Minor Cassane Diterpenoids of *Caesalpinia bonduc*

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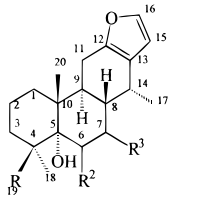
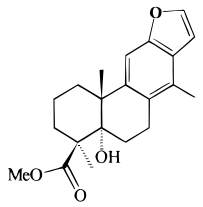
Seven cassane diterpenes, including the known caesaldekarin A, were isolated from the roots of *Caesalpinia bonduc*, collected in Barbados. The ^{1}H and ^{13}C NMR spectra of all seven compounds were completely assigned by using a combination of 2D NMR experiments, which included ^{1}H−^{1}H COSY, HSQC, HMQC, and HMBC sequences.

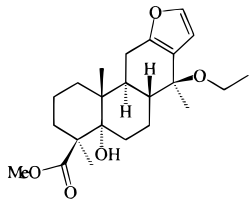
Caesalpinia bonduc (L.) Roxb. (Fabaceae) is a medicinal plant of wide distribution throughout the tropics and subtropics.[1] Early investigations of the seed of this plant led to the isolation[2−6] and structure elucidation[6−8] of the cassane furanoditerpenes, α-, *β*-, *γ*-, and *δ*-caesalpin. Subsequent investigations of the seeds resulted in the isolation and characterization of two further furanoditerpenes, designated *ϵ*-caesalpin[9] and caesalpin F.[10] In contrast, no investigations of the roots of *C. bonduc* were reported in the literature. We have initiated a phytochemical investigation of the roots of *C. bonduc* collected in Barbados and reported previously on the isolation and characterization of 12 new cassane diterpenes from this plant.[11−14] Further investigations of the roots of *C. bonduc* have now resulted in the isolation of seven additional, minor cassane diterpenes. One compound is the recently reported caesaldekarin A (**1**),[15] while the other six compounds (**2**−**7**) have not been reported previously. The



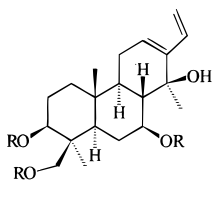
(1) R = -CH_3, R^2 = β-OAc, R^3 = H
(2) R = -CH_2OAc, R^2 = R^3 = H
(3) R = -COOH, R^2 = R^3 = H
(4) R = -CH_2OH, R^2 = H, R^3 = β-OH
(4a) R = -CH_2OAc, R^2 = H, R^3 = β-OAc



(5)



(6)



(7) R = H
(7a) R = Ac

complete proton and carbon assignments for all seven compounds have been determined by the use of a series of 2D NMR experiments.

Results and Discussion

Caesaldekarin A (**1**) was isolated as a white solid and had the molecular formula, $C_{22}H_{32}O_4$, as determined by HREIMS. The IR spectrum had absorptions typical of hydroxyl (3447 cm^{-1}), ester (1732 cm^{-1}), and furan (758 cm^{-1}) functionalities. The ^{1}H NMR spectrum had resonances due to the presence of three tertiary methyl groups at *δ* 0.98, 1.25, and 1.34; one secondary methyl group at *δ* 0.99 (d, J = 6.8 Hz), and one acetoxyl group at *δ* 2.06. The presence of a 1,2-disubstituted furan was evident from resonances at *δ* 7.22 (1H, d, J = 1.7 Hz) and 6.19 (1H, d, J = 1.7 Hz), while an oxymethine proton was observed at *δ* 5.23 (1H, t, J = 3.3 Hz). An examination of the HSQC[16] and HMBC spectra led to structure **1** for this compound. The structure is identical to that reported for caesaldekarin A, a cassane furanoditerpene recently isolated from *C. major* and shown to have an inhibitory effect on mitogen responses of spleen cells from BALB/C mice (IC_{50} = 10 *μ*g/mL) and caused 80% inhibition of interlukin-1 production at 10 *μ*g/mL.[15]

Caesaldekarin H (**2**) was isolated as a white solid and had the molecular formula $C_{22}H_{32}O_4$, as determined by HREIMS. The presence of hydroxyl, ester, and furan groups were evident from IR absorptions at 3487 cm^{-1}, 1741 cm^{-1}, and 757 cm^{-1}, respectively. The ^{1}H NMR spectrum had resonances for two tertiary methyl groups at *δ* 1.02 (H_3-20) and 1.00 (H_3-18), one secondary methyl at *δ* 1.01 (d, J = 6.8 Hz, H_3-17), and one acetoxyl group at *δ* 2.08. There were also two resonances at *δ* 4.43 (d, J = 10.7 Hz) and 4.05 (d, J = 10.7 Hz) associated with oxymethylene protons. In addition, there were resonances at *δ* 7.22 (d, J = 2.4 Hz, H-16) and 6.18 (d, J = 2.4 Hz, H-15) due to the presence of a 1,2-disubstituted furan as in compound **1**. The ^{13}C NMR spectrum exhibited resonances for all 22 carbon atoms. In particular, the carbons of the furan ring had resonances at *δ* 149.8 (C-12), 140.6 (C-16), 122.8 (C-13), and 109.6 (C-15). Resonances were also observed for an oxymethylene carbon at *δ* 67.5 and a nonprotonated oxygenated carbon at *δ* 76.6. The presence of an acetoxyl carbonyl was revealed by a resonance at *δ* 171.5. The HSQC spectrum indicated that the oxymethylene protons at *δ* 4.43 and 4.05 were directly attached to the carbon at *δ* 67.5. The proton at *δ* 4.05 also showed long-range HMBC correlations with the acetoxyl carbonyl at *δ* 171.5, a methyl carbon at *δ* 21.1 (C-18), and a methylene carbon at *δ* 30.8 (C-3). Also, the protons of the

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Table 1. ^{1}H NMR Assignments for Compounds A−G (**1-7A**)

H	1	2	3	4a	5	6[1]	7a
1	1.44 (m)	1.40 (m)	1.46 (m)	1.42 (m)	1.96 (m)	1.41 (m)	1.71 (m)
	1.53 (m)	1.48 (m)	1.51 (m)	1.51 (m)	2.10 (m)	1.50 (m)	1.68 (m)
2	1.51 (m)	1.46 (m)	1.50 (m)	1.49 (m)	1.69 (m)	1.49 (m)	1.65 (m)
	1.71 (m)	1.82 (m)	1.94 (m)	1.51 (m)	2.09 (m)	1.89 (m)	1.82 (m)
3	1.14 (m)	1.50 (m)	1.59 (m)	1.48 (m)	1.76 (12.6, 12.6, 5.0)	1.57 (m)	4.76 (dd, 11.9, 4.8)
	1.71 (m)	1.54 (m)	1.95 (m)	1.48 (m)	2.02 (m)	1.95 (m)	
5							1.49 (m)
6	5.23 (t, 3.3)	1.66 (m)	1.83 (m)	1.69 (dd, 13.8, 10.5)	2.28 (13.7, 7.9, 4.1)	1.85 (m)	1.48 (m)
		1.81 (m)	2.37 (m)	2.16 (dd, 13.8, 5.9)	2.62 (13.7, 8.1, 2.7)	2.24 (m)	1.89 (m)
7	1.51 (m)	1.48 (m)	1.53 (m)	5.28 (ddd, 10.4, 10.4, 5.9)	2.87 (17.8, 8.1, 4.1)	1.68 (m)	4.99 (m)
	2.19 (ddd, 13.4, 13.4, 3.3)	1.58 (m)	1.80 (m)		2.62 (13.7, 8.1, 2.7)	1.81 (m)	
8	1.26 (m)	1.78 (m)	1.81 (m)	1.93 (ddd, 11.0, 10.5, 4.7)		1.96 (m)	2.02 (m)
9	2.34 (m)	2.36 (m)	2.21 (m)	2.55 (dd, 11.0, 4.7		2.23 (m)	1.26 (m)
11	2.47 (dd, 18.0, 10.0)	2.36 (m)	2.34 (dd, 16.7, 11.1)	2.44 (dd, 15.1, 6.3)	7.35 (s)	2.38 (dd, 14.8, 8.2)	2.03 (m)
	2.51 (dd, 18.0, 8.0)	2.48 (dd, 15.9, 9.1)	2.50 (dd, 16.7, 6.1)	2.53 (dd, 15.1, 11.0)		2.48 (dd, 14.8, 6.8)	2.09 (m)
12							5.79 (t, 4.8)
14	2.57 (dq, 6.8, 5.7)	2.60 (m)	2.62 (m)	2.83 (dq, 7.3, 4.7)			
15	6.19 (d, 1.7)	6.18 (d, 2.4)	6.19 (d, 1.9)	6.19 (d, 1.7)	6.73 (d, 2.1)	6.28 (d, 1.8)	6.40 (dd, 17.9, 11.9)
16	7.22 (d, 1.7)	7.22 (d, 2.4)	7.22 (d, 1.9)	7.25 (d, 1.7)	7.54 (d, 2.1)	7.23 (d, 1.8)	5.09 (dd, 11.9, 2.3)
							5.45 (dd, 17.9, 2.3)
17	0.99 (d, 6.8)	1.01 (d, 6.8)	1.02 (d, 6.8)	1.00 (d, 7.3)	2.39 (s)	1.28 (s)	1.29 (s)
18	0.98 (s)	1.00 (s)	1.26 (s)	1.01 (s)	1.34 (s)	1.20 (s)	0.88 (s)
19	1.25 (s)	4.05 (d, 10.7)		4.05 (d, 10.5)			3.68 (d, 12.7)
		4.43 (d, 10.7)		4.40 (d, 10.5)			3.82 (d, 12.7)
20	1.34 (s)	1.02 (s)	0.94 (s)	1.08 (s)	1.15 (s)	0.86 (s)	0.99 (s)
3-Ac							2.12 (s)
6-Ac	2.06						
7-Ac				2.07 (s)			2.03 (s)
19-Ac		2.08 (s)		2.07 (s)			2.09 (s)
OMe					3.70 (s)	3.69 (s)	

[a] C-14−OCH_2CH_3: δ 3.14 (dq, 15.0, 7.0), δ 3.29 (dq, 15.0, 7.0), δ 1.14 (t, 7.0).

tertiary methyl group at δ 1.00 showed long-range correlations to the quaternary carbon at δ 76.6 (C-5), a quaternary carbon at δ 42.7 (C-4), the oxymethylene carbon at δ 67.5 (C-19), and the methylene carbon at δ 30.8 (C-3). This established that the methyl group at δ 1.00 was geminal to the oxymethylene carbon and that they were both attached to the quaternary carbon at δ 42.7 (C-4). The HMBC spectrum also revealed that the tertiary methyl group at δ 1.02 (C-20) had long-range correlations to a quaternary carbon at δ 41.4 (C-10), the oxygenated quaternary carbon at δ 76.6 (C-5), a methine carbon at δ 38.1 (C-9), and a methylene carbon at δ 32.2 (C-1). In addition, the secondary methyl at δ 1.01 showed HMBC correlations to the furan carbon at δ 122.8 (C-13) and a methine carbon at δ 31.4 (C-14). These results are summarized in Tables 1 and 2 and led to structure **2** for caesaldekarin H.

Demethylcaesaldekarin C (**3**), $C_{20}H_{28}O_4$, was the most abundant of these diterpenoids and had IR absorptions due to hydroxyl (3550 cm^{-1}), carboxylic acid (ca. 3300−2506 and 1701 cm^{-1}) and furan (758 cm^{-1}) functionalities. The ^{1}H NMR spectrum had resonances due to two tertiary methyl groups at δ 0.94 (H_3-20) and 1.26 (H_3-18) and one secondary methyl group at δ 1.02 (d, J = 6.8 Hz, H_3-17). A 1,2-disubstituted furan had resonances at δ 7.22 (d, J = 1.9 Hz, H-16) and 6.19 (d, J = 1.9 Hz, H-15). The ^{13}C NMR spectrum had a resonance at δ 77.3 (C-5) due to an oxygenated quaternary carbon and one at δ 181.3 (C-19) due to the carboxylic acid moiety. An examination of an HMBC spectrum of compound **3** indicated that the tertiary methyl group at δ 1.26 showed long-range correlations to the carboxylic acid carbon at δ 181.3 (C-19), a quaternary carbon at δ 49.0 (C-4), a methylene carbon at δ 32.0 (C-3), in addition to the oxygenated carbon at δ 77.3. These results (Tables 1 and 2) established the structure **3** for demethylcaesaldekarin C. The methyl ester of this compound was previously isolated from *C. major* and designated caesaldekarin C.[17]

Table 2. ^{13}C NMR Assigmnents for Compounds A−G (**1**−**7A**)

C no.	1	2	3	4a	5	6[a]	7a
1	34.6	32.2	32.3	32.0	32.9	32.2	36.2
2	18.2	24.2	18.6	17.8	19.4	18.7	23.1
3	38.1	30.8	32.0	30.5	31.6	32.0	73.9
4	38.9	42.7	49.0	42.6	48.7	49.0	40.4
5	76.2	76.6	77.3	77.3	75.5	76.8	43.8
6	72.3	26.4	27.8	32.3	25.5	27.7	26.6
7	31.4	17.8	24.7	71.7	23.7	20.0	75.7
8	30.4	34.4	34.6	39.5	126.6	36.0	46.6
9	37.9	38.1	37.5	36.9	143.0	40.6	46.0
10	41.4	41.4	42.0	40.9	43.9	42.0	36.5
11	21.7	22.2	22.5	22.4	105.8	22.3	24.5
12	149.5	149.8	149.4	149.0	153.8	151.0	122.4
13	122.3	122.8	122.3	121.9	125.7	122.1	141.1
14	31.1	31.4	31.6	27.5	128.3	77.3	73.7
15	109.4	109.6	109.5	109.6	104.9	107.7	134.7
16	140.3	140.6	140.3	140.7	144.3	140.9	114.2
17	17.6	17.5	17.5	17.2	15.9	25.5	23.8
18	27.6	21.1	24.1	21.0	23.9	23.9	13.6
19	25.7	67.5	181.3	67.0	177.5	177.3	64.9
20	16.5	16.9	15.3	17.2	27.5	15.1	14.8
3-Ac							169.4
							20.9
6-Ac	169.8						
	21.8						
7-Ac				170.7			170.6
				21.3			21.2
19-Ac		171.5		171.1			171.0
		21.0		21.1			21.6
OMe					51.6	51.6	

[a] C-14−OCH_2CH_3: δ 57.5 (t), δ 16.1 (q).

Caesaldekarin I (**4**) was purified as the diacetate (**4a**), $C_{24}H_{34}O_6$, and had IR absorptions characteristic of hydroxyl (3440 cm^{-1}), ester (1732 cm^{-1}), and furan (758 cm^{-1})

groups. The ^{1}H NMR spectrum had resonances due to the presence of two tertiary methyl groups at δ 1.01 and 1.08, one secondary methyl group at δ 1.00 (d, J = 7.3 Hz), and two acetoxyl groups at δ 2.07 (6H). An oxymethine proton had a signal at δ 5.28 (ddd, J = 10.4, 10.4, 5.9 Hz, H-7), while an oxymethylene group occurred as doublets at δ 4.40 and 4.05 (J = 10.5 Hz). Resonances at δ 7.25 (1H, d, J = 1.7 Hz) and 6.19 (1H, d, J = 1.7 Hz) were typical of a 1,2-disubstituted furan. The ^{13}C NMR spectrum had two resonances at δ 170.6 and 169.4 due to the acetoxyl carbonyls. There were also signals for three oxygenated carbons at δ 77.3 (s), 71.7 (d), and 67.0 (t). The secondary methyl at δ 1.00 was assigned to C-14 because it showed long-range correlations to carbons at δ 121.9 (C-13) and 39.5 (C-8). The latter carbon was directly attached to a proton at δ 1.93 as observed in an HMQC spectrum. In the ^{1}H−^{1}H COSY spectrum the oxymethine proton at δ 5.28 had cross peaks to H-8 and C-6 methylene protons at δ 2.16 (dd, J = 13.8, 5.9 Hz) and 1.69 (dd, J = 13.8, 10.5 Hz), thus supporting its assignment at C-7. The ^{1}H−^{1}H coupling constants suggested an axial disposition for the oxymethine proton and, hence, an equatorial acetoxyl group. The oxymethylene protons at δ 4.40 and 4.05 showed HMBC correlations to the acetoxyl carbonyl at δ 171.1, a quaternary carbon at δ 42.6 (C-4), a methyl carbon at δ 21.0 (C-18), and a methylene carbon at δ 30.5 (C-3). This indicated that the oxymethylene group had a geminal disposition with respect to the methyl group at C-4. The structure **4a** is, therefore, proposed for caesaldekarin I diacetate, and the NMR results are summarized in Tables 1 and 2.

Caesaldekarin J (**5**), $C_{21}H_{26}O_4$, had IR absorptions due to hydroxyl (3565 cm^{-1}), ester (1724 cm^{-1}), and furan (772 cm^{-1}) groups. The UV spectrum had absorption maxima at 212, 260, 282, and 292 nm, which suggested the presence of a benzofuran moiety in the structure. The ^{1}H NMR spectrum displayed the resonances for the 1,2-disubstituted furan in downfield shifted positions at δ 7.54 (d, J = 2.1 Hz) and 6.73 (d, J = 2.1 Hz). An additional aromatic proton at δ 7.35 (s), along with an aromatic methyl group at δ 2.39, confirmed the presence of a trisubstituted benzofuran moiety. In addition, there was a singlet at δ 3.70 (3H) due to the presence of a methoxycarbonyl group. The ^{13}C NMR spectrum had a resonance at δ 75.5 due to the presence of an oxygenated quaternary carbon. The HSQC spectrum indicated that the aromatic proton at δ 7.35 was directly attached to a carbon at δ 105.8 (C-11). This same proton showed HMBC correlations to aromatic carbons at δ 153.8 (C-12), 125.7 (C-13), and 126.6 (C-8), and a quaternary carbon at δ 43.9 (C-10). This evidence indicated that the aromatic proton was at C-11 in the cassane skeleton. The HMBC spectrum also revealed that the aromatic methyl at δ 2.39 had long-range correlations to the aromatic carbons at δ 128.3 (C-14), 126.6 (C-8), and 125.7 (C-13). On the other hand, the methyl group at δ 1.34 had HMBC correlations to the ester carbonyl at δ 177.5, the oxygenated carbon at δ 75.5 (C-5), the quaternary carbon at δ 48.7 (C-4), and a methylene carbon at δ 31.6 (C-3), thus establishing that it was geminal to the methoxycarbonyl group with both being attached to C-4. Caesaldekarin J was thus assigned structure **5**, and the NMR data are recorded in Tables 1 and 2. It is known that cassane furanoditerpenes bearing a C-14 hydroxyl group can be transformed into benzofurans by the action of mild acid treatment; however, **5** is presumed to be a natural product because no acid was used in its isolation process.[10]

Caesaldekarin K (**6**) was isolated as a white solid and had the molecular formula, $C_{23}H_{34}O_5$, on the basis of HREIMS. The IR spectrum had absorptions characteristic of hydroxyl (3528 cm^{-1}), ester (1718 cm^{-1}), and furan (756 cm^{-1}) functionalities. The ^{1}H NMR spectrum had resonances for three tertiary methyl groups at δ 0.86 (H_3-20), 1.20 (H_3-18), and 1.28 (H_3-17) and a methoxycarbonyl at δ 3.69. There were resonances characteristic of an ethoxy group at δ 3.14 (1H, dq, J = 15.0, 7.0 Hz), 3.29 (1H, dq, J = 15.0, 7.0 Hz), and 1.14 (3H, t, J = 7.0 Hz). The tertiary methyl group at δ 1.20 had HMBC correlations to the methoxycarbonyl at δ 177.3, a methylene carbon at δ 32.0 (C-3), a quaternary carbon at δ 49.0 (C-4), and an oxygenated carbon at δ 76.8 (C-5). On the other hand, the methylene proton at δ 3.14 showed HMBC correlations to the oxygenated quaternary carbon at δ 77.3 (C-14), while the tertiary methyl group at δ 1.28 also showed correlations to this same C-14 carbon, in addition to the furan carbon at δ 122.1 (C-13) and a methine carbon at δ 36.0 (C-8). The structure of caesaldekarin K is thus established as **6**. The ethoxy group at C-14 might have arisen from reaction with the solvent EtOH that was used for extraction of the plant material.

Caesaldekarin L (**7**) was isolated as the triacetate derivative (**7a**) in order to facilitate purification. The molecular formula, $C_{26}H_{38}O_7$, for **7a** was established by HREIMS. The ^{1}H NMR spectrum displayed signals for six methyls—three were tertiary and occurred at δ 0.88, 0.99, and 1.29, while the other three were acetoxyl methyls at δ 2.03, 2.09, and 2.12. Signals typical of oxymethine protons associated with acetoxyl groups were evident at δ 4.76 (1H, dd, J = 11.9, 4.8 Hz, H-3) and 4.99 (1H, m, H-7), while an oxymethylene group was revealed by resonances at δ 3.82 (d, J = 12.7 Hz) and 3.68 (d, J = 12.7 Hz). Signals for olefinic protons typical of a vinyl moiety were observed at δ 6.40 (1H, dd, J = 17.9, 11.9 Hz), 5.45 (1H, dd, J = 17.9, 2.3 Hz), and 5.09 (1H, dd, J = 11.9, 2.3 Hz). An isolated olefinic proton had a signal at δ 5.79 (t, J = 4.8 Hz, H-12). The ^{1}H−^{1}H COSY cross peaks for the oxymethine proton at δ 4.99 (H-7) indicated that it was vicinal to methylene protons at δ 1.89 (m) and 1.48 (m) as well as H-8 at δ 2.02.

The ^{13}C NMR spectrum had signals for three acetoxyl carbonyls at δ 171.0, 170.6, and 169.4 and four oxygenated carbons at δ 75.7 (d), 73.9 (d), 73.7 (s), and 64.9 (t). In the HMQC spectrum, the protons at δ 5.45 and 5.05 showed direct connectivity to a carbon at δ 114.2 (C-16), while the proton at δ 6.40 had direct connectivity to a carbon at δ 134.7. In the HMBC spectrum, the proton at δ 6.40 showed long-range correlation to the carbon at δ 122.4, while the vinyl protons at δ 5.45 and 5.05 correlated with the carbons at δ 141.1 (C-13) and 134.7 (C-15). The methyl group at δ 1.29 and the hydroxyl proton at δ 2.85 correlated with the carbon at δ 141.1 (C-13) as well as the oxygenated carbon at δ 73.7(C-14). Direct attachment of both the methyl and hydroxyl groups to C-14 was therefore established. The oxymethylene protons at δ 3.82 and 3.68, which were bonded to the carbon at δ 64.9 (C-19), as observed in the HMQC spectrum, showed long-range coupling to the acetoxyl carbonyl at δ 171.0, an oxygenated methine at δ 73.9 (C-3), and a quaternary carbon at δ 40.4 (C-4) in the HMBC spectrum. In addition, the methyl protons at δ 0.88 (H_3-18) had long-range correlations to the oxymethylene carbon at δ 64.9 and the quaternary carbon at δ 40.4 (C-4). This indicated that the oxymethylene group and the methyl at δ 0.88 were geminal to each other and attached to C-4, while the oxymethine at δ 73.9 (δ_H = 4.76 from HMQC) was assigned as C-3. The NOE difference spectrum established the β-orientations for H-8, the oxymeth-

ylene group at C-4 as well as the C-11 methylene proton at δ 2.03 from their response to irradiation of the C-10 methyl group. The H-3 and H-7 protons were determined to be α-oriented on the basis of their coupling constants. The structure **7** is therefore proposed for caesaldekarin L and the NMR assignments are recorded in Tables 1 and 2. This is the first report of a cassane diterpene from *C. bonduc* in which a C-5 hydroxyl group is absent; however, such a compound was isolated from *C. decapetala* var. *japonica*.[18]

Experimental Section

General Experimental Procedures. The IR spectra were recorded on a Perkin−Elmer 1725X FT-IR spectrometer. The UV spectra were obtained on a Hewlett-Packard 8452A spectrophotometer in MeOH solutions. The optical rotations were measured on a Perkin−Elmer 341 polarimeter in $CHCl_3$ solutions. All NMR spectra were recorded on a Varian UNITY 500 MHz spectrometer in $CDCl_3$ solutions using TMS as an internal standard. MS were recorded on a VG 70−25S mass spectrometer operating at 70 eV.

Plant Material. The roots of *C. bonduc* were collected in February 1997, along the East Coast Road, St. Andrew, Barbados. The plant material was identified by Dr. Sean Carrington, Department of Biological and Chemical Sciences, University of the West Indies, Barbados, where a voucher specimen (SC1785) was deposited.

Extraction and Isolation. The roots of *C. bonduc* (500 g) were dried, ground, and extracted with 95% EtOH (2.5 L) and the solvent evaporated in vacuo to give a brown viscous syrup (26 g). The extract was dissolved in 90% MeOH in H_2O (100 mL) and extracted with hexane (3 × 100 mL). The aqueous MeOH layer was diluted with H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 300 mL), dried over anhydrous Na_2SO_4, and the solvent evaporated to give a brown gum (24 g). The hexane extract (15.5 g) was flash chromatographed on Si gel using hexane−Me_2CO (9:1) as eluent, to afford nine major fractions. Preparative TLC using the same solvent mixture on fractions 1, 2, 5, and 8 gave compounds A (**1**, 2.4 mg), B (**2**, 2.7 mg), F (**6**, 4.1 mg), and E (**5**, 1.2 mg). The CH_2Cl_2 extract (9.5 g) was flashed chromatographed over Si gel with light petroleum−Me_2CO (4:1) as eluent to give six major fractions. Fraction 1 was rechromatographed using the same solvent, followed by preparative TLC to give compound C (**3**, 4.5 mg). Fraction 3 was acetylated using Ac_2O−pyridine and purified by preparative TLC to give compounds D (**4a**, 2.0 mg) and G (**7a**, 0.8 mg).

Compound A (1): white solid; $[\alpha]^{23}_D$ −20.1° (*c* 0.07, $CHCl_3$); IR(film) ν_{max} 3447, 1732, 758 cm^{-1}; UV(MeOH) λ_{max} (log ϵ) 210 (3.79) nm; EIMS *m/z* 460 $[M]^+$ (71), 318 (13), 267 (16), 233 (27), 215 (44), 197 (26), 145 (41), 109 (100); HREIMS *m/z* 360.2299 (calcd for $C_{22}H_{32}O_4$ 360.2300); ^1H and ^{13}C NMR data, see Tables 1 and 2, respectively.

Compound B (2): white solid; $[\alpha]^{23}_D$ +8.1° (*c* 0.06, $CHCl_3$); IR (film) ν_{max} 3487, 1741, 757 cm^{-1}; UV(MeOH) λ_{max} (log ϵ) 214 (3.08) nm; EIMS *m/z* 360 $[M]^+$ (22), 300 (24), 255 (9), 218 (43), 187 (28), 159 (26), 149 (91), 109 (100); HREIMS *m/z* 360.2296 (calcd for $C_{22}H_{32}O_4$ 360.2300); ^1H and ^{13}C NMR data, see Tables 1 and 2, respectively.

Compound C (3): white solid; $[\alpha]^{23}_D$ +35.2° (*c* 0.08, $CHCl_3$); IR (film) ν_{max} 3550, 1732, 758 cm^{-1}; UV(MeOH) λ_{max} (log ϵ) 228 (3.88) nm; EIMS *m/z* 332 $[M]^+$ (78), 314 (51), 299 (9), 268 (6), 240 (6), 215 (35), 187 (23), 147(100) 109 (53); HREIMS *m/z* 332.1994 (calcd for $C_{20}H_{28}O_4$ 332.1988); ^1H and ^{13}C NMR data, see Tables 1 and 2, respectively.

Compound D diacetate (4a): clear gum; $[\alpha]^{23}_D$ +32.7° (*c* 0.05, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3440, 1735 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 220 (3.67) nm; EIMS *m/z* 418 $[M]^+$ (16), 358 (4), 340 (27), 280 (21), 265 (27), 216 (32), 145 (100), 109 (29); HREIMS *m/z* 418.2373 (calcd for $C_{24}H_{34}O_6$ 418.2355); ^1H and ^{13}C NMR data, see Tables 1 and 2, respectively.

Compound E (5): white solid; $[\alpha]^{23}_D$ +47.6° (*c* 0.07, $CHCl_3$); IR (film) ν_{max} 3565, 1724, 762 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 212 (4.38), 260 (4.33), 282 (4.10), 292 (4.06) nm; EIMS *m/z* 342 $[M]^+$ (23), 325 (33), 324 (100), 249 (52), 209 (60), 185 (37); HREIMS *m/z* 342.1830 (calcd for $C_{21}H_{26}O_4$ 342.1831); ^1H and ^{13}C NMR data, see Tables 1 and 2, respectively.

Compound F (6): white solid; $[\alpha]^{23}_D$ +28.2° (*c* 0.07, $CHCl_3$); IR (film) ν_{max} 3528, 1718, 756 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 216 (3.92) nm; EIMS *m/z* 390 $[M]^+$ (8), 375 (43), 344 (56), 152 (100), 144 (59); HREIMS *m/z* 390.2409 (calcd for $C_{23}H_{34}O_5$ 390.2406); ^1H and ^{13}C NMR data, see Tables 1 and 2, respectively.

Compound triacetate (7a): colorless gum; $[\alpha]^{23}_D$ +10.9° (*c* 0.05, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3400, 1735 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 222, 260 (3.89, 3.71) nm; EIMS *m/z* 462 $[M]^+$ (2), 447 (9), 402 (60), 387 (26), 342 (24), 282 (32), 267 (100), 197 (26), 105 (54); HREIMS *m/z* 462.2522 (calcd for $C_{26}H_{38}O_7$ 462.2618); ^1H and ^{13}C NMR data, see Tables 1 and 2, respectively.

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