MeOH extract (1.5 g) were further subjected to preparative HPLC (eluted with a linear gradient of 30−100% MeOH in H$_2$O in 50 min, 20 mL/min) to yield genistein (5.2 mg), 2′-hydroxygenistein (35 mg), and genistein7-O-β-D-glucoside (3.2 mg).

2-Carboxy-3-(2-hydroxypropanyl)phenol (1): white amorphous solid; $[\alpha]^{20}_D$ −79.8° (*c* 0.188); UV (MeOH) λ_{max} (log ϵ) 210 (4.21), 244 (3.50), 311 (3.43), 337 (sh) (2.82) nm; IR (film) ν_{max} 3113, 2981, 1673, 1620, 1583, 1466, 1364, 1294, 1283, 1167, 1119, 1051, 950, 785, 697, 626 cm^{-1}; ^{1}H and ^{13}C NMR (Table 1); EIMS 196 [M]$^+$ (4), 178 [M − H$_2$O]$^+$ (100), 161 (6), 160 (44), 135 (17), 134 (71), 132 (15), 121 (5), 107 (6), 106 (18), 105 (10), 104 (12), 103 (7); HREIMS *m/z* 196.0729 (calcd for C$_{10}$H$_{12}$O$_4$, 196.0736).

5,7,4′-Trihydroxy-8-(1,1-dimethylprop-2-enyl)isoflavone (2): yellow amorphous solid; UV (MeOH) λ_{max} (log ϵ) 203 (4.16), 265 (4.31), 331 (sh) (3.31) nm; IR (KBr) ν_{max} 3386, 2960, 2927, 1660, 1607, 1517, 1403, 1360, 1260, 1203, 1170, 1064, 1020, 888, 836 cm^{-1}; ^{1}H and ^{13}C NMR (Table 2); EIMS 338 [M]$^+$ (43), 337 (10), 324 (21), 323 [M − CH$_3$]$^+$ (100), 308 (9), 295 (9), 283 (11), 190 (7), 118 (5); HREIMS *m/z* 338.1145 (calcd for C$_{20}$H$_{18}$O$_5$, 338.1154).

5,7,2′,4′-Tetrahydroxy-8-(1,1-dimethylprop-2-enyl)isoflavone (3): yellow amorphous solid; UV (MeOH) λ_{max} (log ϵ) 205 (4.41), 265 (4.35), 336 (sh) (3.51) nm; IR (KBr) ν_{max} 3080, 2968, 2930, 1656,1617, 1554, 1509, 1462, 1407, 1362, 1308, 1267, 1208, 1118, 1058, 1013, 972, 901, 827, 590, 534 cm^{-1}; ^{1}H and ^{13}C NMR (Table 2); EIMS 354 [M]$^+$ (71), 340 (26), 339 [M − CH$_3$]$^+$ (100), 325 (31), 313 (28), 311 (21), 299 (18), 284 (51), 282 (19), 275 (15), 270 (26), 251 (17), 232 (22), 225 (17), 221 (18), 220 (16), 201 (20), 183 (16), 155 (24); HREIMS *m/z* 354.1098 (calcd for C$_{20}$H$_{18}$O$_6$, 354.1103).

5,2′,4′-Trihydroxy-4″,4″,5″(ξ)-trimethyl-4″,5″-dihydrofurano-(7,6,2″,3″)isoflavone (4): brown amorphous solid; $[\alpha]^{19}_D$ −181.82° (*c* 0.11, CHCl$_3$); UV (MeOH) λ_{max} (log ϵ) 207 (4.68), 264 (4.59), 308 (sh) (4.07), 339 (sh) (3.74) nm; IR (film) ν_{max} 3314, 2975, 1652, 1476, 1418, 1301, 1215, 1159, 1117, 1056, 972, 827, 755 cm^{-1}; ^{1}H and ^{13}C NMR (Table 3); EIMS 354 [M]$^+$ (43), 340 (24), 339 [M − CH$_3$]$^+$ (100), 337 (8), 325 (5), 323 (4), 311 (4), 283 (3), 221 (14), 219 (4), 177 (7), 161 (4), 135 (3), 119 (4), 105 (7); HREIMS *m/z* 354.1103 (calcd for C$_{20}$H$_{18}$O$_6$, 354.1103).

5,2′,4′-Trihydroxy-7-(3-methyl-but-2-enyloxy)isoflavone (5 + 2) (1:2): brown amorphous solid; ^{1}H and ^{13}C NMR (Table 4).

Supporting Information Available: Figures showing putative biogenetic pathways to **2**−**4** and to **1**. These materials are available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hooker, J. D. *The Flora of British India*; L. Reeve & Co.: London, 1879; Vol. 2.
(2) Subrahmanyam, K.; Rao, J. M.; Vemuri, V. S. S.; Babu, S. S.; Roy, C. P.; Rao, K. V. J.; Merlini, L. *Indian J. Chem. B* **1982**, *21*, 895−897.
(3) Chen, M.; Lou, S. Q.; Chen, J. H. *Phytochemistry* **1991**, *30*, 3842−3844.
(4) Rao, K. N.; Srimannarayana, G. *Phytochemistry* **1984**, *23*, 927−929, 1875.
(5) Rao, K. N.; Srimannarayana, G. *Phytochemistry* **1983**, *22*, 2287−2290.
(6) Rao, C. P.; Hanumaiah, T.; Vemuri, V. S. S.; Rao, K. V. J. *Phytochemistry* **1983**, *22*, 621−622.
(7) Kojima, H.; Sato, N.; Hatano, A.; Ogura, H. *Phytochemistry* **1990**, *29*, 2351−2355.
(8) Onocha, P. A.; Okorie D. A.; Connolly, J. D.; Rycroft, D. S. *Phytochemistry* **1995**, *40*, 1183−1189.
(9) Gibbons, S. Phytochemical Studies on the Flacourtiaceae and Simaroubaceae. Ph.D. Thesis, University of Strathclyde, Glasgow, U.K., 1994.
(10) Hosny, M.; Rosazza, J. P. N. *J. Nat. Prod.* **1999**, *62*, 1609−1612.
(11) Krishnamurty, H. G.; Prasad, J. S. *Phytochemistry* **1980**, *19*, 2797−2798.
(12) Watanabe, K.; Kinjo, J.; Nohara, T. *Chem. Pharm. Bull.* **1993**, *41*, 394−396.
(13) Murray, R. D. H.; Mendez, J.; Brown, S. A. *The Natural Coumarins−Occurrence, Chemistry and Biochemistry*; John Wiley & Sons: New York, 1982; pp 178−179.
(14) Gray, A. I.; Waterman, P. G. *Phytochemistry* **1978**, *17*, 845−864.
(15) Ollis, W. D. *Recent Developments in the Chemistry of Natural Phenolic Compounds*; Pergamon: Oxford, U.K., 1961; p 81.
(16) Dewick, P. M. *Medicinal Natural Products−A Biosynthetic Approach*, 2nd ed.; John Wiley & Sons: New York, 2002.