Prenylated Isoflavonoids from the Root Bark of *Erythrina vogelii*

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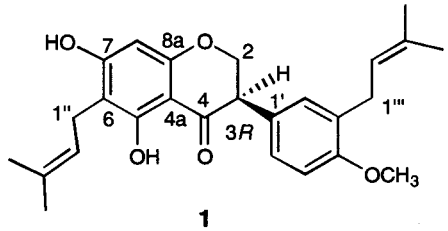
Four new prenylated isoflavonoids, vogelins D−G (**1**−**4**), were isolated from the CH_2Cl_2 extract of *Erythrina vogelii* root bark in addition to the known compounds isolupalbigenin (**5**), ficuisoflavone (**6**) , ulexone (**7**), isochandalon (**8**), and isoderrone (**9**). The structures **1**−**4** were elucidated by spectroscopic and chemical methods. The absolute configuration of compound **1** was determined on the basis of its CD spectrum. Possible biogenetic relationships among the *E. vogelii* isoflavonoids are briefly discussed.

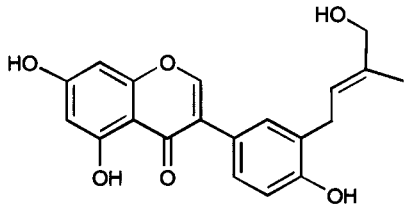
Continuing our studies on the traditional medicinal plants of Ivory Coast, the root bark of *Erythrina vogelii* Hook. f. (Leguminosae) was investigated. Recently, we have described three new prenylated isoflavonoids from this plant[1] and their antifungal activity against *Cladosporium cucumerinum* using a direct TLC bioautographic assay.[2,3] We report here the isolation and structure elucidation of four further prenylated isoflavonoids, vogelin D (**1**), vogelin E (**2**), vogelin F (**3**), and vogelin G (**4**), along with the known compounds isolupalbigenin (**5**),[4] ficuisoflavone (**6**),[5] ulexone A (**7**),[6] isochandalon (**8**),[7] and isoderrone (**9**).[8]

Compound **1** was isolated as an amorphous white powder. The UV spectra in MeOH and after addition of UV−vis shift reagents suggested an isoflavanone- or isoflavone-type structure.[9] The EIMS showed a molecular ion at *m/z* 422 $[M]^+$ and fragment ions at *m/z* 202 $[B_3]^+$ and 220 $[A_1]^+$ resulting from a retro-Diels−Alder fragmentation (RDA),[10] indicating the presence of a prenyl moiety and two hydroxyl groups on ring A and a second prenyl group with a methoxyl on ring B. The signals of a three-proton spin system δ 3.87 (H-3), 4.50 (H-2α), and 4.55 (H-2β) in the ^{1}H NMR spectrum were characteristic of a C-2 unsubstituted isoflavanone nucleus.[11] The substitution of ring A was confirmed by the presence of a chelated OH at δ 12.40 (OH-5), and after analysis of the HMBC spectra, the signal of the aromatic proton at δ 5.95 was attributed to the isolated proton H-8. The correlations observed in the HMBC experiment between the allylic methylene at δ 3.36 and the two oxygenated carbons at δ 161.3 (C-5) and 163.4 (C-7) showed the presence of a prenyl moiety at position C-6.

The ^{1}H NMR spectrum of **1** showed an ABX system at δ 6.81, 7.01, and 7.06, attributed to the aromatic protons at H-5′, H-2′, and H-6′, respectively. This hypothesis was confirmed by the COSY and HMBC data. The HMBC spectrum showed correlations between signals at δ 7.01 (H-2′) and 28.4 (C-1‴), suggesting that a second prenyl group is positioned at C-3′. Moreover, the NOESY spectrum showed correlations between the methoxyl group (δ 3.80) with H-5′ (δ 6.81) and with the protons of the prenyl group at δ 3.28 (H-1‴) and 5.25 (H-2‴), suggesting the presence of the methoxyl at C-4′. The absolute configuration at C-3 was determined using circular dichroism.[12] The 3*R* absolute configuration of compound **1** was deduced by the negative Cotton effect observed at 343 nm.[12] Compound **1**, identified as (3*R*)-5,7-dihydroxy-4′-methoxy-6,3′-di(3-methylbut-2-enyl)isoflavanone, was named vogelin D.



1



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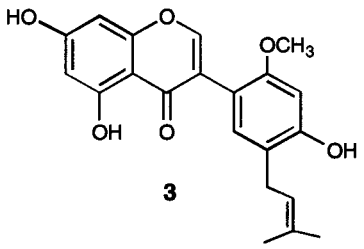

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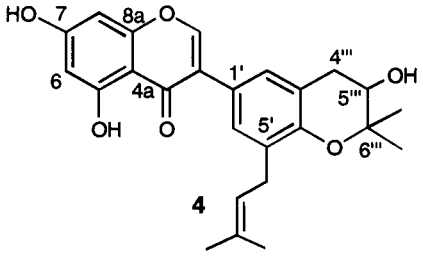

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The UV spectrum of compound **2** gave typical absorption bands for a 5,7-dihydroxyisoflavone. Dihydroxylation of ring A was deduced from the UV shifts observed upon addition of $AlCl_3$ and NaOAc.[9] The ^{1}H NMR spectrum confirmed this hypothesis by the presence of *meta*-coupled

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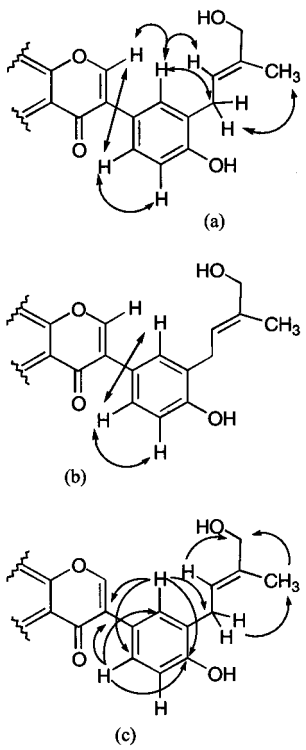

Figure 1. Correlations observed in the (a) NOESY, (b) COSY, and (c) HMBC spectra of compound **2**.

signals at δ 6.32 (H-6) and 6.20 (H-8). The EIMS exhibited a $[M]^+$ ion peak at *m/z* 354 and a fragment ion from a RDA cleavage at *m/z* 152 $[A_1]^+$, indicating the presence of two hydroxyl groups in ring A.[10] The COSY spectrum showed the presence of a three-proton spin system at δ 7.19 (H-6′), 6.80 (H-5′), and 7.24 (H-2′) and a substitution similar to that observed in compound **1** (Figure 1). The presence of a 4-hydroxy prenyl group was deduced from ^{1}H NMR and 2D NMR experiments (Figure 1). The NOESY spectrum showed the correlation between the methyl at δ 1.80 and protons at δ 3.42 (H-1″), suggesting the *trans* (*E*) side chain conformation. Thus, compound **2** was identified as 5,7,4′-trihydroxy-3′-[(2*E*)-4″-hydroxy-3-methylbut-2-enyl]-isoflavone and named vogelin E.

The UV spectrum of compound **3** showed bathochromic shifts with NaOAc and $AlCl_3$, indicative of a 5,7-dihydroxy-isoflavone.[9] In the EIMS, the fragment ion at *m/z* 152 $[A_1]^+$, resulting from a RDA cleavage of the C ring, was in agreement with the presence of two hydroxyl groups on ring A. Another fragment ion at *m/z* 313 $[M - 55]^+$ suggested the presence of a prenyl group, probably attached to the B ring. This hypothesis was confirmed by typical signals observed in the ^{1}H NMR spectrum at δ 3.25 (H-1″) and 5.35 (H-2″) and two methyl group resonances at δ 1.66 and 1.71.[5,6] Two *meta*-coupled aromatic protons at δ 6.21 and 6.34 were observed in the ^{1}H NMR spectrum, which were attributed to the protons H-6 and H-8. The ^{1}H NMR spectrum also exhibited two other signals at δ 6.88 (H-6′) and 6.50 (H-3′). The HMBC spectrum showed a clear correlation between the proton at δ 6.88 and the carbon at δ 26.1 (C-1″), indicating the attachment of the prenyl group at C-5′. The NOESY correlation between δ 3.25 (H-1″) and 6.88 (H-6′) confirmed this hypothesis, while a correlation between the aromatic proton at δ 6.50 (H-3′) and 3.70 ($-OCH_3$) was observed, indicating the presence of the methoxyl group at C-2′. Therefore, a hydroxyl group was attributed to position 4′. Compound **3** was identified as 5,7,-dihydroxy-2′-methoxy-5′-(3-methylbut-2-enyl)isoflavone and named vogelin F.

Compound **4** was also an isoflavone derivative, and this was deduced from the UV spectra.[9] The EIMS exhibited a $[M]^+$ ion peak at *m/z* 422 and a fragment ion from a RDA cleavage at *m/z* 152 $[A_1]^+$, indicating the presence of two hydroxyls in ring A.[9] The ions at *m/z* 367 $[M - 55]^+$ and 352 $[M - 70]^+$ suggested the presence of a prenyl group.[5,6] The ^{1}H NMR spectrum confirmed this hypothesis from the signals at δ 3.40 (H-1″) and 5.35 (H-2″) and the two methyls at δ 1.65 and 1.82. Two doublet signals at δ 6.25 and 6.32, respectively, were assigned to H-6 and H-8 in ring A. Signals for two aromatic protons were recorded at δ 7.20 and 7.26, and these could be readily assigned to H-2′ and H-6′ in the B ring. The NOESY spectrum showed a correlation between H-6′ (δ 7.26) and H-1″ (3.40), suggesting the attachment of the prenyl group at C-5′. The presence of a 2,2-dimethylchromane moiety with a secondary hydroxyl group attached to ring D was indicated by the proton signals at δ 1.24 and 1.27 (3H each, s), 2.80 (H-4‴), 3.00 (H-4‴), and 4.40 (H-5‴).[4] The NOESY spectrum showed a correlation between H-2′ and H-4‴, indicating the exact position of the chromane moiety. On the basis of the above evidence, compound **4** was identified as 5,7-dihydroxy-5′-(3-methylbut-2-enyl)-6‴,6‴-dimethyl-5‴-hydroxy-3′,4′-pyranoisoflavone and named vogelin G.

The NMR chemical shifts and MS data of the known compounds were identical to values of isolupalbigenin (**5**), ficuisoflavone (**6**), ulexone A (**7**), isochandalon (**8**), and isoderrone (**9**), respectively, reported in the literature.[4−8]

It was demonstrated that prenyl cyclization probably occurs with various oxygenase enzymes.[13−15] On the other hand, Mizutani et al.[16] demonstrated the existence of the transitory epoxy intermediates in the conversion of the prenyl group to diverse oxygenated cyclic substituents in the fungal metabolism of prenylated isoflavones. As the authors suggested the presence of the same epoxy intermediates in plant biogenesis, these compounds seem to originate through a stereospecific epoxidation.[17] These different pathways may be used to explain a variety of isoflavones with pyrano, dihydrofurano, dihydropyrano, and other acyclic substituents found in different species of the family Leguminosae.[15] Including the previously reported compounds,[1] a total of 11 isoflavonoids were isolated from the root bark of *Erythrina vogelii*.

The antifungal activity against *Cladosporium cucumerinum*[3] of the isolated compounds was investigated, but no activity was detected.

Experimental Section

General Experimental Procedures. Optical rotations were determined using a Perkin-Elmer 241 polarimeter (MeOH, *c* in g/100 mL). UV spectra were measured on a Perkin-Elmer Lambda 20 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Inova 500 spectrometer (500 and 125 MHz, respectively) in $CDCl_3$ or CD_3OD: chemical shifts in ppm as δ relative to Me_4Si (internal standard). Mass spectra were obtained on a Finnigan-MAT/TSQ-700 triple-stage quadrupole instrument: EIMS 70 eV; D/CI-MS NH_3, positive ion mode. HRESIMS were recorded on a Bruker FTMS 4.7T. TLC was carried out on silica gel 60 F_{254} Al sheets (Merck), with detection at 254 nm and using vanillin-sulfuric acid reagent.[18] Open column chromatography was performed using silica gel 60 (40−63 and 63−200 μm; Merck). Analytical HPLC was carried out on a HP 1090 system equipped with a photodiode array detector (Agilent Technologies). Extracts and fractions were analyzed on a Nova-Pak C_{18} column (5 μm, 4.6 × 250 mm; Waters). MPLC separations were done with a Büchi 681

pump equipped with a Knauer UV detector using a Lichroprep C_{18} column (15−25 μm, 40 × 500 mm, Merck). Semipreparative HPLC was carried out with a Shimadzu LC-8A pump equipped with a Knauer UV detector using a μBondapak C_{18} prepacked column (10 μm, 25 × 100 mm; Waters) or a Symmetry prep column (7 μm, 19 × 150 mm; Waters).

Plant Material. The roots of *Erythrina vogelii* Hook. f. were collected near Petit Yapo (region of Agbovelli) in Ivory Coast, in September 1999. The plant was identified by Henri Téré from the Centre Suisse de Recherches Scientifiques (CSRS) in Abidjan, Ivory Coast, and a voucher specimen was deposited at the CSRS herbarium (number HGT 2797).

Extraction and Isolation. The root bark (3 kg) was exhaustively extracted with CH_2Cl_2 (2.0 L, 3 × 24 h), followed by MeOH (2.0 L, 3 × 24 h), and concentrated under vacuum to give 15 g of CH_2Cl_2 extract and 10 g of MeOH extract. The CH_2Cl_2 extract was fractionated by open columm chromatography on silica gel (675 g), with a stepwise gradient of CH_2Cl_2−MeOH (95:5 to 0:100) to give 20 fractions (F1 to F20). Fraction F6 (796 mg) was re-subjected to column chromatography (silica gel 60; 230−400 μm, 3.08 g), eluted with a stepwise gradient CH_2Cl_2−AcOEt (99:1 to 93:7), to give five fractions (F6-1 to F6-5). Fractions F6-2 (140 mg) was purified by semipreparative HPLC using a μBondapak C_{18} prepacked column (10 μm, 25 × 100 mm, Waters, MeOH−H_2O, 68:32, flow rate 10 mL/min, UV 210 nm) and yielded **1** (7.6 mg, t_R = 40 min) and **9** (5.2 mg, t_R = 59 min). Fraction F6-4 (275 mg) was purified by semipreparative HPLC using (MeOH−H_2O, 40:60), yielding **4** (4.5 mg, t_R = 18 min), **6** (5.2 mg, t_R = 27 min), **7** (7.3 mg, t_R = 35 min), and **8** (7 9.1 mg, t_R = 37 min). Fraction 12 (950 mg) was re-subjected to column chromatography (silica gel 60; 230−400 μm, 28 g), eluted with the CH_2Cl_2−EtOAc (96:4), to give 20 fractions (F14.1 to F14.20). Fraction F14.16 (245 mg), was purified by HPLC using a μBondapak C_{18} prepacked column (MeOH−H_2O, 75:25, flow rate 15 mL/min, UV 210 nm) and yielded **5** (9.4 mg, t_R = 22 min) and **3** (12.7 mg, t_R = 17 min). Fraction 18 (600 mg) was purified by MPLC using a C_{18} column packed with Lichroprep eluted with MeOH−H_2O (gradient: 40% to to 100% in 5 days, UV 210 nm) to give 70 fractions (F20.1 to F20.70). Fractions F20.45 to F20.65 (145 mg) were purified by semipreparative HPLC using a Symmetry Prep column (MeOH−H_2O, 1:1, flow rate 10 mL/min, UV 210 nm) and yielded **2** (9.8 mg, t_R = 57 min).

Vogelin D (1): amorphous white powder; $[\alpha]_D^{23}$ −25.9 ° (*c* 0.1, MeOH); CD (MeCN; *c* 1.85 μmol/L; 200−400 nm) $[\theta]_{315}$ +110, $[\theta]_{343}$ − 100; UV (MeOH) λ_{max} (log ϵ) 227 (sh), 295 (4.07), 321 (sh) nm; UV (MeOH + NaOMe) λ_{max} 251 (sh), 332.9 (MeOH + NaOAc) λ_{max} 297, 331 (sh) nm; UV (MeOH + $AlCl_3$) λ_{max} 224, 314.4 nm; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.66 (3H, s, CH_3-4‴), 1.71 (3H, s, CH_3-5‴), 1.75 (3H, s, CH_3-4″), 1.81 (3H, s, CH_3-5″), 3.28 (2H, d, J = 7.2 Hz, H-1‴), 3.36 (2H, d, J = 6.8 Hz, H-1″), 3.80 (3H, s, −OCH_3), 3.87 (1H, dd, J = 5.3 and 8.3 Hz, H-3), 4.50 (1H, dd, J = 8.3 and 11.2 Hz, H-2α), 4.55 (2H, dd, J = 5.3 and 11.2 Hz, H-2β), 5.25 (4H, m, H-2″ and H-2‴), 5.95 (H, s, H-8), 6.81 (1H, d, J = 8.3 Hz, H-5′), 7.01 (1H, d, J = 1.9 Hz, H-2′), 7.06 (1H, dd, J = 1.9 and 8.3 Hz, H-6′), 12.40 (1H, s, 5-OH); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.8 (C-4‴), 17.7 (C-4″), 21.1 (C-1″), 25.7 (C-5‴), 25.7 (C-5″), 28.4 (C-1‴), 50.6 (C-3), 55.4 (−OCH_3), 71.3 (C-2), 95.1 (C-8), 102.4 (C-4a), 106.1 (C-6), 110.1 (C-5′), 121.3 (C-2″), 122.0 (C-2‴), 126.8 (C-2′), 126.5 (C-1′), 129.5 (C-6′), 130.6 (C-3′), 132.8 (C-3″), 135.7 (C-3‴), 156.9 (C-4′), 157.9 (C-8a), 161.3 (C-5), 163.4 (C-7), 196.0 (C-4); EIMS *m*/*z* 422 $[M]^+$ (85), 404 (22), 367 $[M - 55]^+$ (23), 220 $[A_1]^+$ (32), 202 $[B_3]^+$ (100), 189 (29), 164.9 (22); D/CI-MS *m*/*z* 440 $[M + NH_4]^+$; HRESIMS *m*/z 445.1985 (calcd for $C_{26}H_{30}O_5$ $[M + Na]^+$).

Vogelin E (2): amorphous yellow powder; UV (MeOH) λ_{max} (log ϵ) 262 (3.7), 325 (sh) nm; UV (MeOH + NaOMe) λ_{max} 275.5, 325 (sh) nm. UV (MeOH + NaOAc) λ_{max} 270, 324 (sh) nm; UV (MeOH + $AlCl_3$) λ_{max} 203, 273.2, 378 (sh) nm; ^{1}H NMR (CD_3OD, 500 MHz) δ 1.80 (3H, s, CH_3-5″), 3.42 (2H, d, J = 7.32 Hz, CH_2-1″), 3.95 (2H, s, H-4″), 5.40 (1H, t, J = 7.32 Hz, CH-2″), 6.20 (1H, d, J = 1.9 Hz, H-6), 6.32 (1H, d, J = 1.9 Hz, H-8), 6.80 (1H, d, J = 8.3 Hz, H-5′), 7.19 (1H, dd, J = 1.9 and 8.3 Hz, H-6′), 7.24 (1H, d, J = 1.9 Hz, H-2′), 8.00 (1H, s, H-2); ^{13}C NMR (CD_3OD, 125 MHz) δ 18.5 (C-5″), 32.2 (C-1″), 72.4 (C-4″), 94.5 (C-6), 105.2 (C-8), 109.1 (C-4a), 120.6 (C-5′), 123.8 (C-1′), 125.3 (C-3), 126.7 (C-3′), 129.5 (C-2″), 132.5 (C-6′), 135.5 (C-2′), 140.1 (C-3″), 154.2 (C-2), 160.1 (C-4′), 164.2 (C-8a), 166.1 (C-5), 168.0 (C-7), 180.1 (C-4); EIMS *m*/*z* 354 $[M]^+$ (20), 336 $[M - 18]^+$ (90), 320.9 (100), 309 $[M - 72]^+$ (17), 295 (20), 152 $[A_1]^+$ (35); D/CI-MS *m*/z 372 $[M + NH_4]^+$, 355 $[M + H]^+$; HRESIMS *m*/z 377.0995 (calcd for $C_{20}H_{18}O_6$ $[M + Na]^+$).

Vogelin F (3): amorphous white powder; UV (MeOH) λ_{max} (log ϵ) 210 (sh), 259 (4.02), 288 (sh) nm. UV (MeOH + NaOMe) λ_{max} 210 (sh), 269.1, 320.1 (sh) nm; UV (MeOH + NaOAc) λ_{max} 264.8, 322.9 (sh) nm; UV (MeOH + $AlCl_3$) λ_{max} 210.8 (sh), 269.1, 368 (sh) nm; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.66 (3H, s, CH_3-4″), 1.71 (3H, s, CH_3-5″), 3.25 (2H, d, J = 7.2 Hz, H-1″), 3.70 (3H, s, −OCH_3), 5.35 (1H, m, H-2″), 6.21 (H, d, J = 1.9 Hz, H-6), 6.34 (H, d, J = 1.9 Hz, H-8), 6.50 (1H, s, H-3′), 6.88 (1H, s, H-6′), 7.90 (1H, s, H-2); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 17.8 (C-4″), 25.6 (C-5″), 26.1 (C-1″), 56.0 (−OCH_3), 95.7 (C-6), 103.2 (C-4a), 104.2 (C-3′), 105.1 (C-8), 112.0 (C-5′), 121.8 (C-2″), 122.3 (C-3), 120.3 (C-1′), 129.5 (C-6′), 132.2 (C-3″), 153.0 (C-2), 156.7 (C-4′), 157.3 (C-2′), 160.0 (C-8a), 162.2 (C-5), 163.2 (C-7), 184.0 (C-4); EIMS *m*/*z* 368 $[M]^+$ (76), 353 $[M - 15]$ (27), 313 $[M - 55]^+$ (100), 297 (15), 227 (15), 163 (19), 152.0 $[A_1]^+$ (30), 111 (22), 83 (28); D/CI-MS *m*/z 386 $[M + NH_4]^+$; HRESIMS *m*/z 391.1154 (calcd for $C_{21}H_{20}O_6$ $[M + Na]^+$).

Vogelin G (4): amorphous yellow powder; UV (MeOH) λ_{max} (log ϵ) 216 (sh), 262.9 (3.80), 295 (sh) nm; UV (MeOH + NaOMe) λ_{max} 275, 325 (sh) nm; UV (MeOH + NaOAc) λ_{max} 203 (sh), 270.3, 324.8 (sh) nm; UV (MeOH + $AlCl_3$) λ_{max} 216.8 (sh), 272.8, 310 (sh) nm; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.65 (3H, s, CH_3-4″), 1.63 (3H, s, CH_3-7‴), 1.82 (3H, s, CH_3-5″), 1.87 (3H, s, CH_3-8‴), 2.80 (1H, dd, J = 14.1 and 8.7 Hz, H-4‴), 3.00 (1H, dd, J = 14.1 and 1.9 Hz, H-4‴), 3.40 (2H, m, H-1″), 4.40 (1H, d, J = 8.7 and 1.9 Hz, H-5‴), 5.35 (1H, m, H-2″), 6.25 (1H, d, J = 1.9 Hz, H-6), 6.32 (1H, d, J = 1.9 Hz, H-8), 7.20 (1H, d, J = 1.9 Hz, H-2′), 7.25 (1H, d, J = 1.9 Hz, H-6′), 7.80 (1H, s, H-2), 12.9 (OH-5); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.0 (C-4″), 18.5 (C-7‴), 26.3 (C-5″ and C-8‴), 28.3 (C-1″), 40.2 (C-4‴), 72.3 (C-5‴), 79.7 (C-6‴), 94.5 (C-6), 100.1 (C-8), 104.5 (C-4a), 106.2 (C-3′), 117.5 (C-5′), 121.3 (C-2″), 122.3 (C-3), 124.3 (C-1′), 129.4 (C-6′), 130.2 (C-2′), 132.0 (C-3″), 154.3 (C-2), 155.6 (C-4′), 159.2 (C-8a), 164.0 (C-5), 164.3 (C-7), 182.0 (C-4); EIMS *m*/*z* 422 $[M]^+$ (38), 367 $[M - 55]^+$ (87), 352 (100), 313 (40), 293 (33), 266.9 (25), 167 (35), 152.0 $[A_1]^+$; D/CI-MS *m*/z 440 $[M + NH_4]^+$, 423 $[M + H]^+$; HRESIMS *m*/z 445.1621 (calcd for $C_{25}H_{26}O_6$ $[M + Na]^+$).

Antifungal Assay. The antifungal testing of pure compounds, fractions, and extracts against *Cladosporium cucumerinum* was performed using a TLC biautography assay,[3] with a LB (Luria−Bertani) medium.

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Supporting Information Available: Spectral data for the known compounds **5**−**9** are available free of charge via the Internet at http://pubs.acs.org.

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