Supporting Information for

Thirteen Novel Cycloartane-type Triterpenes from *Combretum quadrangulare*

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Esterification of 1–13 with Diazomethane. To a MeOH solution of each acid, excess CH_2N_2 in ether was added and the mixture was left overnight at room temperature. Evaporattion under reduced pressure yielded each methyl ester.

Dimethyl Quadrangularate F (1a): colorless amorphous solid; ^{1}H NMR (pyridine-d_5) δ 6.50 (1H, d, J = 6.0 Hz, OH-3), 6.05 (1H, d, J = 16.0 Hz, H-24), 5.91 (1H, d, J = 3.0 Hz, OH-1), 5.84 (1H, dt, J = 16.0, 6.0 Hz, H-23), 5.36 (1H, dd, J = 12.5, 4.5 Hz, H-3), 3.85 (1H, td, J = 4.0, 3.0 Hz, H-1), 3.69 (3H, s, MeO-21), 3.66 (3H, s, MeO-28), 3.27 (1H, dd, J = 12.0, 4.5 Hz, H-5), 2.41 (1H, ddd, J = 13.0, 4.5, 4.0 Hz, H-2), 2.22 (1H, ddd, J = 13.0, 12.0, 3.5 Hz, H-2), 1.61 (3H, s, H_3-29), 1.54 (3H, s, H_3-26), 1.52 (3H, s, H_3-27), 1.18 (3H, s, H_3-18), 0.98 (3H, s, H_3-30), 0.76 (1H, d, J = 4.5 Hz, H-19), 0.48 (1H, d, J = 4.5 Hz, H-19); HRFABMS *m/z* 585.3420 [calcd for $C_{32}H_{50}O_8Na$ $(M + Na)^+$, 585.3403].

Dimethyl Quadrangularate G (2a): colorless amorphous solid; ^{1}H NMR (pyridine-d_5) δ 6.45 (1H, d, J = 5.5 Hz, OH-3), 6.41 (1H, d, J = 4.0 Hz, OH-24), 5.85 (1H, d, J = 3.0 Hz, OH-1), 5.35 (1H, ddd, J = 12.0, 5.5, 4.5 Hz, H-3), 5.20 (1H, br s, H-26), 4.93 (1H, br s, H-26), 4.40 (1H, td, J = 5.0, 4.0 Hz, H-24), 3.84 (1H, td, J = 4.0, 3.0 Hz, H-1), 3.68 (3H, s, MeO-21), 3.65 (3H, s, MeO-28), 3.22 (1H, dd, J = 12.5, 4.5 Hz, H-5), 2.64 (1H, dt, J = 12.0, 5.0 Hz, H-11), 2.56 (1H, td, J = 10.5, 4.5 Hz, H-17), 2.42 (1H, ddd, J = 13.0, 4.5, 4.0 Hz, H-2), 2.34 (1H, m, H-20), 2.20 (1H, ddd, J = 13.0, 12.0, 3.5 Hz, H-2), 1.89 (3H, s, H_3-27), 1.60 (3H, s, H_3-29), 1.19 (3H, s, H_3-18), 0.98 (3H, s, H_3-30), 0.77 (1H, d, J = 4.5 Hz, H-19), 0.46 (1H, d, J = 4.5 Hz, H-19); HRFABMS *m/z* 569.3427 [calcd for $C_{32}H_{50}O_7Na$ $(M + Na)^+$, 569.3455].

Dimethyl 24-Epiquadrangularate G (3a): colorless amorphous solid; ^{1}H NMR (pyridine-d_5) δ 6.50 (1H, d, J = 6.0 Hz, OH-3), 6.44 (1H, d, J = 4.0 Hz, OH-24), 5.90 (1H, d, J = 3.0 Hz, OH-1), 5.37 (1H, ddd, J = 12.0, 6.0, 4.0 Hz, H-3), 5.31 (1H, br s, H-26), 4.95 (1H, br s, H-26), 4.43 (1H, ddd, J = 5.5, 5.0, 4.0 Hz, H-24), 3.84 (1H, td, J = 4.0, 3.0 Hz, H-1), 3.67 (3H, s, MeO-21), 3.65 (3H, s, MeO-28), 3.24 (1H, dd, J = 12.5, 4.5 Hz, H-5), 2.64 (2H, m, H-11), 2.44 (1H, dt, J = 13.0, 4.0 Hz, H-2), 2.35 (1H, m, H-20), 2.21 (1H, ddd, J = 13.0, 12.0, 3.5 Hz, H-2), 1.88 (3H, s, H_3-27), 1.62 (3H, s, H_3-29), 1.20 (3H, s, H_3-18), 1.00 (3H, s, H_3-30), 0.75 (1H, d, J = 4.5 Hz, H-19), 0.45 (1H, d, J = 4.5 Hz, H-19); HRFABMS *m/z* 569.3459 [calcd for $C_{32}H_{50}O_7Na$ $(M + Na)^+$, 569.3454].

Methyl Quadrangularate H (4a): colorless amorphous solid; ^{1}H NMR (pyridine-d_5) δ 6.52 (1H, d, J = 6.0 Hz, OH-3), 5.96 (1H, br s, H-26), 5.89 (1H, br s, OH-1), 5.68 (1H, br s, H-26), 5.38 (1H, ddd, J = 12.5, 6.0, 4.5 Hz, H-3), 3.85 (1H, br s, H-1), 3.70 (3H, s, MeO-21), 3.66 (3H, s, MeO-28), 3.24 (1H, dd, J = 12.0, 4.5 Hz, H-5), 2.85 (1H, ddd, J = 17.0, 9.0, 6.5 Hz, H-23), 2.67 (1H, br t, J = 8.0 Hz, H-17), 2.58 (1H, td, J = 11.0, 3.5 Hz, H-11), 2.44 (1H, ddd, J = 13.0, 4.5, 4.0 Hz, H-2), 2.33 (1H, br q, J = 9.0 Hz, H-20), 2.22 (1H, ddd, J = 13.0, 12.0, 3.5 Hz, H-2), 1.88 (3H, s, H_3-27), 1.61 (3H, s, H_3-29), 1.58 (3H, s, H_3-18), 0.99 (3H, s, H_3-30), 0.76 (1H, d, J = 4.5 Hz, H-19), 0.45 (1H, d, J = 4.5 Hz, H-19); HRFABMS *m/z* 567.3296 [calcd for $C_{32}H_{48}O_7Na$ $(M + Na)^+$, 567.3298].

Methyl Quadrangularate J (6a): colorless amorphous solid; ^{1}H NMR (pyridine-d_5) δ 6.51 (1H, d, J = 6.0 Hz, OH-3), 5.90 (1H, d, J = 3.0 Hz, OH-1), 5.66 (1H, ddd, J = 15.5, 8.5, 6.0 Hz, H-23), 5.56 (1H, d, J = 15.5 Hz, H-24), 5.39 (1H, ddd, J = 12.0, 6.0, 4.5 Hz, H-3), 3.88 (1H, td, J = 4.0, 3.0 Hz, H-1), 3.66 (3H, s, MeO-28), 3.27 (1H, dd, J = 12.0, 4.5 Hz, H-5), 3.21 (3H, s, MeO-25), 2.73 (1H, ddd, J = 13.0, 9.0, 8.0 Hz, H-11), 2.45 (1H, ddd, J = 13.0, 4.5, 4.0 Hz, H-2), 2.24 (2H, m, H-2, H-22), 1.63 (3H, s, H_3-29), 1.32 (6H, s, H_3-26, H_3-27), 1.05 (3H, s, H_3-18), 0.99 (3H, s, H_3-30), 0.96 (3H, d, J = 6.5 Hz, H_3-21), 0.78 (1H, d, J = 4.5 Hz, H-19), 0.53 (1H, d, J = 4.5 Hz, H-19); HRFABMS *m/z* 539.3698 [calcd for $C_{32}H_{52}O_5Na$ $(M + Na)^+$, 539.3713].

Methyl Quadrangularate K (7a): colorless amorphous solid; ^{1}H NMR (pyridine-d_5) δ 6.47 (1H, d, J = 6.0 Hz, OH-3), 5.94 (2H, m, H-23, H-24), 5.86 (1H, d, J = 3.0 Hz, OH-1),

5.37 (1H, ddd, J = 12.0, 6.0, 4.5 Hz, H-3), 3.87 (1H, td, J = 4.0, 3.0 Hz, H-1), 3.64 (3H, s, MeO-28), 3.25 (1H, dd, J = 12.0, 4.5 Hz, H-5), 2.72 (1H, ddd, J = 13.0, 9.0, 8.0 Hz, H-11), 2.43 (1H, ddd, J = 13.0, 4.5, 4.0 Hz, H-2), 2.30 (1H, m, H-23), 2.23 (1H, ddd, J = 13.0, 12.0, 3.5 Hz, H-2), 1.62 (3H, s, H_3-29), 1.55 (6H, s, H_3-26, H_3-27), 1.03 (3H, s, H_3-18), 0.97 (3H, s, H_3-30), 0.95 (3H, d, J = 6.5 Hz, H_3-21), 0.77 (1H, d, J = 4.5 Hz, H-19), 0.52 (1H, d, J = 4.5 Hz, H-19); HRFABMS *m/z* 525.3553 [calcd for $C_{31}H_{50}O_5Na$ $(M + Na)^+$, 525.3556].

Methyl Quadrangularate L (8a): colorless amorphous solid; ^{1}H NMR (pyridine-d_5) δ 6.50 (1H, d, J = 6.0 Hz, OH-3), 6.88 (1H, d, J = 4.0 Hz, OH-24), 5.79 (1H, d, J = 3.0 Hz, OH-1), 5.36 (1H, ddd, J = 12.0, 6.0, 4.5 Hz, H-3), 3.85 (1H, td, J = 4.0, 3.0 Hz, H-1), 3.76 (1H, ddd, J = 9.0, 4.0, 2.5 Hz, H-24), 3.63 (3H, s, MeO-28), 3.25 (1H, dd, J = 12.0, 4.5 Hz, H-5), 2.69 (1H, ddd, J = 13.0, 9.0, 8.0 Hz, H-11), 2.41 (1H, ddd, J = 12.5, 4.5, 4.0 Hz, H-2), 2.22 (1H, dd, J = 12.5, 12.0, 3.5 Hz, H-2), 1.61 (3H, s, H_3-29), 1.54 (3H, s, H_3-26), 1.51 (3H, s, H_3-27), 1.02 (3H, s, H_3-18), 0.98 (3H, d, J = 6.5 Hz, H_3-21), 0.95 (3H, s, H_3-30), 0.75 (1H, d, J = 4.5 Hz, H-19), 0.50 (1H, d, J = 4.5 Hz, H-19); HRFABMS *m/z* 543.3668 [calcd for $C_{31}H_{52}O_6Na$ $(M + Na)^+$, 543.3662].

Methyl 7β-Hydroxy-23-deoxojessate (12a): colorless amorphous solid; ^{1}H NMR (pyridine-d_5) δ 6.55 (1H, d, J = 6.0 Hz, OH-3), 6.00 (1H, d, J = 5.5 Hz, OH-7), 5.50 (1H, d, J = 3.0 Hz, OH-1), 5.40 (1H, ddd, J = 12.0, 6.0, 4.5 Hz, H-3), 4.86 (1H, br s, H-31), 4.85 (1H, br s, H-31), 4.07 (1H, ddd, J = 11.0, 8.5, 4.0 Hz, H-7), 3.94 (1H, td, J = 4.0, 3.0 Hz, H-1), 3.52 (3H, s, MeO-28), 3.52 (1H, dd, J = 13.0, 4.0 Hz, H-5), 2.61 (1H, ddd, J = 13.0, 8.0, 4.0 Hz, H-11), 2.47 (1H, ddd, J = 13.0, 4.5, 4.0 Hz, H-2), 2.25 (3H, m, H-2, H-6, H-23), 2.05 (1H, d, J = 8.5 Hz, H-8), 1.62 (3H, s, H_3-29), 1.30 (3H, s, H_3-30), 1.14 (3H, s, H_3-18), 1.06 (3H, d, J = 7.0 Hz, H_3-26), 1.05 (3H, d, J = 7.0 Hz, H_3-27), 1.00 (1H, d, J = 4.5 Hz, H-19), 0.98 (3H, d, J = 5.0 Hz, H_3-21), 0.55 (1H, d, J = 4.5 Hz, H-19); HRFABMS *m/z* 539.3704 [calcd for $C_{32}H_{52}O_5Na$ $(M + Na)^+$, 539.3712].

Dimethyl Norquadrangularate A (13a): colorless amorphous solid; ^{1}H NMR (pyridine-d_5) δ 6.50 (1H, d, J = 6.0 Hz, OH-3), 5.91 (1H, s, OH-1), 5.40 (1H, ddd, J = 12.0, 6.0, 4.5 Hz, H-3), 3.87 (1H, br s, H-1), 3.67 (6H, s, MeO-24, MeO-28), 3.27 (1H,

dd, J = 11.5, 4.5 Hz, H-5), 2.44 (3H, m, H-11, H_2-23), 2.33 (1H, m, H-2), 2.24 (1H, ddd, J = 12.5, 12.0, 2.0 Hz, H-2), 1.63 (3H, s, H_3-29), 1.00 (3H, s, H_3-18), 0.97 (3H, s, H_3-30), 0.87 (3H, d, J = 5.0 Hz, H_3-21), 0.76 (1H, d, J = 4.5 Hz, H-19), 0.51 (1H, d, J = 4.5 Hz, H-19); HRFABMS *m/z* 513.3196 [calcd for $C_{29}H_{46}O_6Na$ $(M + Na)^+$, 513.3192].

Acetylation of Methyl Quadrangularate G (2a) and Methyl 7β-Hydroxy-23-deoxojessate (12a). A solution of **2a** (10.0 mg) or **12a** (6.0 mg) in dry pyridine (0.5 mL) and acetic anhydride (0.5 mL) was stirred overnight at room temperature. After aqueous work-up, the reaction mixture was extracted with $CHCl_3$ (5 mL x 3), and the $CHCl_3$ extract was washed with water, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to yield a triacetate **2b** (10.5 mg; 85.3%) or **12b** (5.5 mg, 73.7%).

Methyl 1,3,24-Tri-*O*-acetylquadrangularate G (2b): colorless amorphous solid; ^{1}H NMR (pyridine-d_5) δ 5.95 (1H, dd, J = 12.5, 4.5 Hz, H-3), 5.43 (1H, t, J = 5.0 Hz, H-24), 5.10 (1H, br s, H-26), 4.97 (1H, br s, H-26), 4.89 (1H, br s, H-1), 3.76 (3H, s, MeO-21), 3.70 (3H, s, MeO-28), 2.94 (1H, dd, J = 12.0, 4.0 Hz, H-5), 2.42 (2H, m, H-11, H-17), 2.26 (1H, m, H-20), 2.37 (1H, ddd, J = 13.0, 4.5, 4.0 Hz, H-2), 2.17 (1H, ddd, J = 13.0, 12.5, 3.5 Hz, H-2), 2.07, 2.03, 1.98 (each 3H, s, Ac × 3), 1.74 (3H, s, H_3-27), 1.63 (1H, t, J = 8.0 Hz, H-8), 1.80 (3H, s, H_3-29), 1.35 (3H, s, H_3-18), 0.96 (3H, s, H_3-30), 0.80 (1H, d, J = 4.5 Hz, H-19), 0.50 (1H, d, J = 4.5 Hz, H-19); HRFABMS *m/z* 695.3781 [calcd for $C_{38}H_{56}O_{10}Na$ $(M + Na)^+$, 695.3771].

Methyl 1,3,7-Tri-*O*-acetyl-23-deoxojessate (12b): colorless amorphous solid; ^{1}H NMR (pyridine-d_5) δ 5.96 (1H, dd, J = 12.0, 4.5 Hz, H-3), 5.17 (1H, ddd, J = 11.0, 8.5, 4.0 Hz, H-7), 5.05 (1H, br s, H-1), 4.87 (1H, br s, H-31), 4.85 (1H, br s, H-31), 3.65 (3H, s, MeO-28), 3.23 (1H, dd, J = 13.0, 4.0 Hz, H-5), 2.44 (1H, ddd, J = 13.0, 4.5, 4.0 Hz, H-2), 2.26 (1H, m, H-25), 2.20 (1H, m, H-2), 2.05, 2.02, 1.98 (each 3H, s, Ac × 3), 1.44 (3H, s, H_3-29), 1.13 (1H, d, J = 4.5 Hz, H-19), 1.10 (3H, s, H_3-30), 1.07 (3H, d, J = 7.0 Hz, H_3-26), 1.06 (3H, d, J = 7.0 Hz, H_3-27), 0.95 (3H, s, H_3-18), 0.91 (3H, d, J = 5.0 Hz, H_3-21), 0.54 (1H, d, J = 4.5 Hz, H-19); HRFABMS *m/z* 665.4009 [calcd for $C_{38}H_{58}O_8Na$ $(M + Na)^+$, 665.4029].

^{13}C NMR Data (100 MHz) of Compounds **1a–4a**, **6a–8a**, **12a**, **13a**, **2b** and **12b** in Pyridine-d_5

position	**1a**	**2a**	**2b**[a]	**3a**	**4a**	**6a**	**7a**	**8a**	**12a**	**12b**[b]	**13a**
1	72.2	72.2	75.2	72.2	72.2	72.2	72.3	72.2	72.3	74.6	72.2
2	38.7	38.6	38.9	38.7	38.7	38.8	38.7	38.7	38.7	36.9	38.1
3	70.4	70.5	73.5	70.4	70.4	70.5	70.5	70.5	70.4	73.0	70.5
4	56.0	56.0	53.1	56.0	56.0	56.0	56.1	56.1	55.7	52.6	56.0
5	37.9	37.8	35.0	37.8	37.8	37.9	38.0	37.9	37.1	35.5	38.6
6	23.1	23.1	22.2	23.1	23.1	23.3	23.4	23.4	34.0	32.6	23.3
7	25.6	27.2	26.9	27.2	27.1	28.2	28.3	28.4	69.4	71.4	28.2
8	47.6	47.7	45.9	47.7	47.6	48.1	48.1	48.2	55.0	52.2	48.0
9	20.7	20.8	20.8	20.7	20.7	20.8	20.8	20.8	21.0	21.4	20.7
10	30.3	30.3	28.4	30.3	30.3	30.1	30.0	30.0	30.6	28.4	30.0
11	25.3	26.0	26.0	25.9	26.0	26.1	26.1	26.0	26.6	24.5	26.0
12	30.5	30.6	30.2	30.5	30.6	33.1	33.1	33.2	33.3	31.7	31.3
13	45.5	45.5	45.3	45.5	45.5	45.5	45.5	45.5	46.0	45.7	44.5
14	48.8	48.5	48.0	48.2	48.9	49.1	49.1	49.1	49.2	48.7	49.1
15	35.4	33.7	30.5	33.6	35.3	35.8	35.9	35.8	37.6	36.4	35.7
16	27.0	25.6	24.6	25.6	25.6	25.8	25.8	25.8	28.8	28.2	25.8
17	49.2	48.8	49.0	48.8	49.5	52.2	51.5	52.9	52.0	48.8	52.3

18	18.1	18.1	17.8	18.3	18.1	18.4	18.4	18.4	17.7	16.4	18.3
19	29.5	29.5	28.0	29.5	29.5	29.7	29.7	29.7	27.9	26.8	29.6
20	49.6	49.7	49.4	49.8	47.8	36.6	36.9	36.3	36.5	35.2	35.9
21	175.5	176.5	176.0	176.4	176.1	18.5	18.6	18.5	18.7	18.5	18.0
22	36.0	29.3	27.5	29.0	27.5	39.6	39.5	34.1	35.4	34.0	31.0
23	126.6	35.4	30.9	35.4	35.3	128.7	124.5	28.9	31.7	30.9	31.0
24	138.0	75.3	77.3	74.5	200.8	137.5	141.6	79.0	156.7	156.6	174.4
25	81.0	149.3	143.4	150.3	144.5	74.8	69.7	72.7	34.0	32.6	
26	24.9	110.8	113.8	110.1	124.7	26.5	30.9	26.1	22.1	22.1	
27	24.7	17.7	17.7	18.1	17.7	25.9	30.1	26.1	22.0	21.9	
28	178.2	178.1	175.9	178.2	178.1	178.2	178.2	178.2	178.0	175.4	176.9
29	9.5	9.4	10.1	9.5	9.4	9.5	9.5	9.5	9.4	9.9	9.5
30	19.3	19.4	18.9	19.3	19.3	19.4	19.4	19.5	19.1	18.9	19.4
31									106.6	106.7	
MeO-21	50.9	51.0	51.1	51.0	51.1						
MeO-24											51.3
MeO-25						50.1					
MeO-28	51.5	51.4	52.1	51.5	51.4	51.5	52.3	51.5	51.4	51.7	51.4

[a] The signals of the three acetyl groups appeared at δ 170.0, 169.9, 169.8, 21.4, 21.0, 20.9.

[a, b] The signals of the three acetyl groups appeared at δ 169.9, 21.8, 21.3, 20.9.