Notes

Cassane Diterpenoids of *Caesalpinia pulcherrima*

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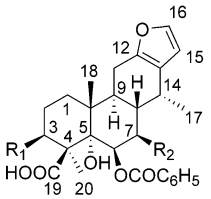
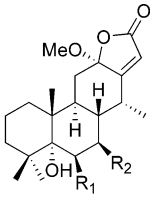
Five new cassane diterpenoids (**1**−**5**) were isolated from the roots of *Caesalpinia pulcherrima*, along with the known isovouacapenol C (**6**), pulcherrimin A (**11**), and 6*β*-cinnamoyl-7*β*-hydroxyvouacapen-5α-ol (**12**). Compounds **3**−**5** possess the α,*β*-butenolide moiety, whereas compounds **1** and **2** contain a more usual 2,3-disubstituted furan unit. Compounds **7** and **8** were derived from hydrolysis of **6**, while **9** and **10** were derived from acetylation and oxidation of **6**, respectively. The ^{1}H and ^{13}C NMR spectra of all compounds were completely assigned using a combination of 2D NMR experiments, including ^{1}H−^{1}H COSY, HSQC, HMBC, and T-ROESY sequences.

Caesalpinia pulcherrima Swartz. (Fabaceae) is an ornamental plant in the Caribbean due to its variety of flowers, which appear yellow, pink, off-white, and red with yellow margins. The red with yellow margins variety is the national flower of Barbados, known as Pride of Barbados, and it is the roots of this variety that were used for this investigation. *C. pulcherrima* also has uses in traditional medicine: the stem is used as an abortifacient and emmenagogue, while decoctions of the leaves, roots, and bark are used as a febrifuge and to treat liver disorders as well as ulcers of the mouth and throat.[1] The genus *Caesalpinia* has been a rich source of cassane-type diterpenoids, and the roots of *C. pulcherrima* have yielded pulcherrimins A−D, vouacapen-5α-ol, 6*β*-cinnamoyl-7*β*-hydroxyvouacapen-5α-ol, and 8,9,11,14-didehydrovouacapen-5α-ol, while isovouacapenols A−D were isolated from the leaves.[2−4] Pulcherrimins A and B were found to be active in DNA repair-deficient yeast mutant, and isovouacapenols A−D were found to be active against several bacteria and fungi.[2,4] Peltogynoids and homoisoflavanoids have also been isolated from *C. pulcherrima*.[5] As part of an investigation of the chemical constituents of *Caesalpinia* we report here the isolation and structure elucidation of five new cassane diterpenoids (**1**−**5**), along with the known isovouacapenol C (**6**), pulcherrimin A (**11**), and 6*β*-cinnamoyl-7*β*-hydroxyvouacapen-5α-ol (**12**).

The dichloromethane extract of the roots of *C. pulcherrima* was fractionated by silica gel flash chromatography and preparative HPLC to give compounds **1**−**6**, **11**, and **12**. A combination of 1D and 2D NMR spectroscopy and HREIMS was used to elucidate the structures for the new compounds (**1**−**5**) as described in the following paragraphs.

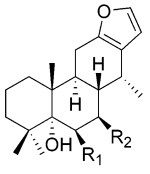
The molecular formula of compound **1** was established as $C_{36}H_{38}O_{10}$ by HREIMS. The ^{1}H NMR spectrum showed two tertiary methyl groups at *δ* 1.28 and 1.62, one secondary methyl group at *δ* 0.99 (d, *J* = 7.0 Hz), and an acetoxy methyl group at *δ* 1.95. Three oxymethine protons were observed at *δ* 5.33 (dd, *J* = 12.2, 4.9 Hz, H-3), 5.50 (dd, *J* = 11.7, 4.0 Hz, H-7), and 5.95 (d, *J* = 4.0 Hz, H-6). A 2,3-disubstituted furan ring was evident from resonances at *δ* 6.18 (d, *J* = 1.9 Hz) and 7.25 (d, *J* = 1.9 Hz), while the presence of two monosubstituted benzene rings was indicated by resonances in the range *δ* 7.24−7.92 (Table 1). In the ^{13}C NMR spectrum, the carbons of the furan ring resonated at *δ* 148.7, 140.9, 121.4, and 109.5, while the carbons of the two benzene rings occurred in the range *δ* 133.5−128.5. A quaternary oxygenated carbon was seen at *δ* 79.4, and three secondary oxygenated carbons had signals at *δ* 77.0, 71.0, and 69.0, corresponding to C-5, C-3, C-7, and C-6, respectively. Three ester carbonyls had signals at *δ* 171.2 and 162.1 (2C each), while a resonance at *δ* 176.1 was due to a carboxylic acid moiety. The full ^{1}H and ^{13}C NMR assignments and connectivities were determined from a combination of ^{1}H−^{1}H COSY, HSQC, and HMBC spectral data. The coupled HSQC spectrum showed

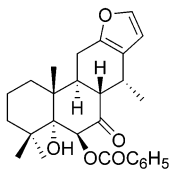




1 R_1 = $OCOC_6H_5$, R_2 = $OCOCH_3$
2 R_1 = H, R_2 = $OCOCH_3$
11 R_1 = OH, R_2 = $OCOC_6H_5$

3 R_1 = R_2 = H
4 R_1 = $OCOC_6H_5$, R_2 = OH
5 R_1 = $OCOCH{=}CHC_6H_5$, R_2 = OH





6 R_1 = $OCOC_6H_5$, R_2 = OH
7 R_1 = R_2 = OH
8 R_1 = OH, R_2 = $OCOC_6H_5$
9 R_1 = $OCOC_6H_5$, R_2 = $OCOCH_3$
12 R_1 = $OCOCH{=}CHC_6H_5$, R_2 = OH

10

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Table 1. NMR Spectral Data for Compounds **1** and **2** ($CDCl_3$)[a]

	1		**2**	
position	δ_C	δ_H (mult. *J*, Hz)	δ_C	δ_H (mult. *J*, Hz)
1	32.9	1.68 (dd, 13.2, 3.8)	34.5	1.57 (m)
		2.02 (dd, 13.2, 3.8)		1.70 (m)
2	24.3	1.93 (m)	18.5	1.51 (m)
		2.61 (m)		2.06 (m)
3	77.0	5.33 (dd, 12.2, 4.9)	33.7	1.55 (m)
				1.88 (m)
4	53.4		48.7	
5	79.4		77.8	
6	69.0	5.95 (d, 4.0)	69.1	5.95 (d, 3.6)
7	71.0	5.50 (dd, 11.7, 4.0)	71.5	5.55 (dd, 11.6, 3.6)
8	35.2	2.29 (dt, 11.7, 5.0)	35.3	2.28 (dt, 11.6, 5.0)
9	36.9	2.58 (m)	37.3	2.45 (m)
10	41.6		41.2	
11	22.2	2.62 (m)	22.3	2.60 (dd, 14.8, 9.5)
		2.66 (m)		2.66 (dd, 14.8, 5.0)
12	148.7		149.0	
13	121.4		121.3	
14	27.3	2.83 (dq, 7.0, 5.0)	27.2	2.82 (dq, 7.0, 5.0)
15	109.5	6.18 (d, 1.9)	109.4	6.18 (d, 1.9)
16	140.9	7.27 (d, 1.9)	140.8	7.23 (d, 1.9)
17	17.1	0.99 (d, 7.0)	17.0	0.99 (d, 7.0)
18	17.2	1.62 (s)	17.8	1.40 (s)
19	176.4		179.7	
20	19.9	1.28 (s)	24.1	1.24 (s)
1′	162.1		166.0	
2′	130.0		130.4	
3′/7′	129.6	7.96 (dd, 8.5, 1.1)	129.6	7.94 (dd, 8.4, 1.4)
4′/6′	128.5	7.39 (dd, 8.5, 8.5)	128.5	7.42 (dd, 8.4, 8.4)
5′	133.2	7.56 (tm, 8.5)	132.8	7.53 (tm, 8.4)
1″	162.1			
2″	130.2			
3″/7″	129.4	7.91 (dd, 8.4, 1.3)		
4″/6″	128.6	7.24 (dd, 8.4, 8.4)		
5″	133.1	7.46 (tm, 8.4)		
$OCOCH_3$	171.2		171.0	
$OCOCH_3$	20.9	1.95 (s)	20.9	1.95 (s)

[a] Chemical shifts (δ) in ppm.

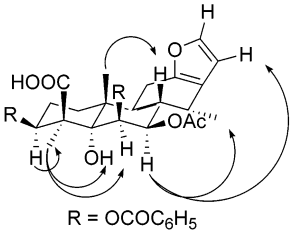

Figure 1. Key T-ROESY correlations for **1**.

that the oxymethine proton at δ 5.33 (dd, J = 12.2, 4.9 Hz, H-3) is directly attached to a carbon resonating at δ 77.0 (C-3). In the HMBC spectrum, H-3 showed correlations to C-1′, C-2, C-4, C-19, and C-20, which supported the placement of the benzoate ester at C-3. Further, the H-7 proton showed HMBC correlations to the acetoxy carbonyl carbon at δ 171.2, in addition to carbons at δ 27.3 (C-14) and 35.2 (C-8). An analysis of the coupling constants, as well as T-ROESY correlations, enabled the stereochemistry at C-3, C-6, and C-7 to be determined (Figure 1).[6] Therefore, the structure of pulcherrimin E (**1**) was assigned as 7β-acetyl-3β,6β-dibenzoyl-12,16-epoxy-5α-hydroxy-12α-methoxycassa-12,15-dien-19β-oic acid.

Compound **2**, $C_{29}H_{34}O_8$, had ^{1}H NMR data similar to **1** except that the oxymethine proton at C-3 was replaced by methylene protons resonating at δ 1.55 and 1.88, along with the absence of the associated benzoate ester. Two oxymethine protons had resonances at δ 5.55 (dd, J = 11.6, 3.6 Hz, H-7) and 5.95 (d, J = 3.6 Hz, H-6) and showed COSY cross-peaks to each other. In addition, the H-7 proton showed HMBC correlations to the benzoate carbonyl carbon at δ 166.0, along with the carbons at δ 77.8 (C-5), 71.5 (C-7), 41.2 (C-10), and 35.3 (C-8). The stereochemical orientations at C-6 and C-7 were the same as in compound **1**, since the coupling constants of the associated protons were similar, and this was confirmed by T-ROESY experiments. Accordingly, pulcherrimin F (**2**) was assigned as 7β-acetyl-6β-benzoyl-12,16-epoxy-5α-hydroxy-12α-methoxycassa-12,15-dien-19β-oic acid.

The molecular formula of **3**, $C_{21}H_{32}O_4$, was established by HREIMS. The IR spectrum had absorption bands at 3500 and 1748 cm^{-1}, indicative of hydroxy and α,β-unsaturated γ-lactone functionalities, respectively. The ^{1}H NMR spectrum had a one-proton singlet at δ 5.79 due to an α,β-butenolide, instead of the resonances associated with a 2,3-disubstituted furan as in **1** and **2**. There were also resonances for three tertiary methyl groups at δ 0.95, 0.97, and 1.05, a secondary methyl group at δ 1.17 (d, J = 7.3 Hz), and a methoxy group at δ 3.19. The ^{13}C NMR spectrum of compound **3** showed signals at δ 171.9, 170.3, 115.3, and 108.4, attributable to a fused α,β-butenolide moiety, while a methoxy carbon resonated at δ 50.8. HMBC correlations indicated that the two methyl groups at δ 0.95 and δ 1.05 are geminal to each other and are attached to the carbon at δ 38.4 (C-4), while the methoxy group at δ 3.19 showed a correlation to the acetal carbon at δ 108.4 (C-12). The secondary methyl group at δ 1.17 (H_3-17) had T-ROESY cross-peaks with the methoxy group, which indicated that they were on the same side of the molecule and that they were α-oriented. Therefore, compound **3** was assigned as 12,16-epoxy-5α-hydroxy-12α-methoxycassa-13-(15)-en-16-one.

The ^{1}H NMR spectrum of compound **4**, $C_{28}H_{36}O_7$, was similar to that of **3** except at C-6 and C-7, where the methylene protons were replaced by a benzoate ester and a hydroxy group, respectively. There were resonances for two oxymethine protons at δ 4.47 (dd, J = 11.1, 4.1 Hz, H-7) and δ 5.77 (d, J = 4.1 Hz, H-6), which also showed COSY cross-peaks to each other. The oxymethine proton at δ 5.77 showed HMBC correlations to the benzoate ester carbonyl carbon at δ 167.5, in addition to carbons at δ 78.0 (C-5), 68.1 (C-7), 42.3 (C-8), and 40.9 (C-10). In the T-ROESY spectrum, the secondary methyl group at δ 1.22 (J = 7.3 Hz) had cross-peaks to the methoxy protons at δ 3.21 and H-9 at δ 2.39, thus establishing that the methoxy group had the same relative stereochemistry as in **3**. Compound **4** was assigned as 6β-benzoyl-5α,7β-dihydroxy-12,16-epoxy-12α-methoxycassa-13(15)-en-16-one.

Compound **5**, $C_{30}H_{38}O_7$, had ^{1}H NMR data similar to **4** except at C-6, where the benzoate ester was replaced by a cinnamoyl moiety. Two oxymethine protons had resonances at δ 4.43 (dd, J = 11.1, 4.0 Hz, H-7) and 5.61 (d, J = 4.0 Hz, H-6), while a methoxy group appeared as a sharp singlet at δ 3.21. The oxymethine proton at δ 5.61 had HMBC correlations to the cinnamate ester carbonyl at δ 167.6 and the carbons at δ 77.9 (C-5), 68.2 (C-7), 42.3 (C-8), and 41.0 (C-10). Compound **5** was assigned as 6β-cinnamoyl-5α,7β-dihydroxy-12,16-epoxy-12α-methoxycassa-13(15)-en-16-one. The trivial names proposed for compounds **3**−**5** are neocaesalpins E, F, and G, respectively. This is the first isolation of α,β-butenolide cassane diterpenoids from *C. pulcherrima*; neocaesalpins A and B were isolated from the seeds of *Caesalpinia bonduc* (L.) Roxb. (Fabaceae),[7] while neocaesalpins C and D were isolated from the Philippine crude drug calumbibit, which is derived from *C. bonduc*.[8]

Table 2. NMR Spectral Data for Compounds **3**−**5** ($CDCl_3$)

	3		**4**		**5**	
position	δ_C	δ_H (mult. *J*, Hz)	δ_C	δ_H (mult. *J*, Hz)	δ_C	δ_H (mult. *J*, Hz)
1	32.4	⟨1.41⟩[a] (m)	34.7	⟨1.55⟩[a] (m)	34.7	⟨1.53⟩[a] (m)
2	18.2	1.49 (m)	18.1	1.54 (m)	18.0	1.52 (m)
		1.64 (m)		1.70 (m)		1.60 (m)
3	36.3	1.23 (m)	37.7	1.20 (m)	37.8	1.20 (m)
		1.63 (m)		1.65 (m)		1.65 (m)
4	38.4		39.2		39.2	
5	76.5		78.0		77.9	3.49 (s, OH)
6	25.5	1.61 (m)	73.7	5.77 (d, 4.1)	73.4	5.61 (d, 4.0)
		1.75 (dt, 13.5, 4.4)				
7	23.9	1.33 (m)	68.1	4.47 (dd, 11.1, 4.1)	68.2	4.43 (dd, 11.1, 4.0)
		1.90 (dq, 13.0, 5.0)				
8	40.2	1.62 (m)	42.3	1.86 (dt, 11.1, 4.7)	42.3	1.84 (dt, 11.1, 5.0)
9	37.0	2.33 (m)	36.8	2.39 (m)	36.8	2.36 (m)
10	40.9		40.9		41.0	
11	37.4	1.27 (m)	37.2	1.44 (m)	37.3	1.42 (m)
		2.31 (m)		2.40 (m)		2.39 (m)
12	108.4		108.0		108.0	
13	170.3		170.2		170.2	
14	37.1	2.89 (dq, 7.3, 4.8)	32.4	3.36 (dq, 7.3, 5.0)	32.4	3.38 (dq, 7.3, 4.9)
15	115.3	5.79 (s)	116.0	5.82 (s)	116.0	5.83 (s)
16	171.9		171.1		171.2	
17	11.7	1.17 (d, 7.3)	11.2	1.22 (d, 7.3)	11.3	1.22 (d, 7.3)
18	16.7	0.97 (s)	17.4	1.43 (s)	17.1	1.34 (s)
19	28.1	0.95 (s)	27.8	1.08 (s)	27.8	1.06 (s)
20	24.6	1.05 (s)	25.4	1.16 (s)	25.4	1.19 (s)
OMe	50.8	3.19 (s)	50.9	3.21 (s)	50.9	3.21 (s)
1′			167.5		167.6	
2′			129.6		117.5	6.43 (d, 16.0)
3′[b]			129.9	8.03 (dd, 8.4, 1.3)	146.4	7.72 (d, 16.0)
4′[b]			128.7	7.47 (dd, 8.4, 8.4)	134.0	
5′[c]			133.5	7.59 (tm, 8.4)	129.0	7.39 (m)
6′[c]					128.3	7.54 (m)
7′					130.7	7.41 (m)

[a] Average value for an incompletely resolved methylene group. [b] Compound **4**: 3′ = 7′ and 4′ = 6′. [c] Compound **5**: 5′ = 9′ and 6′ = 8′.

The known cassane diterpenoids, isovouacapenol C (**6**), pulcherrimin A (**11**), and 6*β*-cinnamoyl-7*β*-hydroxyvouacapen-5α-ol (**12**), were identified by comparison with literature data.[2−4] Hydrolysis of compound **6** with methanolic Na_2CO_3 gave **7**, the product of complete hydrolysis, along with the transesterification product **8**, while acetylation and oxidation gave compounds **9** and **10**, respectively. The spectral data for compounds **7**−**10** were in complete accord with the proposed structures, and these were confirmed by analysis of their 2D NMR spectra. To date, all cassane diterpenes with a 6,7-dihydroxylation pattern isolated from *C. pulcherrima* possess the 6*β*,7*β*-orientation, while those isolated from the related *C. bonduc* possess the 6α,7*β*-orientation.[2−4,9−11]

Experimental Section

General Experimental Procedures. Melting points were determined using a Fisher/Johns melting point apparatus. Optical rotations were measured on a Perkin-Elmer 341 polarimeter with Na 589 nm at 20 °C. UV spectra were recorded on a HP8452A diode array spectrophotometer, and IR spectra were recorded on a Nexus 670 FT-IR spectrophotometer. NMR spectra were recorded on a Varian Unity 500 MHz spectrometer in $CDCl_3$ with TMS as internal standard. The high- and low-resolution EIMS were recorded on a Micromass 70-250S (double focusing) mass spectrometer at an ionizing voltage of 70 eV. Flash column chromatography was performed using Merck Grade 9385 silica gel 60 (230−400 mesh). TLC was performed using precoated silica gel plates of 0.2 mm thickness; the plates were visualized by spraying with Ehrlich's reagent and warming.

Plant Material. The plant material was collected at Spring Garden, Barbados, in January 2002. It was identified by Professor Sean Carrington at the University of the West Indies Cave Hill Campus as *Caesalpinia pulcherrima* (L.) Swartz, and a voucher specimen (JSR1) is maintained in the Department of Biological and Chemical Sciences.

Extraction and Isolation. The ground, air-dried roots (150 g) were soaked in MeOH (1.5 L) for 2 weeks, the mixture was filtered, and the filtrate was concentrated in vacuo to afford a crude extract (19 g). This extract was suspended in MeOH−H_2O, 9:1 (200 mL), and extracted with hexane (4 × 200 mL). Water (100 mL) was added to the aqueous layer, and this was extracted with CH_2Cl_2 (3 × 200 mL) to give a CH_2Cl_2 extract (3.76 g). The CH_2Cl_2 extract was fractionated by silica gel chromatography using increasing proportions of acetone in hexane (starting at 10%) as eluents. The 10% acetone fractions afforded **3** (4 mg) and **6** (253 mg), while the 15% acetone fractions afforded **1** (16 mg), all three crystallizing spontaneously from solution. Subsequent concentration of the 10% and 15% acetone fractions in vacuo followed by TLC analysis gave six grouped fractions (I−VI). Reversed-phase HPLC in 65% acetonitrile−H_2O on fractions III−VI afforded **2** (3 mg), **4** (17 mg), **5** (17 mg), **11** (4 mg), and **12** (12 mg). Hydrolysis of **6** (50 mg) for 6 h using MeOH (10 mL) saturated with Na_2CO_3 at 24 °C afforded **7** (5.4 mg) and **8** (10.6 mg) after usual workup. Acetylation of **6** (30 mg) using a 1:1 mixture of pyridine−acetic anhydride (0.5 mL) overnight, followed by usual workup and preparative TLC, afforded **9** (25 mg), while oxidation of **6** (50 mg) for 5 h in CH_2Cl_2 (2 mL) using pyridinium chlorochromate (50 mg) in CH_2Cl_2 (5 mL) yielded **10** (17 mg) after workup and preparative TLC.

Pulcherrimin E (1): white crystalline solid (acetone−*n*-hexane); mp 222−224 °C; $[\alpha]^{20}_D$ +30.7° (*c* 0.29, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 204 (4.49), 230 (4.70) nm; IR (KBr) ν_{max} 3446, 1731, 1274, 1110, 1069, 1026, 710, 669 cm^{-1}; ^1H NMR and ^{13}C NMR data, Tables 1 and 2; EIMS *m*/*z* 630 $[M]^+$ (46), 448 (22), 415 (31), 308 (11), 293 (19), 105 (100), 77 (25); HREIMS *m*/*z* 630.2463 (calcd for $C_{36}H_{38}O_{10}$, 630.2465).

Pulcherrimin F (2): white gum; $[\alpha]^{20}_D$ +38.5° (*c* 0.26, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 224 (3.79) nm; IR (film) ν_{max} 3501, 1717, 1276, 1113, 1070, 1026, 755, 710, 668 cm^{-1}; ^1H NMR and ^{13}C NMR data, Tables 1 and 2; EIMS *m*/*z* 510 $[M]^+$ (19), 310 (19), 295 (26), 105 (100), 77 (31); HREIMS *m*/*z* 510.2263 (calcd for $C_{29}H_{34}O_8$, 510.2254).

Neocaesalpin E (3): fine needles (acetone−*n*-hexane); mp 173−175 °C; $[\alpha]^{20}_D$ −62.5° (*c* 0.20, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 224 (4.07) nm; IR (film) ν_{max} 3500, 1748, 1635, 1280, 1173, 1065, 978, 960, 921, 757 cm^{-1}; ^1H NMR and ^{13}C NMR data, Table 2; EIMS *m*/*z* 330 $[M]^+$ (24), 298 (24), 232 (56), 109 (100), 82 (69), 55 (30); HREIMS *m*/*z* 348.2305 (calcd for $C_{21}H_{32}O_4$, 348.2301).

Neocaesalpin F (4): colorless gum ($CHCl_3$); $[\alpha]^{20}_D$ −70.9° (*c* 0.33, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 224 (4.07); IR (film) ν_{max} 3526, 1748, 1715, 1275, 1070, 961, 923, 862, 755, 715, 667 cm^{-1}; ^1H NMR and ^{13}C NMR data, Table 2; EIMS *m*/*z* 485 $[M + H]^+$ (31), 453 (16), 362 (52), 344 (100); HREIMS *m*/*z* 485.2551 (calcd for $C_{28}H_{37}O_7$, 485.2539).

Neocaesalpin G (5): white crystals; mp 108−110 °C; $[\alpha]^{20}_D$ −61.8° (*c* 0.11, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 210 (4.50), 278 (3.98) nm; IR (film) ν_{max} 3500, 1748, 1701, 1635, 1280, 1173, 1065, 978, 960, 921, 757 cm^{-1}; ^1H NMR and ^{13}C NMR data, Table 2; EIMS *m*/*z* 510 $[M]^+$ (90), 492 (16), 479 (74), 362 (76), 344 (100); HREIMS *m*/*z* 510.2618 (calcd for $C_{30}H_{38}O_7$, 510.2617).

6*β*-Hydroxyisovouacapenol C (7): white solid; mp 105−107 °C; $[\alpha]^{20}_D$ +25.7° (*c* 0.07, $CHCl_3$); ^1H NMR and ^{13}C NMR data, Tables S1 and S2.

7*β*-Acetyl-6*β*-hydroxyisovouacapenol C (8): white solid; mp 125−127 °C; $[\alpha]^{20}_D$ +23.7° (*c* 0.27, $CHCl_3$); ^1H NMR and ^{13}C NMR data, Tables S1 and S2.

Isovouacapenol C monoacetate (9): white solid; mp 120−122 °C; $[\alpha]^{20}_D$ +26.2° (*c* 1.70, $CHCl_3$); ^1H NMR and ^{13}C NMR data, Tables S1 and S2.

7-Keto-isovouacapenol C (10): white solid; mp 128−130 °C; $[\alpha]^{20}_D$ −9.0° (*c* 0.50, $CHCl_3$); ^1H NMR and ^{13}C NMR data, Tables S1 and S2.

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Supporting Information Available: Tables of NMR spectroscopic data for compounds **7**−**10**. This information is available free of charge on the Internet at http://www.pubs.acs.org.

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