Total Synthesis of (–)-Reveromycin A

Mariana El Sous, Danny Ganame, Peter A. Tregloan and Mark A. Rizzacasa*

School of Chemistry, The University of Melbourne, Victoria 3010, Australia

masr@unimelb.edu.au

Supporting Information

General. Unless otherwise stated, ^1H NMR (300 MHz or 400 MHz) and proton decoupled ^{13}C NMR spectra (75.5 MHz or 100 MHz) were recorded for deuteriochloroform solutions with residual chloroform as internal standard. Optical rotations were recorded in a 10cm microcell. HRMS (ESI) mass spectra were run at Monash University, Clayton, Victoria.

Spiroketal 4: $[\alpha]_{\text{D}}^{21} +55.0$ (*c*, 0.15, CH_2Cl_2); IR ν_{max} (film) 3032, 2956, 2931, 2860, 1462, 1256, 1160, 1089, 982 cm^{-1} ; ^1H NMR (300 MHz) δ 0.004 (s, 3H), 0.003 (s, 3H), 0.82 (d, $J = 6.6$ Hz, 3H), 0.86 (s, 9H), 0.87 (t, $J = 6.6$ Hz, 3H), 1.20–2.30 (m, 17H), 3.41 (dt, $J = 9.9, 2.1$ Hz, 1H), 3.49 (dt, $J = 9.6, 6$ Hz, 1H), 3.71 (dt, $J = 9.9, 5.1$ Hz, 1H), 3.98 (ABq, $J = 11.4$ Hz, 2H), 4.56 (ABq, $J = 12.3$ Hz, 2H), 7.26–7.38 (m, 5H); ^{13}C NMR (75.5 MHz) δ -5.3, -5.3, 14.0, 17.7, 18.3, 21.8, 22.7, 25.9, 27.9, 31.3, 31.5, 32.0, 34.7, 34.9, 36.5, 60.7, 66.7, 71.8, 73.1, 94.6, 113.3, 127.3, 127.5, 128.2, 138.7, 141.2; MS (ESI): m/z 520 ($[\text{M}+\text{H}_2\text{O}]^+$, 100%), 503 ($[\text{M}+1]^+$, 17%), 271 (17%); HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{50}\text{O}_4\text{SiNa}$ $[\text{M}+\text{Na}]^+$: 525.3376. Found: 525.3355; Anal. Calcd for $\text{C}_{30}\text{H}_{50}\text{O}_4\text{Si}$: C, 71.66; H, 10.02%. Found: C, 71.80; H, 10.00%.

Ene adduct 9: IR ν_{max} (film) 3528, 2957, 2930, 2859, 1682, 1471, 1255, 1095, 836 cm^{-1} ; ^1H NMR (300 MHz) δ 0.002 (s, 6H), 0.83 (t, $J = 3$ Hz, 3H), 0.84 (s, 9H), 0.87 (d, $J = 1.5$ Hz, 3H), 1.08–1.96 (m, 12H), 2.21–2.42 (m, 2H), 3.26–3.45 (m, 3H), 3.51 (dt, $J = 8.1, 2.7$ Hz, 1H), 3.67 (m, 1H), 4.41 (m, 1H), 4.51 (s, 2H), 4.86 (s, 1H), 5.13 (s, 1H), 7.26–7.28 (m, 5H); ^{13}C NMR (75.5 MHz) δ -5.3, 14.1, 17.7, 18.3, 22.8, 25.9, 28.7, 29.7, 30.5, 30.6, 31.1, 35.7, 41.1, 59.6, 73.5, 75.4, 77.3, 77.6, 77.7, 98.7, 109.4, 127.5, 127.7, 128.2, 138.4, 149.8, 149.9, 151.6; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{50}\text{O}_4\text{SiNa}$ $[\text{M}+\text{Na}]^+$: 525.3376. Found: 525.3382.

Alcohol 10: $[\alpha]_{\text{D}}^{21} +34.7$ (*c*, 0.75, CH_2Cl_2); IR ν_{max} (film) 3446, 2957, 2861, 1650, 1459, 1253, 1086, 973 cm^{-1} ; ^1H NMR δ (300 MHz) 0.047 (s, 6H), 0.82 (d, $J = 6$ Hz, 3H), 0.88 (s, 9H), 0.90 (t, $J = 6.6$ Hz, 3H), 1.20–1.88 (m, 17H), 2.27–2.32 (m, 1H), 2.76 (s, 1H), 3.56–3.73 (m, 5H), 4.48 (ABq, $J = 11.7$ Hz, 2H), 7.26–7.34 (m, 5H); ^{13}C NMR (100 MHz) δ -5.2, -5.2, 14.1, 17.9, 18.3, 23.4, 24.5, 26.0, 27.5, 29.7, 29.8, 31.8, 33.6, 34.8, 36.3, 59.2, 70.1, 71.3, 72.3, 73.6, 76.0, 97.0, 127.8, 127.9, 128.5, 137.5; MS (ESI): m/z 538 ($[\text{M}+\text{H}_2\text{O}]^+$, 100%), 521 ($[\text{M}+1]^+$, 53%); HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{52}\text{O}_5\text{SiNa}$ $[\text{M}+\text{Na}]^+$: 543.3482. Found: 543.3464.

Alcohol 11: $[\alpha]^{32}_D +12.8$ (*c*, 1.35, CH₂Cl₂); IR $\nu_{\max}$ (film) 3436, 2956, 2930, 2859, 1472, 1463, 1256, 1086, 835 cm⁻¹; ¹H NMR (300 MHz) δ 0.062 (s, 3H), 0.072 (s, 3H), 0.099 (s, 3H), 0.12 (s, 3H), 0.80-0.93 (m, 6H), 0.86 (s, 9H), 0.90 (s, 9H), 1.25-1.92 (m, 16H), 2.24 (m, 1H), 2.33 (bs, 1H), 3.45 (dd, *J* = 7.5, 3.3 Hz, 1H), 3.65-3.77 (m, 5H); ¹³C NMR (75.5 MHz) δ 5.3, -5.2, -1.9, -1.8, 14.1, 17.9, 18.3, 23.2, 24.8, 25.8, 26.0, 27.6, 30.1, 30.9, 33.2, 34.1, 34.8, 36.3, 59.2, 61.9, 72.9, 74.6, 80.1, 96.6; HRMS (ESI) calcd for C₂₉H₆₀O₅Si₂Na [M+Na⁺]: 567.3877. Found: 567.3879.

Alkyne 3: $[\alpha]^{19}_D +12.9$ (*c*, 0.954, CH₂Cl₂); IR $\nu_{\max}$ (film) 3434, 2958, 2931, 2859, 2097, 1641, 1256, 1088 cm⁻¹; ¹H NMR (300 MHz) δ 0.052 (s, 6H), 0.088 (s, 6H), 0.85 (d, *J* = 6.6 Hz, 3H), 0.88 (s, 9H), 0.89 (s, 9H), 0.90 (t, *J* = 6.6 Hz, 3H), 1.25-2.04 (m, 17H), 2.31 (d, *J* = 2.7 Hz, 1H), 3.64-3.84 (m, 3H), 4.26 (brs, 1H); ¹³C NMR (75.5 MHz) δ -5.2, -2.5, -2.3, 14.1, 17.9, 18.4, 18.6, 23.2, 24.3, 25.9, 26.0, 27.7, 27.8, 31.9, 34.0, 35.5, 35.9, 38.5, 59.8, 70.2, 72.9, 73.2, 74.6, 82.9, 95.7; HRMS (ESI) calcd for C₃₀H₅₈O₄Si₂Na [M+Na⁺]: 561.3771. Found: 561.3772.

Ester 12: $[\alpha]^{19}_D -5.2$ (*c*, 1.04, CH₂Cl₂); IR $\nu_{\max}$ (film) 3307, 2956, 2931, 2859, 1720, 1622, 1463, 1435, 1258, 1170 cm⁻¹; ¹H NMR (300 MHz) δ 0.093 (s, 6H), 0.82 (d, *J* = 6.6 Hz, 3H), 0.89 (s, 9H), 0.90 (t, *J* = 6.6 Hz, 3H), 1.25-2.08 (m, 14H), 1.77 (s, 3H), 1.83-2.55 (m, 3H), 2.27 (d, *J* = 2.1 Hz, 1H), 3.75 (s, 3H), 3.84 (m, 1H), 4.29 (s, 1H), 5.76 (d, *J* = 15.9 Hz, 1H), 6.15 (t, *J* = 6.3 Hz, 1H), 7.36 (d, *J* = 15.6 Hz, 1H); ¹³C NMR (75.5 MHz) δ -2.6, -2.3, 12.3, 14.1, 17.7, 18.6, 23.2, 24.2, 25.9, 27.4, 27.7, 31.5, 31.9, 33.8, 38.9, 51.4, 70.0, 72.7, 74.5, 74.6, 83.1, 95.8, 114.6, 133.2, 139.3, 150.1, 168.1; HRMS (ESI) calcd for C₃₀H₅₀O₅SiNa [M+Na⁺]: 541.3325. Found: 541.3346.

Aldol adduct 15: $[\alpha]^{19}_D +64.7$ (*c*, 0.78, CH₂Cl₂); IR $\nu_{\max}$ (film) 3453, 3307, 2958, 2932, 2859, 2113, 1703, 1650, 1462, 1365, 1327, 1264, 1090 cm⁻¹; ¹H NMR (300 MHz) δ 0.088 (s, 6H), 0.80 (d, *J* = 6.3 Hz, 3H), 0.85-0.93 (m, 9H), 0.88 (s, 9H), 1.16-1.50 (m, 6H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.56-2.49 (m, 12H), 1.73 (s, 3H), 2.29 (d, *J* = 2.4 Hz, 1H), 2.57 (bs, 1H), 3.77 (m, 1H), 4.27 (s, 1H), 4.37 (d, *J* = 5.7 Hz, 2H), 4.64 (t, *J* = 5.4 Hz, 1H), 4.75 (dd, *J* = 9.3, 5.4 Hz, 1H), 5.05 (m, 1H), 5.57 (dd, *J* = 15.9, 6.6 Hz, 1H), 5.72 (t, *J* = 6.9 Hz, 1H), 6.36 (d, *J* = 15.9 Hz, 1H); ¹³C NMR (75.5 MHz) δ -2.6, -2.3, 11.5, 12.6, 14.1, 14.8, 17.7, 18.2, 18.6, 23.2, 24.2, 25.9, 27.4, 27.8, 29.0, 29.7, 31.3, 33.6, 35.9, 38.9, 42.8, 63.3, 67.3, 70.0, 72.7, 73.8,

74.7, 83.0, 95.8, 124.7, 130.5, 133.2, 137.3, 176.7, 186.1; HRMS (ESI) calcd for $C_{38}H_{63}NO_6SSiNa$ $[M+Na^+]$: 712.4043. Found: 712.4028.

Diol 16: $[\alpha]_D^{20} -9.0$ (c, 0.40, CH_2Cl_2); IR ν_{max} (film) 3403, 3309, 2959, 2933, 2861, 2113, 1649, 1461, 1384 cm^{-1} ; 1H NMR (300 MHz) δ 0.09 (s, 6H), 0.81 (d, $J = 6$ Hz, 3H), 0.84-0.92 (m, 6H), 0.88 (s, 9H), 1.25-1.68 (m, 6H), 1.75 (s, 3H), 1.80-2.44 (m, 14H), 2.28 (d, $J = 2.4$ Hz, 1H), 3.62-3.72 (m, 2H), 3.77 (dd, $J = 14.1, 5.1$ Hz, 1H), 4.28 (s, 1H), 4.34 (dd, $J = 6.9, 3.9$ Hz, 1H), 5.60 (dd, $J = 15.9, 6.9$ Hz, 1H), 5.71 (t, $J = 6.9$ Hz, 1H), 6.29 (d, $J = 15.6$ Hz, 1H); ^{13}C NMR (75.5 MHz) δ -2.5, -2.3, 11.7, 12.7, 14.1, 17.7, 18.6, 23.2, 24.2, 25.9, 27.5, 27.8, 29.6, 31.3, 31.6, 33.6, 35.9, 38.9, 40.2, 66.4, 70.0, 72.7, 74.7, 83.0, 95.9, 125.6, 130.2, 133.2, 137.0; HRMS (ESI) calcd for $C_{32}H_{56}O_5SiNa$ $[M+Na^+]$: 571.3795. Found: 571.3804.

Alcohol 17: $[\alpha]_D^{24} +8.4$ (c, 1.33, CH_2Cl_2); IR ν_{max} (film) 3400, 3309, 2950, 2858, 1647, 1461 cm^{-1} ; 1H NMR (400 MHz) δ -0.01 (s, 3H), 0.02 (s, 6H), 0.03 (s, 3H), 0.85 (t, $J = 6.6$ Hz, 3H), 0.88 (s, 9H), 0.89 (s, 9H), 0.89-0.93 (m, 6H), 1.30-1.69 (m, 14H), 1.71 (s, 3H), 1.79 (td, $J = 13.6, 4.8$ Hz, 1H), 2.10-2.15 (m, 1H), 2.25-2.32 (m, 1H), 2.30 (d, $J = 2.4$ Hz, 1H), 2.46 (ddd, $J = 15.4, 6.8, 4.2$ Hz, 1H), 3.39 (dd, $J = 10.0, 6.4$ Hz, 1H), 3.57 (dd, $J = 9.6, 6.4$ Hz, 1H), 3.74-3.79 (m, 1H), 4.24 (dd, $J = 6.8, 4.4$ Hz, 1H), 4.27 (t, $J = 2.0$ Hz, 1H), 5.49 (dd, $J = 15.6, 6.8$ Hz, 1H), 5.60 (t, $J = 7.0$ Hz, 1H), 6.11 (d, $J = 15.6$ Hz, 1H); ^{13}C NMR (100 MHz) δ -5.35, -5.32, -4.9, -4.0, 11.3, 12.7, 14.0, 17.7, 18.23, 18.26, 23.1, 24.0, 25.9, 26.9, 27.7, 31.5, 31.6, 33.8, 36.2, 38.2, 43.0, 65.0, 69.8, 71.2, 73.4, 73.7, 75.2, 81.8, 96.0, 128.2, 128.7, 133.5, 134.7; HRMS (ESI) calcd for $C_{38}H_{70}O_5Si_2Na$ $[M+Na^+]$: 685.4659. Found: 685.4661.

Ester 19: $[\alpha]_D^{21} +6.7$ (c, 1.73, CH_2Cl_2); IR ν_{max} (film) 3309, 3269, 2929, 2858, 1735, 1461 cm^{-1} ; 1H NMR (400 MHz) δ -0.01 (s, 3H), 0.021 (s, 6H), 0.026 (s, 3H), 0.03 (s, 9H), 0.83-0.90 (m, 9H), 0.88 (s, 9H), 0.89 (s, 9H), 0.98 (t, $J = 8.6$ Hz, 2H), 1.25-1.68 (m, 14H), 1.71 (s, 3H), 1.98-2.18 (m, 2H), 2.22 (m, 1H), 2.28 (d, $J = 2.4$ Hz, 1H), 2.44-2.52 (m, 1H), 2.54-2.66 (m, 4H), 3.38 (dd, $J = 10.0, 6.4$ Hz, 1H), 3.57 (dd, $J = 9.6, 6.4$ Hz, 1H), 3.72-3.77 (m, 1H), 4.17 (t, $J = 8.6$ Hz, 2H), 4.24 (dd, $J = 6.6, 4.2$ Hz, 1H), 4.84 (bs, 1H), 5.49 (dd, $J = 15.6, 6.8$ Hz, 1H), 5.61 (t, $J = 7.0$ Hz, 1H), 6.11 (d, $J = 15.6$ Hz, 1H); ^{13}C NMR (100 MHz) δ -5.35, -5.32, -4.9, -3.9, -1.5, 11.3, 12.6, 13.9, 17.2, 17.8, 18.23, 18.26, 22.7, 24.0, 24.1, 25.8, 25.9, 27.7, 29.3, 30.0, 31.4, 33.7, 34.0, 36.3, 43.0,

62.9, 65.0, 66.5, 73.6, 73.7, 75.1, 81.3, 83.1, 95.6, 128.3, 128.7, 133.4, 134.7, 171.2, 172.3; HRMS (ESI) calcd for $C_{47}H_{86}O_8Si_3Na$ $[M+Na^+]$: 885.5528. Found: 885.5522.

Alcohol 20: $[\alpha]_D^{18} +10.8$ (*c*, 1.10, CH_2Cl_2); IR ν_{max} (film) 3450, 3309, 2929, 2859, 1732, 1631 cm^{-1} ; 1H NMR (400 MHz) δ 0.021 (s, 3H), 0.028 (s, 9H), 0.06 (s, 3H), 0.78 (d, $J = 7.2$ Hz, 2H), 0.82-0.89 (m, 6H), 0.89 (s, 9H), 0.97 (t, $J = 8.6$ Hz, 2H), 1.18-1.69 (m, 14H), 1.72 (s, 3H), 1.98-2.16 (m, 2H), 2.27 (d, $J = 2.4$ Hz, 1H), 2.29-2.31 (m, 1H), 2.48-2.51 (m, 1H), 2.53-2.64 (m, 4H), 2.99 (d, $J = 4.4$ Hz, 1H), 3.44-3.50 (m, 1H), 3.65 (t, $J = 9.8$ Hz, 1H), 3.73-3.78 (m, 1H), 4.16 (t, $J = 8.6$ Hz, 2H), 4.29 (dd, $J = 7.0, 3.8$ Hz, 1H), 4.84 (t, $J = 2.0$ Hz, 1H), 5.54 (dd, $J = 15.8, 7.0$ Hz, 1H), 5.66 (t, $J = 7.0$ Hz, 1H), 6.17 (d, $J = 16.0$ Hz, 1H); ^{13}C NMR (100 MHz) δ -5.0, -4.2, -1.5, 12.5, 12.6, 13.8, 17.2, 17.7, 18.0, 22.7, 24.0, 24.1, 25.7, 25.8, 27.7, 29.3, 30.0, 31.4, 31.5, 33.7, 33.9, 36.3, 41.2, 62.8, 65.9, 66.5, 73.5, 75.0, 77.9, 81.3, 83.0, 95.6, 125.3, 129.4, 133.1, 136.4, 171.2, 172.2; HRMS (ESI) calcd for $C_{41}H_{72}O_8Si_2Na$ $[M+Na^+]$: 771.4663. Found: 771.4648.

Diester 23: $[\alpha]_D^{23} -105.8$ (*c*, 0.31, CH_2Cl_2); IR ν_{max} (film) 3450, 2956, 2858, 1710, 1612, 1458 cm^{-1} ; 1H NMR (400 MHz) δ 0.02 (s, 3H), 0.03 (s, 9H), 0.04 (s, 9H), 0.07 (s, 3H), 0.76-0.84 (m, 9H), 0.89 (s, 9H), 0.96-1.04 (m, 4H), 1.17-1.76 (m, 14H), 1.73 (s, 3H), 1.98-2.05 (m, 2H), 2.26 (s, 3H), 2.29-2.41 (m, 2H), 2.54-2.66 (m, 1H), 3.01 (d, $J = 4.4$ Hz, 1H), 3.39-3.51 (m, 2H), 3.67 (t, $J = 9.0$ Hz, 1H), 4.15-4.23 (m, 4H), 4.29 (dd, $J = 6.8, 4.4$ Hz, 1H), 4.60 (d, $J = 7.6$ Hz, 1H), 5.54-5.59 (m, 2H), 5.79 (bs, 1H), 6.18 (d, $J = 16.0$ Hz, 1H), 6.32-6.34 (m, 1H); ^{13}C NMR (100 MHz) δ -5.0, -4.1, -1.5, -1.4, 12.5, 12.8, 13.9, 14.2, 17.2, 17.3, 17.6, 18.0, 22.7, 24.0, 24.5, 25.8, 27.4, 29.3, 30.0, 31.7, 33.3, 34.0, 35.7, 41.2, 62.0, 62.9, 65.9, 74.5, 78.0, 78.3, 83.0, 95.6, 120.4, 125.7, 127.9, 132.8, 134.2, 136.2, 137.9, 151.0, 167.1, 171.4, 172.3; HRMS (ESI) calcd for $C_{50}H_{90}O_{10}Si_3Na$ $[M+Na^+]$: 957.5739. Found: 957.5730.

Triester 24: $[\alpha]_D^{31} -69.6$ (*c*, 0.21, CH_2Cl_2); IR ν_{max} (film) 2957, 2931, 2860, 1733, 1654, 1460 cm^{-1} ; 1H NMR (400 MHz) δ -0.01 (s, 3H), 0.031 (s, 3H), 0.039 (s, 9H), 0.04 (s, 9H), 0.05 (s, 9H), 0.76 (d, $J = 6.4$ Hz, 3H), 0.80-0.84 (m, 6H), 0.88 (s, 9H), 0.96-1.04 (m, 6H), 1.10-1.80 (m, 14H), 1.70 (s, 3H), 1.95 (td, $J = 13.6, 4.0$ Hz, 1H), 2.26 (s, 3H), 2.28-2.30 (m, 1H), 2.34-2.48 (m, 2H),

2.54–2.66 (m, 4H), 3.38–3.45 (m, 1H), 4.09 (dd, $J = 7.0, 5.0$ Hz, 1H), 4.14–4.24 (m, 6H), 4.61 (d, $J = 8.0$ Hz, 1H), 5.43 (dd, $J = 15.6, 7.2$ Hz, 1H), 5.53 (t, $J = 7.0$ Hz, 1H), 5.75 (d, $J = 1.2$ Hz, 1H), 5.78–5.80 (m, 1H), 6.14 (d, $J = 15.6$ Hz, 1H), 6.32–6.35 (m, 2H), 6.99 (dd, $J = 15.8, 7.4$ Hz, 1H); ^{13}C NMR (100 MHz) δ -4.8, -4.0, -1.5, -1.48, -1.44, 12.8, 13.8, 14.2, 17.2, 17.3, 17.4, 17.6, 18.2, 22.7, 24.0, 24.5, 25.8, 27.5, 29.4, 29.7, 30.1, 31.7, 31.8, 33.2, 34.0, 35.7, 43.7, 62.0, 62.2, 62.9, 74.5, 76.9, 78.3, 83.0, 95.6, 120.4, 121.1, 127.2, 127.7, 132.8, 134.2, 135.9, 137.9, 151.0, 151.3, 166.8, 167.0, 171.4, 172.3; HRMS (ESI) calcd for $\text{C}_{57}\text{H}_{102}\text{O}_{11}\text{Si}_4\text{Na}$ $[\text{M}+\text{Na}^+]$: 1097.6396. Found: 1097.6386.

(–)Reveromycin A (1): $[\alpha]_{\text{D}}^{22} -122.4$ (c , 0.16, MeOH); Lit.¹ $[\alpha]_{\text{D}}^{23} -115$ (c , 0.1, MeOH); λ_{max} (MeOH) nm (ϵ) 238 (36513 $\text{M}^{-1} \text{cm}^{-1}$); IR ν_{max} (film) 3450, 2940, 2852, 1693, 1610, 1480 cm^{-1} ; ^1H NMR

(400 MHz, CD_3OD) δ 0.77 (d, $J = 6.0$ Hz, 3H), 0.83 (t, $J = 6.0$ Hz, 3H), 1.07 (d, $J = 6.8$ Hz, 3H), 1.17–1.72 (m, 14H), 1.74 (s, 3H), 1.83 (td, $J = 13.2, 3.9$ Hz, 1H), 2.01 (td, $J = 12.6, 4.4$ Hz, 1H), 2.25 (s, 3H), 2.26–2.40 (m, 3H), 2.48–2.60 (m, 4H), 3.41–3.48 (m, 4H), 4.03–4.07 (m, 1H), 4.61 (d, $J = 7.6$ Hz, 1H), 5.51 (dd, $J = 16.0, 7.2$ Hz, 1H), 5.58 (t, $J = 7.0$ Hz, 1H), 5.80 (d, $J = 16.0$ Hz, 1H), 5.87 (bs, 1H), 6.24 (d, $J = 16.0$ Hz, 1H), 6.42–6.44 (m, 2H), 6.97 (dd, $J = 15.6, 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 13.1, 14.3, 14.7, 15.3, 18.1, 23.9, 25.2, 25.5, 28.8, 30.0, 31.2, 32.9, 33.1, 34.9, 35.3, 37.0, 44.3, 76.4, 77.0, 79.8, 84.3, 97.1, 121.8, 122.7, 128.0, 129.6, 134.3, 135.6, 137.9, 139.4, 152.6, 152.9, 170.3, 170.3, 173.5, 176.0; HRMS (ESI) calcd for $\text{C}_{36}\text{H}_{52}\text{O}_{11}\text{Na}$ $[\text{M}+\text{Na}^+]$: 683.3407. Found: 683.3406.

(1) Takahashi, H.; Osada, H.; Koshino, H.; Kudo, T.; Amano, S.; Shimizu, S.; Yoshihama, M.; Isono, K. *J. Antibiot.* **1992**, *45*, 1409.

¹H NMR (400 MHz, CD₃OD)

Reveromycin A (1)

Synthetic ¹H NMR (400 MHz, CD₃OD)

Reveromycin A (1)

Natural Sample

RP-HPLC traces

Synthetic

Natural

Co-injection

^{13}C NMR chemical shift comparison (ppm in CD_3OD solvent) for natural² and synthetic reveromycin A (1)

Carbons	Nat. ²	Syn.	$\Delta\delta$	Carbons	Nat. ²	Syn.	$\Delta\delta$	Carbons	Nat. ²	Syn.	$\Delta\delta$
C1	170.0	170.3	-0.3	C13	28.6	28.8	-0.2	C25	35.2	35.3	-0.1
C2	122.5	122.7	-0.2	C14	36.9	37.0	-0.1	C26	25.1	25.2	-0.1
C3	152.9	152.9	0	C15	97.0	97.1	-0.1	C27	23.8	23.9	-0.1
C4	44.1	44.3	-0.2	C16	32.8	32.9	-0.1	C28	14.2	14.3	-0.1
C5	76.9	77.0	-0.1	C17	25.4	25.5	-0.1	4-Me	15.4	15.3	0.1
C6	128	128.0	0	C18	84.2	84.3	-0.1	8-Me	13.0	13.1	-0.1
C7	137.9	137.9	0	C19	79.7	79.8	-0.1	12-Me	18.1	18.1	0
C8	135.2	135.6	-0.4	C20	134.2	134.3	-0.1	22-Me	14.7	14.7	0
C9	129.2	129.6	-0.4	C21	139.2	139.4	-0.2	C1'	173.1	173.5	-0.4
C10	33.0	33.1	-0.1	C22	152.5	152.6	-0.1	C2'	29.9	30.0	-0.1
C11	76.2	76.4	-0.2	C23	121.5	121.8	-0.3	C3'	31.2	31.2	0
C12	34.8	34.9	-0.1	C24	170.1	170.3	-0.2	C4'	176.0	176.0	0

(2) Koshino, H.; Takahashi, H.; Osada, H.; Isono, K. *J. Antibiot.* **1992**, 45, 1420.