Supporting Information

(9 Pages)

Total Syntheses of Sesterpenic Acids: Refuted (±)-Bilosespenes A and B

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compound **1**:

IR (neat) ν 3500-2500, 1691, 1639, 1439, 1251, 1169, 886 cm^{-1}; MS (EI, 70 eV) *m/z* (% base peak) 372 (M^+, 32), 289 (100), 243 (29), 207 (18), 189 (58), 147 (35), 135 (66), 121 (86), 107 (58), 95 (66); HRMS (EI) calcd for $C_{25}H_{40}O_2$ 372.3028, Found 372.3025. Anal.Calcd for $C_{25}H_{40}O_2$: C, 80.59; H, 10.82. Found: C, 80.62; H, 10.78.

compound **2**:

IR (neat) ν 3500-2500, 1691, 1638, 1440, 1376, 1251, 1170, 932, 867 cm^{-1}; MS (EI, 70 eV) *m/z* (% base peak) 372 (M^+, 4), 289 (29), 243 (7), 189 (12), 135 (22), 121 (18), 107 (22), 95 (21), 32 (89), 28 (100); HRMS (EI) calcd for $C_{25}H_{40}O_2$ 372.3028, Found 372.3026.

compound **3**:

IR (neat) ν 3016, 2960, 2879, 1729, 1448, 1376, 1221, 1119, 1051, 952, 868, 743 cm^{-1}; ^1H NMR (C_6D_6, 400 MHz) δ 0.93 (s, 3H), 1.30 (d, *J* = 7.2 Hz, 3H), 1.34 (s, 3H), 1.50-1.62 (m, 3H), 1.74-1.90 (m, 4H), 2.26 (d, *J* = 6.0 Hz, 1H), 2.43 (dq, *J* = 7.2, 7.2 Hz, 1H), 2.67-2.72 (m, 1H), 3.21 (s, 3H), 3.48 (d, *J* = 8.0 Hz, 1H), 3.56-3.58 (m, 4H), 3.70 (dd, *J* = 3.2, 8.0 Hz, 1H), 5.32-5.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.7 (CH_3), 19.5 (CH_2), 23.7 (CH_3), 24.9 (CH_2), 29.8 (CH_3), 33.8 (CH), 36.6 (C), 37.5 (CH_2), 41.7 (CH), 45.2 (CH), 52.0 (CH_3), 57.8 (CH), 64.6 (CH_2×2), 73.1 (CH_2), 105.2 (C), 109.9 (C), 125.5 (CH), 129.9 (CH), 208.9 (C); MS (EI, 70 eV) *m/z* (% base peak) 350 (M^+, 7), 335 (3), 291 (3), 235 (6), 201 (21), 166 (13), 125 (31), 107 (21), 87 (100); HRMS (EI) calcd for $C_{20}H_{30}O_5$ 350.2093, Found 350.2102. Anal.Calcd for $C_{20}H_{30}O_5$: C, 68.54; H, 8.63. Found: C, 68.48; H, 8.73.

compound **4**:

IR (neat) ν 3473, 2949, 2880, 1664, 1443, 1375, 1253, 1204, 1052, 998, 953, 865 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.33 (s, 3H), 1.38 (ddd, *J* = 2.0, 3.2, 13.2 Hz, 1H), 1.65 (s, 3H), 1.66-1.70 (m, 2H), 1.81 (d, *J* = 2.4 Hz, 3H), 1.85 (dm, *J* = 13.2 Hz, 1H), 2.05-2.21 (m, 3H), 2.43 (ddd, *J* = 3.2, 3.2, 6.4 Hz, 1H), 2.86 (dd, *J* = 1.8, 4.2 Hz, 1H), 3.29 (s, 3H), 3.75 (d, *J* = 7.2 Hz, 1H), 3.92-3.96 (m, 4H), 4.03 (dd, *J* = 4.0, 7.2 Hz, 1H), 4.25 (s, 1H), 5.50 (dd, *J* = 6.8, 8.0 Hz, 1H), 5.88-5.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.8 (CH_3), 20.7 (CH_3), 22.9 (CH_2), 23.7 (CH_3), 30.7 (CH_2), 36.0 (CH), 38.5 (CH_2), 42.5 (CH), 47.2 (CH), 51.2 (CH_3), 64.6 (CH_2×2), 73.1 (CH_2), 81.8 (C), 110.0 (C), 110.3 (C), 126.3 (CH), 128.7 (CH), 131.7 (C), 137.0 (C); MS (EI, 70 eV) *m/z* (% base peak) 350 (M^+, 2), 335 (2), 318 (8), 248 (8), 175 (5), 111 (13), 107 (61), 87 (100), 70 (33); HRMS (EI) calcd for $C_{20}H_{30}O_5$ 350.2093, Found 350.2113.

compound **9**:

IR (neat) ν 2963, 2936, 2868, 1727, 1459, 1448, 1378, 1222, 1093, 1041, 971, 931, 865 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.83 (ddd, *J* = 3.6, 13.2, 13.2 Hz, 1H), 0.96-1.07 (m, 1H), 1.08 (s, 3H), 1.23 (d, *J* = 7.2 Hz, 3H), 1.35 (s, 3H), 1.17-1.47 (m, 4H), 1.55-1.82 (m, 4H), 2.16 (d, *J* = 6.4 Hz, 1H), 2.25-2.35 (m, 2H), 2.63 (dq, *J* = 7.2, 8.8 Hz, 1H), 3.18 (s, 3H), 3.70 (d, *J* = 8.4 Hz, 1H), 3.88 (dd, *J* = 3.6, 8.4 Hz, 1H), 3.92-4.00 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.5 (CH_3), 19.4 (CH_2), 19.5 (CH_2), 23.7 (CH_3), 26.8 (CH_2), 27.1 (CH_3), 29.4 (CH_2), 35.9 (C), 37.6 (CH), 38.3 (CH_2), 41.3 (CH), 47.2 (CH), 51.5 (CH_3), 59.5 (CH), 64.6 (CH_2×2), 72.4 (CH_2), 105.0 (C), 110.0 (C), 209.8 (C); MS (EI, 70 eV) *m/z* (% base peak)

352 (M^+, 0.1), 337 (5), 293 (12), 169 (35), 168 (20), 110 (17), 86 (100); HRMS (EI) calcd for $C_{20}H_{32}O_5$ 352.2250, Found 352.2276. Anal.Calcd for $C_{20}H_{32}O_5$: C, 68.15; H, 9.15. Found: C, 67.90; H, 9.11.

compound **10**:

IR (neat) ν 2968, 2940, 2870, 1717, 1459, 1378, 1090, 1056, 1038, 996, 970, 858 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.82-0.91 (m, 1H), 0.97-1.10 (m, 1H), 1.08 (s, 3H), 1.22 (s, 3H), 1.22-1.33 (m, 1H), 1.33 (s, 3H), 1.42-2.06 (m, 12H), 1.56 (s, 3H), 1.66 (s, 3H), 2.18 (d, *J* = 6.4 Hz, 1H), 2.29-2.37 (m, 1H), 3.11 (s, 3H), 3.63 (d, *J* = 8.8 Hz, 1H), 3.80 (dd, *J* = 4.4, 8.8 Hz, 1H), 3.91-3.99 (m, 4H), 4.96-4.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7 (CH_3), 19.2 (CH_2), 19.6 (CH_3), 19.7 (CH_2), 22.5 (CH_2), 23.7 (CH_3), 25.7 (CH_3), 26.8 (CH_3), 27.4 (CH_2), 29.7 (CH_2), 36.3 (C), 37.4 (CH), 41.1 (CH_2), 42.1 (CH_2), 50.4 (CH_3), 50.6 (C), 54.5 (CH), 59.3 (CH), 64.6 (CH_2×2), 71.7 (CH_2), 104.3 (C), 110.0 (C), 123.8 (CH), 131.6 (C), 208.9 (C); MS (EI, 70 eV) *m/z* (% base peak) 419 (M^+ - 15, 3), 320 (100), 292 (10), 243 (6), 218 (40), 190 (46), 168 (41), 153 (14), 109 (21), 87 (18); HRMS (EI) calcd for $C_{25}H_{39}O_5$ (M^+ - 15) 419.2798, Found 419.2788. Anal.Calcd for $C_{26}H_{42}O_5$: C, 71.85; H, 9.74. Found: C, 71.75; H, 9.72.

compound **11**:

IR (neat) ν 3449, 2966, 2927, 2875, 1700, 1450, 1378, 1058, 857 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.03-1.16 (m, 1H), 1.10 (s, 3H), 1.14 (s, 3H), 1.26-1.33 (m, 1H), 1.33 (s, 3H), 1.39-1.89 (m, 15H), 1.61 (s, 3H), 1.67 (s, 3H), 2.11 (dd, *J* = 5.2, 14.8 Hz, 1H), 2.13-2.21 (m, 1H), 2.57 (dd, *J* = 13.2, 14.8 Hz, 1H), 3.43-3.45 (m, 2H), 3.90-3.99 (m, 4H), 5.04-5.08 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7 (CH_3), 19.8 (CH_2), 21.1 (CH_2), 22.4 (CH_3), 23.2 (CH_2), 23.5 (CH_2), 23.6 (CH_3), 24.6 (CH_3), 25.7 (CH_3), 26.7 (CH_2), 34.7 (CH_2), 37.8 (C), 38.6 (CH_2), 38.7 (C), 41.9 (CH_2), 42.8 (CH), 52.2 (C), 53.2 (CH), 64.6 (CH_2×2), 65.4 (CH_2), 109.9 (C), 124.4 (CH), 131.3 (C), 216.5 (C); MS (EI, 70 eV) *m/z* (% base peak) 406 (M^+, 1), 391 (5), 324 (4), 262 (5), 222 (100), 198 (37), 154 (8), 136 (51), 108 (94), 87 (70); HRMS (EI) calcd for $C_{25}H_{42}O_4$ 406.3083, Found 406.3079. Anal.Calcd for $C_{25}H_{42}O_4$: C, 73.85; H, 10.41. Found: C, 73.89; H, 10.41.

compound **12**:

IR (neat) ν 3386, 2963, 2927, 2869, 1451, 1376, 1061, 1027, 857 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (dd, *J* = 3.6, 3.6 Hz, 1H), 0.91 (s, 3H), 0.98 (s, 3H), 0.98-2.00 (m, 20H), 1.33 (s, 3H), 1.59 (s, 3H), 1.67 (s, 3H), 2.00-2.08 (m, 1H), 3.45-3.55 (m, 2H), 3.89-3.97 (m, 4H), 5.04-5.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4 (CH_2), 17.5 (CH_3), 19.9 (CH_3), 20.2 (CH_2), 21.6 (CH_2), 21.7 (CH_2), 23.4 (CH_3), 24.5 (CH_2), 25.0 (CH_3), 25.7 (CH_3), 27.2 (CH_2), 37.2 (C), 37.4 (CH_2), 38.2 (CH), 39.4 (C), 42.8 (CH_2), 44.6 (CH_2), 44.9 (CH), 56.5(CH), 64.5 (CH_2×2), 66.6 (CH_2), 110.1 (C), 125.2 (CH), 130.7 (C); MS (EI, 70 eV) *m/z* (% base peak) 392 (M^+, 4), 377 (2), 330 (1), 307 (2), 247 (3), 229 (2), 189 (2), 115 (9), 87 (100); HRMS (EI) calcd for $C_{25}H_{44}O_3$ 392.3290, Found 392.3283.

compound **13**:

IR (neat) ν 2964, 2928, 2867, 1591, 1566, 1514, 1332, 1060, 853, 731 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (dd, *J* = 3.4, 3.4 Hz, 1H), 0.92 (s, 3H), 0.96 (s, 3H), 1.03-1.11 (m, 1H), 1.17-1.78 (m, 16H), 1.33 (s, 3H), 1.60 (s, 3H), 1.68 (s, 3H), 1.83-1.96 (m, 2H), 2.20-2.29 (m, 1H),

2.77-2.88 (m, 2H), 3.89-3.97 (m, 4H), 5.04-5.08 (m, 1H), 7.28-7.32 (m, 1H), 7.51-7.52 (m, 2H), 8.28 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.0 (CH_2), 17.6 (CH_3), 19.9 (CH_3), 20.3 (CH_2), 21.7 (CH_2), 22.0 (CH_2), 23.5 (CH_3), 24.9 (CH_3), 25.7 (CH_3), 26.7 (CH_2), 28.3 (CH_2), 32.0 (CH_2), 34.9 (CH), 37.3 (C), 37.4 (CH_2), 39.9 (C), 42.8 (CH_2), 44.6 (CH_2), 48.1 (CH), 56.5 (CH), 64.5 (CH_2×2), 110.1 (C), 125.1 (CH), 125.2 (CH), 126.4 (CH), 129.2 (CH), 130.8 (C), 133.4 (CH), 134.2 (C), 147.0 (C); MS (EI, 70 eV) *m/z* (% base peak) 577 (M^+, 6), 547 (10), 492 (3), 375 (3), 313 (8), 229 (17), 189 (15), 121 (18), 115 (25), 87 (100); HRMS (EI) calcd for $C_{31}H_{47}NO_4$ Se 577.2670, Found 577.2669.

compound **14**:

IR (neat) ν 2962, 2926, 2853, 1715, 1590, 1512, 1331, 1303, 1037, 852, 730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (dd, J = 3.4, 3.4 Hz, 1H), 0.93 (s, 3H), 0.94 (s, 3H), 0.98-1.06 (m, 1H), 1.16-1.71 (m, 14H), 1.60 (s, 3H), 1.68 (s, 3H), 1.87-1.97 (m, 2H), 2.13 (s, 3H), 2.19-2.28 (m, 1H), 2.43-2.58 (m, 2H), 2.79-2.87 (m, 2H), 5.03-5.07 (m, 1H), 7.28-7.33 (m, 1H), 7.51-7.52 (m, 2H), 8.28 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.9 (CH_2), 17.6 (CH_3), 19.7 (CH_3), 19.8 (CH_2), 21.7 (CH_2), 21.9 (CH_2), 25.1 (CH_3), 25.7 (CH_3), 26.6 (CH_2), 28.4 (CH_2), 29.8 (CH_3), 31.9 (CH_2), 34.9 (CH), 37.3 (C), 37.4 (CH_2), 39.9 (C), 44.7 (CH_2), 47.8 (CH), 48.0 (CH_2), 56.4 (CH), 125.0 (CH), 125.1 (CH), 126.4 (CH), 129.2 (CH), 131.0 (C), 133.4 (CH), 134.1 (C), 147.0 (C), 209.0 (C); MS (EI, 70 eV) *m/z* (% base peak) 533 (M^+, 4), 516 (12), 432 (11), 327 (8), 247 (47), 229 (100), 189 (29), 149 (20), 135 (53), 109 (53), 81 (51); HRMS (EI) calcd for $C_{29}H_{43}NO_3$ Se 533.2408, Found 533.2408.

compound **15**:

IR (neat) ν 3066, 2964, 2927, 2866, 1718, 1645, 1455, 1375, 1160, 886 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (dd, *J* = 3.6, 3.6 Hz, 1H), 0.86 (s, 3H), 0.94 (s, 3H), 0.99-1.06 (m, 1H), 1.20-1.93 (m, 14H), 1.60 (s, 3H), 1.68 (s, 3H), 2.06-2.19 (m, 2H), 2.13 (s, 3H), 2.48-2.52 (m, 2H), 4.61-4.64 (m, 2H), 5.04-5.07 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 17.7 (CH_3), 19.8 (CH_3), 19.9 (CH_2), 22.2 (CH_2), 23.3 (CH_2), 25.7 (CH_2), 25.9 (CH_3), 26.7 (CH_3), 27.1 (CH_2), 29.3 (CH_3), 31.5 (CH_2), 37.7 (C), 37.8 (CH_2), 39.9 (C), 45.1 (CH_2), 47.6 (CH_2), 54.9 (CH), 56.5 (CH), 108.7 (CH_2), 125.7 (CH), 130.8 (C), 152.3 (C), 206.0 (C); MS (EI, 70 eV) *m/z* (% base peak) 330 (M^+, 28), 315 (5), 247 (100), 229 (78), 189 (39), 173 (41), 161 (29), 147 (42), 135 (67), 121 (70), 107 (64), 93 (62), 69 (36); HRMS (EI) calcd for $C_{23}H_{38}O$ 330.2923, Found 330.2923. Anal.Calcd for $C_{23}H_{38}O$: C, 83.57; H, 11.59. Found: C, 83.63; H, 11.59.

compound **16**:

IR (neat) ν 3066, 2962, 2928, 2866, 1717, 1646, 1444, 1383, 1222, 1147, 1039, 886 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (dd, *J* = 3.8, 3.8 Hz, 1H), 0.89 (s, 3H), 0.94 (s, 3H), 1.03-1.13 (m, 1H), 1.22-1.97 (m, 14H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.60 (s, 3H), 1.69 (s, 3H), 2.08-2.22 (m, 4H), 2.17 (s, 3H), 4.15 (q, *J* = 7.2 Hz, 2H), 4.61-4.65 (m, 2H), 5.05-5.08 (m, 1H), 5.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4 (CH_3), 17.7 (CH_3), 19.1 (CH_3), 19.9 (CH_3), 21.7 (CH_2), 23.0 (CH_2), 24.4 (CH_2), 25.3 (CH_2), 25.7 (CH_3), 26.5 (CH_3), 27.0 (CH_2), 31.1 (CH_2), 37.5 (CH_2), 37.6 (C), 39.7 (C), 44.7 (CH_2), 44.8 (CH_2), 54.5 (CH), 56.4 (CH), 59.5 (CH_2), 108.2 (CH_2), 115.0 (CH), 125.1 (CH), 131.1 (C), 152.3 (C), 160.1 (C), 167.0 (C); MS (EI, 70 eV) *m/z* (% base peak) 400 (M^+, 27), 317 (74), 243

(43), 189 (44), 165 (73), 135 (67), 121 (84), 107 (58), 93 (65), 69 (100); HRMS (EI) calcd for $C_{27}H_{44}O_2$ 400.3341, Found 400.3341.

Selective Comparison of ^{1}H-NMR Data of 1

Natural (500 MHz, $CDCl_3$) δ (ppm)	Synthetic (400 MHz, $CDCl_3$) δ (ppm)
0.72 (s, 3H)	0.90 (s, 3H)
0.87 (s, 3H)	0.94 (s, 3H)
1.58 (s, 3H)	1.61 (s, 3H)
1.67 (s, 3H)	1.69 (s, 3H)
2.18 (s, 3H)	2.19 (s, 3H)
4.47 (s, 1H)	4.62 (s, 1H)
4.82 (s, 1H)	4.64 (s, 1H)
5.10 (t, 1H)	5.07 (t, 1H)
5.70 (s, 1H)	5.69 (s, 1H)

Comparison of ^{13}C-NMR Data of 1

Natural (125 MHz, $CDCl_3$) δ (ppm)		Synthetic (100 MHz, $CDCl_3$) δ (ppm)	
15.4 (CH_3)	37.9 (CH_2)		37.5 (CH_2)
17.5 (CH_3)	39.1 (CH_2)	17.7 (CH_3)	
19.1 (CH_2)	39.3 (CH_2)		
19.3 (CH_3)	39.8 (C)	19.5 (CH_3)	39.7 (C)
	43.5 (CH_2)	19.8 (CH_3)	44.7 (CH_2)
21.5 (CH_2)		21.7 (CH_2)	45.0 (CH_2)
23.0 (CH_2)	56.5 (CH)	23.0 (CH_2)	54.5 (CH)
	57.7 (CH)	24.4 (CH_2)	56.5 (CH)
25.3 (CH_2)	106.2 (CH_2)	25.3 (CH_2)	108.3 (CH_2)
25.7 (CH_3)	114.7 (CH)	25.8 (CH_3)	114.4 (CH)
	125.5 (CH)	26.5 (CH_3)	125.0 (CH)
	131.0 (C)	27.0 (CH_2)	131.1 (C)
29.3(CH_3)	148.1 (C)		152.2 (C)
32.8 (CH_2)	164.0 (C)	31.1 (CH_2)	164.0 (C)
37.6 (C)	173.0 (C)	37.6 (C)	171.5 (C)