Supporting Information

Toward a Synthesis of Reidispongiolide A: Synthesis of the C₁₇-C₂₂ and C₂₃-C₃₅ Degradation Fragments

Ian Paterson,^{*} Kate Ashton, Robert Britton, Henner Knust

University Chemical Laboratory, Cambridge CB2 1EW, UK

General

Thin layer chromatography was carried out on commercial glass backed silica gel 60 F₂₅₄ plates. Visualization of chromatograms was accomplished using ultraviolet light (254 nm) and/or heating the plate after staining with either a solution of 20% ceric ammonium molybdate w/v in H₂O or 20% potassium permanganate w/v in H₂O. Melting points were measured on a Shandon melting point apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 241 polarimeter at 589 nm (sodium D line) and concentrations (*c*) are reported in g/100 mL. Infrared (IR) spectra were recorded on a Perkin-Elmer 1620 FT-IR spectrophotometer with internal calibration. Only selected, characteristic IR absorption data are provided for each compound. NMR spectra were recorded using deuteriochloroform (CDCl₃) or deuteriomethanol (CD₃OD) as the solvent. Signal positions (δ) are given in parts per million from tetramethylsilane (δ 0) and were measured relative to the signal of the solvent in which the sample was analyzed (CDCl₃: δ 7.26 ¹H NMR; δ 77.0, ¹³C NMR; CD₃OD: δ 3.34, ¹H NMR; δ 49.0, ¹³C NMR). Coupling constants (*J* values) are given in Hertz (Hz) and are reported to the nearest 0.1 Hz. ¹H NMR spectral data are tabulated in the order: number of protons, multiplicity (br, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet), coupling constant and proton assignment where applicable. Where ¹H NMR data for a mixture of diastereomers is presented, an asterisk (*) follows the assignment of a resolved resonance that corresponds to a proton of the minor diastereomer. Where ¹³C NMR data for a mixture of diastereomers is presented, resolved resonances that correspond to the minor diastereomer are indicated in brackets (). Where APT (attached proton test) data is given, signals with negative phases (methyl and methine carbons) and signals with positive phases (methylene and quaternary carbons) are indicated in brackets (-ve) or (+ve) respectively, following the ¹³C NMR chemical shift.

Characterization Data for Intermediates in the Synthesis of the C₁₇-C₂₂ Degradation Fragment

(2S, 3S, 5R, 6E)-1-*t*-Butyldimethylsiloxy-2-methyloct-6-en-3,5-diol (10)

R_f 0.20 (20% EtOAc / 40-60 petroleum ether); **[α]_D** +5.8 (c 1.09, CHCl₃); **IR** (thin film) 3374, 2955, 2857, 1462, 1255 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃) δ 5.69 (1H, ddq, *J* = 15.2, 6.4, 0.9 Hz, H7), 5.49 (1H, dqd, *J* = 15.2, 6.8, 1.5 Hz, H6), 4.31 (1H, m, H5), 4.02 (1H, m, H3), 3.73 (1H, dd, *J* = 9.9, 4.2 Hz, H1), 3.65 (1H, dd, *J* = 9.9, 6.4 Hz, H1), 1.77 (1H, m, H2), 1.70 (1H, m, H4), 1.68 (3H, dt, *J* = 6.4, 1.5 Hz, H8), 1.47 (1H, ddd, *J* = 14.1, 2.9, 2.3 Hz, H4), 0.89 (3H, d, *J* = 7.1 Hz, H9), 0.88 (9H, s, SiC(CH₃)₃), 0.07 (6H, br s, Si(CH₃)₂); **¹³C NMR** (100.6 MHz, CDCl₃) δ 133.9, 126.2, 75.7, 73.4, 67.8, 40.1, 39.5, 25.8, 18.1, 17.7, 11.0, -5.4, -5.4; **HRMS** calc. for C₁₅H₃₂O₃Si [M+H]⁺ 289.2199, found 289.2200.

(2S, 3S, 5R, 6E)-1-*t*-Butyldimethylsiloxy-3,5-dimethoxy-2-methyloct-6-ene

R_f 0.50 (20% EtOAc / 40-60 petroleum ether); **[α]_D** +9.8 (c 1.25, CHCl₃); **IR** (thin film) 2928, 2856, 1464, 1255 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃) δ 5.65 (1H, dq, *J* = 15.2, 6.4 Hz, H7), 5.25 (1H, dqd, *J* = 15.2, 8.5, 1.6 Hz, H6), 3.60 (1H, dd, *J* = 9.8, 6.9 Hz, H1), 3.57 (1H, m, H5), 3.42 (1H, dd, *J* = 9.8, 6.7 Hz, H1), 3.37 (1H, ddd, *J* = 8.2, 5.0, 3.3 Hz, H3), 3.32 (3H, s, OCH₃), 3.22 (3H, s, OCH₃), 1.85 (1H, ddd, *J* = 13.8, 8.2, 6.3 Hz, H4), 1.78 (1H, dddq, *J* = 6.9, 6.7, 3.3, 6.9 Hz, H2), 1.73 (3H, dd, *J* = 6.4, 1.6 Hz, H8), 1.47 (1H, ddd, *J* = 13.8, 7.6, 5.0 Hz, H4), 0.89 (9H, s, SiC(CH₃)₃), 0.84 (3H, d, *J* = 6.9 Hz, H9), 0.03 (6H, br s, Si(CH₃)₂); **¹³C NMR** (100.6 MHz, CDCl₃) δ 131.6, 129.7, 80.2, 78.4, 64.9, 57.8, 55.8, 39.0, 37.5, 25.9, 18.2, 17.7, 11.2, -5.4, -5.4; **HRMS** calc. for C₁₇H₃₆O₃Si [M+H]⁺ 317.2512, found 317.2514.

(2R, 4S, 5S)-6-*t*-Butyldimethylsiloxy-2,4-dimethoxy-5-methylhexan-1-ol

R_f 0.15 (20% EtOAc / 40-60 petroleum ether); **[α]_D** -8.8 (c 1.1, CHCl₃); **IR** (thin film) 3423, 2928, 1462, 1255 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃) δ 3.67 (1H, br dt, *J* = 11.0, 5.5 Hz, H1), 3.61 (1H, dd, *J* = 9.8, 6.4 Hz, H6), 3.52 (1H, br dt, *J* = 11.0, 5.5 Hz, H1), 3.45 (1H, dd, *J* = 9.8, 6.4 Hz, H6), 3.41-3.36 (2H, m, H2, H4), 3.38 (3H, s, OCH₃), 3.32 (3H, s, OCH₃), 2.28 (1H, br t, *J* = 5.5 Hz, C1-OH), 1.85 (1H, dddq, *J* = 6.4, 6.4, 3.8, 7.0 Hz, H5), 1.78 (1H, ddd, *J* = 14.6, 8.2, 5.3 Hz, H3), 1.60 (1H, ddd, *J* = 14.6, 6.6, 4.5 Hz, H3), 0.88 (9H, s, SiC(CH₃)₃), 0.87 (3H, d, *J* = 7.0 Hz, H7), 0.03 (6H, br s, Si(CH₃)₂); **¹³C NMR** (100.6 MHz, CDCl₃) δ 79.0, 78.3, 64.5, 63.7, 57.6, 57.0, 38.5, 31.7, 25.9, 18.2, 11.7, -5.4, -5.4; **HRMS** calc. for C₁₅H₃₄O₄Si [M+H]⁺ 307.2304, found 307.2308.

(2R, 4S, 5S)-2,4-Dimethoxy-5-methylhexan-1,6-diol (4)

R_f 0.10 (EtOAc); **[α]_D** +4.1 (c 0.17, MeOH); **IR** (thin film) 3386, 2933, 1464, 1255 cm⁻¹; **¹H NMR** (400 MHz, CD₃OD) δ 3.63 (1H, dd, *J* = 11.7, 4.0 Hz, H1), 3.59 (1H, dd, *J* = 10.5, 6.5 Hz, H6), 3.52 (1H, br dt, *J* = 11.7, 5.3 Hz, H1), 3.43 (1H, dd, *J* = 10.5, 6.9 Hz, H6), 3.42 (1H, ddd, *J* = 6.9, 5.9, 3.4 Hz, H4), 3.39 (3H, s, OCH₃), 3.34 (3H, s, OCH₃), 3.31 (1H, m, H2), 1.85 (1H, dddq, *J* = 6.9, 6.5, 3.4, 6.9 Hz, H5), 1.73 (1H, dt, *J* = 14.2, 6.9 Hz, H3), 1.63 (1H, dt, *J* = 14.2, 5.9 Hz, H3), 0.89 (3H, d, *J* = 6.9 Hz, H7); **¹³C NMR** (100 MHz, CD₃OD) δ 80.7, 80.1, 65.3, 64.2, 57.8, 57.5, 39.7, 33.3, 11.6; **HRMS** calc. for C₉H₂₀O₄ [M+NH₄]⁺ 210.1705, found 210.1709.

(2R, 4S, 5S)-2,4-dimethoxy-1,6-di-*p*-nitrobenzoyloxy-5-methylhexane (11)

R_f 0.20 (20% EtOAc / 40-60 petroleum ether); **[α]_D** -8.0 (c 0.56, CHCl₃); **IR** (thin film) 2932, 1724, 1608, 1527, 1347, 1274, 1102 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃) δ 8.29 (4H, br d, *J* = 8.8 Hz), 8.22 (2H, d, *J* = 8.8 Hz), 8.21 (2H, d, *J* = 8.8 Hz), 4.55 (1H, dd, *J* = 12.0, 3.5 Hz), 4.45 (1H, dd, *J* = 11.0, 6.6 Hz), 4.38 (1H, dd, *J* = 12.0, 5.4 Hz), 4.31 (1H, dd, *J* = 11.0, 6.9 Hz), 3.67 (1H, m), 3.47 (1H, m), 3.43 (3H, s), 3.39 (3H, s), 2.31 (1H, m), 1.93 (1H, ddd, *J* = 14.5, 7.3, 7.3 Hz), 1.79 (1H, ddd, *J* = 14.5, 5.5, 5.5 Hz), 1.04 (3H, d, *J* = 6.9 Hz); **¹³C NMR** (125.8 MHz, CDCl₃) δ 164.6, 164.5, 150.7, 150.6, 135.7, 135.3, 130.7, 130.6, 123.6, 123.6, 78.2, 76.4, 67.6, 66.7, 57.6, 57.5, 35.0, 32.0, 11.8; **HRMS** calc. for C₂₃H₂₆N₂O₁₀Na [M+Na]⁺ 513.1485, found 513.1483.

Characterization Data for Intermediates in the Synthesis of the C₂₃-C₃₅ Degradation Fragments(2S, 4S, 5S, 6S)-5-Hydroxy-1-(*p*-methoxybenzyloxy)-7-triisopropylsiloxy-2,4,6-trimethylheptan-3-one (13) and (2S, 4R, 5R, 6S)-5-Hydroxy-1-(*p*-methoxybenzyloxy)-7-triisopropylsiloxy-2,4,6-trimethylheptan-3-one

(13) major diastereomer

minor diastereomer (tentative assignment)

Isolated as a 95:5 mixture of diastereomers

13: **R_f** 0.13 (10% EtOAc / 40-60 petroleum ether); **[α]_D** +17.5 (c 1.5, CHCl₃); **IR** (thin film) 3500, 2940, 2865, 1713, 1513, 1462 cm⁻¹; **¹H NMR** (400 MHz, C₆D₆) δ 7.25° (2H, d, *J* = 8.6 Hz, H3), 6.88° (2H, d, *J* = 8.6 Hz, H4), 4.35° (1H, d, *J* = 11.6 Hz, H1), 4.30° (1H, d, *J* = 11.6 Hz, H1), 3.89° (1H, dd, *J* = 9.7, 4.9 Hz, H7), 3.85° (1H, dd, *J* = 9.9, 4.9 Hz, H7), 3.80° (1H,

dt, $J = 7.2, 5.5$ Hz, H5), 3.73° (1H, br t, $J = 8.6$ Hz, H1), 3.42° (1H, d, $J = 7.2$ Hz, C5-OH), 3.39° (3H, s, OCH₃), 3.35° (1H, dd, $J = 8.6, 5.0$ Hz, H1), 3.17° (1H, br q, $J = 7.3$ Hz, H4), 3.10° (1H, m, H2), 1.86° (1H, m, H6), 1.23° (3H, d, $J = 7.3$ Hz, H9), 1.20 - 1.21° (3H, m, Si(CH(CH₃)₂)), 1.19 - 1.20° (18H, m, Si(CH(CH₃)₂)), 1.12° (3H, d, $J = 7.1$ Hz, H10), 1.09° (3H, d, $J = 7.0$ Hz, H8); ¹³C NMR (100.6 MHz, CDCl₃) δ 217.7, 159.2, 130.2, 129.2, 113.7, 77.8, 73.0, 72.3, 65.7, 55.2, 49.9, 46.5, 36.7, 18.0, 15.2, 13.5, 13.4, 11.8; HRMS calc. for C₂₇H₄₈O₅Si [M+H]⁺ 481.3349, found 481.3343.

minor diastereomer: R_f 0.11 (10% EtOAc / 40-60 petroleum ether); $[\alpha]_D$ 0.0 (c 1.0, CHCl₃); IR (thin film) 3485, 2940, 2865, 1711, 1612, 1513 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.21[°] (2H, d, $J = 8.6$ Hz, H3), 6.84[°] (2H, d, $J = 8.6$ Hz, H4), 4.42[°] (1H, d, $J = 11.6$ Hz, H1), 4.37[°] (1H, d, $J = 11.6$ Hz, H1), 3.98[°] (1H, ddd, $J = 9.2, 3.5, 2.5$ Hz, H5), 3.78[°] (3H, s, OCH₃), 3.73[°] (2H, br d, $J = 5.3$ Hz, H7), 3.67[°] (1H, dd, $J = 9.0, 7.7$ Hz, H1), 3.39[°] (1H, dd, $J = 9.0, 5.9$ Hz, H1), 3.11[°] (1H, d, $J = 3.5$ Hz, C5-OH), 3.08[°] (1H, br dd, $J = 7.5, 5.9$ Hz, H2), 2.91[°] (1H, dd, $J = 9.2, 7.0$ Hz, H4), 1.74[°] (1H, m, H6), 1.06[°] (3H, d, $J = 6.9$ Hz, H8), 1.04-1.05[°] (18H, m, Si(CH(CH₃)₂)), 1.03-1.04[°] (3H, m, Si(CH(CH₃)₂)), 0.98[°] (3H, d, $J = 7.0$ Hz, H9), 0.92[°] (3H, d, $J = 7.0$ Hz, H10); ¹³C NMR (100.6 MHz, CDCl₃) δ 218.0, 159.2, 130.0, 129.3, 113.7, 75.2, 72.9, 72.1, 68.0, 55.2, 49.0, 46.6, 36.5, 17.9, 13.6, 13.4, 11.8, 9.2. HRMS calc. for C₂₇H₄₈O₅Si [M+H]⁺ 481.3349, found 481.3347.

(2S, 3S, 4R, 5S, 6S)-1-(p-Methoxybenzyloxy)-7-triisopropylsiloxy-2,4,6-trimethylheptan-3,5-diol (14)

R_f 0.10 (10% EtOAc / 40-60 petroleum ether); $[\alpha]_D$ +2.3 (c 1.0, CHCl₃); IR (thin film) 3420, 2939, 2865, 1513, 1461 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.26[°] (2H, d, $J = 8.6$ Hz, H3), 6.87[°] (2H, d, $J = 8.6$ Hz, H4), 4.68[°] (1H, d, $J = 3.1$ Hz, C5-OH), 4.49[°] (1H, d, $J = 11.6$ Hz, H1), 4.45[°] (1H, d, $J = 11.6$ Hz, H1), 4.29[°] (1H, s, C3-OH), 3.86[°] (1H, dd, $J = 9.7, 4.5$ Hz, H7), 3.83[°] (1H, br d, $J = 10.2$ Hz, H3), 3.80[°] (3H, s, OCH₃), 3.76[°] (1H, dd, $J = 9.7, 7.8$ Hz, H7), 3.65[°] (1H, dd, $J = 8.9, 5.5$ Hz, H1), 3.56[°] (1H, dt, $J = 8.6, 3.1$ Hz, H5), 3.46[°] (1H, dd, $J = 8.9, 6.4$ Hz, H1), 2.02[°] (1H, m, H6), 1.94[°] (1H, m, H2), 1.80[°] (1H, m, H4), 1.07-1.08[°] (18H, m, Si(CH(CH₃)₂)), 1.06-1.07[°] (3H, m, Si(CH(CH₃)₂)), 1.05[°] (3H, d, $J = 8.0$ Hz, H9), 0.86[°] (3H, d, $J = 6.6$ Hz, H8), 0.84[°] (3H, d, $J = 6.8$ Hz, H10); ¹³C NMR (100.6 MHz, CDCl₃) δ_c 159.1, 130.6, 129.4, 113.7, 82.2, 74.1, 73.6, 72.9, 69.5, 55.2, 37.5, 36.5, 34.8, 18.0, 13.5, 13.4, 11.7, 10.4; HRMS calc. for C₂₇H₅₀O₅Si [M+H]⁺ 483.3506, found 483.3503.

(2S, 3S, 4S, 5S, 6S, 1S)-1,3-(p-Methoxybenzyldioxy)-7-triisopropylsiloxy-2,4,6-trimethylheptan-5-ol

R_f 0.20 (10% EtOAc / 40-60 petroleum ether); $[\alpha]_D$ +31.9 (c 1.15, CHCl₃); IR (thin film) 3509, 2865, 1518, 1460 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.38[°] (2H, d, $J = 8.5$ Hz, H3), 6.86[°] (2H, d, $J = 8.5$ Hz, H4), 5.50[°] (1H, s, H1), 4.11[°] (1H, dd, $J = 11.1, 4.6$ Hz, H1), 4.02[°] (1H, br d, $J = 10.1$ Hz, H3), 3.95[°] (1H, dd, $J = 9.7, 4.4$ Hz, H7), 3.89[°] (3H, s, OCH₃), 3.86[°] (1H, dd, $J = 9.5, 6.9$ Hz, H7), 3.54[°] (1H, dd, $J = 11.1, 11.1$ Hz, H1), 3.48[°] (1H, dt, $J = 9.2, 7.0$ Hz, H5), 3.22[°] (1H, d, $J = 9.2$ Hz, C5-OH), 2.10[°] (1H, m, H2), 1.98[°] (1H, br q, $J = 7.0$ Hz, H4), 1.82[°] (1H, m, H6), 1.14[°] (3H, d, $J = 7.0$ Hz, H10), 1.08[°] (18H, m, Si(CH(CH₃)₂)),

1.07° (3H, m, Si(CH₂(CH₃)₂), 1.02° (3H, d, J = 7.0 Hz, H₉), 0.75° (3H, d, J = 6.7 Hz, H₈); ¹³C NMR (100.6° MHz, CDCl₃) δ 159.8, 131.4, 127.4, 113.5, 101.0, 82.3, 76.4, 73.2, 65.8, 55.3, 36.8, 36.5, 30.3, 18.0, 15.4, 12.0, 11.8, 10.5; HRMS calc. for C₂₇H₄₈O₅Si [M+H]⁺ 481.3349, found 481.3348.

(2S, 3S, 4S, 5S, 6S, 1 S)-5-Methoxy-1,3-(*p*-methoxybenzyldioxy)-7-triisopropylsiloxy-2,4,6-trimethylheptane

R_f 0.30 (10% EtOAc / 40-60 petroleum ether); **[α]_D** +28.9 (c 1.5, CHCl₃); **IR** (thin film) 2940, 2865, 1518, 1461 cm⁻¹; **¹H NMR** (400° MHz, CDCl₃) δ 7.42° (2H, d, J = 8.6 Hz, H₃), 6.89° (2H, d, J = 8.6 Hz, H₄), 5.47° (1H, s, H₁), 4.12° (1H, dd, J = 11.1, 4.6 Hz, H₁), 3.84° (1H, dd, J = 9.6, 6.5 Hz, H₇), 3.81° (3H, s, OCH₃), 3.77° (1H, br d, J = 10.7 Hz, H₃), 3.53° (1H, dd, J = 11.1, 11.1 Hz, H₁), 3.47° (1H, dd, J = 9.6, 7.4 Hz, H₇), 3.44° (3H, s, OCH₃), 3.22° (1H, br d, J = 10.4 Hz, H₅), 2.06° (1H, m, H₂), 2.04° (1H, m, H₄), 2.02° (1H, m, H₆), 1.07° (3H, d, J = 6.8 Hz, H₁₀), 1.06° (18H, m, Si(CH₂(CH₃)₂), 1.05° (3H, m, Si(CH₂(CH₃)₂), 0.95° (3H, d, J = 6.9 Hz, H₉), 0.74° (3H, d, J = 6.7 Hz, H₈); ¹³C NMR (100.6° MHz, CDCl₃) δ 159.8, 131.7, 127.3, 113.5, 100.8, 84.8, 82.0, 73.4, 64.1, 61.6, 55.3, 38.2, 36.7, 30.4, 18.1, 16.1, 11.9, 10.2; HRMS calc. for C₂₈H₅₀O₅Si [M+H]⁺ 495.3506, found 495.3507.

(2S, 3S, 4S, 5S, 6S, 1 S)-5-Methoxy-1,3-(*p*-methoxybenzyldioxy)-2,4,6-trimethylheptan-7-ol (15)

R_f 0.40 (50% EtOAc / petroleum ether); **[α]_D** +72.1 (c 0.19, CHCl₃); **mp**: 104-105 °C; **IR** (thin film) 3439, 2931, 1615, 1518, 1248, 1081, 1031 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃) δ 7.40 (2H, d, J = 8.7 Hz), 6.89 (2H, d, J = 8.7 Hz), 5.46 (1H, s), 4.13 (1H, dd, J = 11.1, 4.6 Hz), 3.90 (1H, dd, J = 11.1, 2.1 Hz), 3.80 (3H, s), 3.77 (1H, dd, J = 10.1, 1.5 Hz), 3.54 (2H, m, H₁), 3.49 (3H, s), 3.30 (1H, dd, J = 10.1, 1.7 Hz), 2.89 (1H, br d, J = 7.2 Hz), 2.09 (1H, m), 2.00 (1H, m), 1.87 (1H, m), 1.21 (3H, d, J = 7.2 Hz), 0.91 (3H, d, J = 7.0 Hz), 0.76 (3H, d, J = 6.7 Hz); ¹³C NMR (125.8 MHz, CDCl₃) δ 159.9, 131.5, 127.3, 113.6, 100.9, 87.5, 81.6, 73.4, 64.2, 62.1, 55.3, 37.2, 35.6, 30.4, 16.2, 12.0, 10.1; HRMS calc. for C₁₉H₃₀O₅Na [M+Na]⁺ 361.1991, found 361.1991.

(2R, 3R, 4S, 5S, 6S, 1 S)-3-Methoxy-5,7-(*p*-methoxybenzyldioxy)-2,4,6-trimethylheptanal (18)

R_f: 0.4 (25% Et₂O / petroleum ether); [**α**]_D +41.1 (c 0.54, CHCl₃); **IR** (thin film) 2934, 1721, 1615, 1518, 1385, 1249, 1092 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃) δ 9.75 (1H, d, *J* = 1.9 Hz), 7.41 (2H, d, *J* = 8.7 Hz), 6.89 (2H, d, *J* = 8.7 Hz), 5.47 (1H, s), 4.12 (1H, dd, *J* = 11.1, 4.6 Hz), 3.80 (3H, s), 3.80 (1H, m), 3.53 (1H, dd, *J* = 11.1, 11.0), 3.52 (1H, d, *J* = 10.7 Hz), 3.46 (3H, s), 2.66 (1H, m), 2.08 (1H, m), 1.98 (1H, m), 1.23 (3H, d, *J* = 7.0 Hz), 0.90 (3H, d, *J* = 7.0 Hz), 0.74 (3H, d, *J* = 6.7 Hz); **¹³C NMR** (125.8 MHz, CDCl₃) δ 204.5 (-ve), 159.9 (+ve), 131.5 (+ve), 127.3 (-ve), 113.6 (-ve), 101.0 (-ve), 83.6 (-ve), 81.5 (-ve), 73.3 (+ve), 60.6 (-ve), 55.3 (-ve), 48.5 (-ve), 37.2 (-ve), 30.3 (-ve), 11.9 (-ve), 11.0 (-ve), 9.7 (-ve); **HRMS** calc. for C₁₉H₂₈O₅Na [M+Na]⁺ 359.1834, found 359.1839.

(3*R*, 4*S*)-1-*t*-Butyldimethylsiloxy-3-methoxy-4-methylhex-4-ene

R_f: 0.80 (25% Et₂O / petroleum ether); [**α**]_D +11.8 (c 2.8, CHCl₃); **IR** (thin film) 2929, 1640, 1463, 1255, 1094, 835 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃) δ 5.77 (1H, m, H5), 5.02 (2H, m, H6), 3.68 (2H, m, H1), 3.35 (3H, s, OCH₃), 3.25 (1H, ddd, *J* = 8.1, 4.1, 4.1 Hz, H3), 2.47 (1H, m, H4), 1.58 (2H, m, H2), 1.00 (3H, d, *J* = 6.9 Hz, H7), 0.89 (9H, s, SiC(CH₃)₃), 0.04 (3H, s, SiCH₃), 0.04 (3H, s, SiCH₃); **¹³C NMR** (125.8 MHz, CDCl₃) δ 140.7, 114.5, 81.3, 59.9, 57.7, 40.0, 33.9, 25.9, 18.2, 14.4, -5.3, -5.4; **HRMS** calc. for C₁₄H₃₁O₂Si [M+H]⁺ 259.2093, found 259.2094.

(3*S*, 4*R*)-1-*t*-Butyldimethylsiloxy-3-methoxy-4-methylhex-4-ene

The characterization data (**R_f**, **IR**, **¹H NMR**, **¹³C NMR**, **HRMS**) was identical to that listed above for the enantiomer; [**α**]_D -9.8 (c 0.40, CHCl₃).

(3*R*, 4*R*)-6-*t*-Butyldimethylsiloxy-4-methoxy-3-methylhexan-2-one (9)

R_f: 0.5 (90:8:1:1 - petroleum ether:CH₂Cl₂:MeOH:acetone); [**α**]_D -19.3 (c 6.8, CHCl₃); **IR** (thin film) 2929, 1714, 1254, 1093, 833 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃) δ 3.67 (2H, m, H6), 3.60 (1H, ddd, *J* = 7.1, 7.1, 3.5 Hz, H4), 3.30 (3H, s, OCH₃), 2.82 (1H, dq, *J* = 7.1, 7.0 Hz, H3), 2.15 (3H, s, H7), 1.59 (2H, m, H5), 0.99 (3H, d, *J* = 7.0 Hz, H7), 0.87 (9H, s, SiC(CH₃)₃), 0.03 (3H, s, SiCH₃), 0.02 (3H, s, SiCH₃); **¹³C NMR** (125.8 MHz, CDCl₃) δ 211.2 (+ve, C2), 79.2 (-ve, C4), 59.4 (+ve, C6), 57.6 (-ve, OCH₃), 50.1 (-ve, C3), 33.8 (+ve, C5), 29.7 (-ve, C1), 25.9 (-ve, SiC(CH₃)₃), 18.2 (+ve, SiC(CH₃)₃), 11.5 (-ve, C7), -5.4 (-ve, SiCH₃), -5.5 (-ve, SiCH₃); **HRMS** calc. for C₁₄H₃₀O₃SiNa [M+Na]⁺ 297.1862, found 297.1854.

(3S, 4S)-6-*t*-Butyldimethylsiloxy-4-methoxy-3-methylhexan-2-one (**ent-9**)

The characterization data (R_f , IR, ^1H NMR, ^{13}C NMR, HRMS) recorded for **ent-9** was identical to that listed above for enantiomer **9**; $[\alpha]_D^{+17.2}$ (c 1.1, CHCl_3).

(3R, 4R, 7S, 8S, 9S, 10S, 11S, 12S, 1 S)-1-*t*-Butyldimethylsiloxy-3,9-dimethoxy-7-hydroxy-11,13-(*p*-methoxybenzyldioxy)-4,8,10,12-tetramethyltridecan-5-one (**19**) and (3R, 4R, 7R, 8S, 9S, 10S, 11S, 12S, 1 S)-1-*t*-butyldimethylsiloxy-3,9-dimethoxy-7-hydroxy-11,13-(*p*-methoxybenzyldioxy)-4,8,10,12-tetramethyltridecan-5-one (**7-epi-19**)

R_f : 0.20 (25% Et_2O / petroleum ether); IR (thin film) 3498, 2929, 1707, 1615, 1518, 1249, 1093 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.40 (2H, d, J = 8.6 Hz, H3), 6.89 (2H, d, J = 8.6 Hz, H4), 5.44 (1H, s, H1), 4.51 (1H, m, H7), 4.24 (1H, m, H7), 4.13 (1H, dd, J = 11.0, 4.5 Hz, H13 β)*, 4.11 (1H, dd, J = 11.0, 4.5 Hz, H13 β), 3.80 (3H, s, OCH_3), 3.76 (1H, br d, J = 10.1 Hz, H11), 3.71 (2H, m, H1, H3), 3.59 (1H, ddd, J = 15.4, 7.7, 3.4 Hz, H1), 3.52 (1H, dd, J = 11.2, 11.0 Hz, H13 α), 3.49 (3H, s, OCH_3)*, 3.45 (3H, s, OCH_3), 3.36 (1H, m, OH), 3.30 (3H, s, OCH_3)*, 3.29 (3H, s, OCH_3), 3.22 (1H, dd, J = 10.1, 2.3 Hz, H9), 2.88 (1H, m, H4), 2.82 (1H, m, H6), 2.59 (1H, m, H6), 1.90-2.10 (3H, m, H8, H10, H12), 1.72 (1H, m, H2), 1.60 (1H, m, H2), 1.09 (3H, d, J = 7.1 Hz, H15)*, 1.02 (3H, d, J = 7.1 Hz, H15), 1.02 (3H, d, J = 7.0 Hz, H14), 0.95 (3H, d, J = 6.9 Hz, H16), 0.90 (9H, s, $\text{SiC}(\text{CH}_3)_3$), 0.89 (9H, s, $\text{SiC}(\text{CH}_3)_3$)*, 0.77 (3H, d, J = 7.0 Hz, H17)*, 0.72 (3H, d, J = 6.7 Hz, H17), 0.06 (6H, s, $\text{Si}(\text{CH}_3)_2$), 0.05 (6H, s, $\text{Si}(\text{CH}_3)_2$)*; ^{13}C NMR (125.8 MHz, CDCl_3) δ 215.4, 159.8, 131.6, 127.3, 113.5, (100.9), 100.8, (88.4), 85.8, 81.7, 79.8, (79.4), 73.4, 68.2, 61.7, (59.0), 58.9, 57.8, (57.6), 55.3, 50.4, (50.1), 47.4, (47.0), 40.0, 37.7, (36.3), 33.9, (33.8), (30.3), 30.3, 25.9, 18.2, 14.6, 12.3, (12.0), (12.0), 11.9, (11.5), 10.1, (9.9), -5.3, -5.4; HRMS calc. for $\text{C}_{33}\text{H}_{58}\text{O}_8\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 633.3799, found 633.3812.

(3R, 4R, 6E, 8S, 9S, 10S, 11S, 12S, 1 S)-1-*t*-Butyldimethylsiloxy-3,9-dimethoxy-11,13-(*p*-methoxybenzyldioxy)-4,8,10,12-tetramethyltridec-6-en-5-one (**20**)

R_f : 0.60 (20% EtOAc / hexane); $[\alpha]_D^{+27.8}$ (c 0.45, CHCl_3); IR (thin film) 2930, 1693, 1669, 1617, 1518, 1250, 1094 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.41 (2H, d, J = 8.7 Hz, H3), 6.91 (1H, dd, J = 16.0, 8.8 Hz, H7), 6.89 (2H, d, J = 8.7 Hz, H4), 6.16 (1H, d, J = 16.0 Hz, H6), 5.46 (1H, s, H1), 4.11 (1H, dd, J = 11.1, 4.6 Hz, H13 β), 3.81 (3H, s, OCH_3), 3.75 (1H, dd, J = 10.1, 1.5 Hz, H11), 3.67-3.72 (2H, m, H1), 3.59 (1H, ddd, J = 7.7, 7.7, 3.2 Hz, H3), 3.52 (1H, dd, J = 11.0, 11.0 Hz, H13 α), 3.47 (3H, s, OCH_3), 3.28 (3H, s, OCH_3), 3.23 (1H, dd, J = 10.2, 1.8 Hz, H9), 3.13 (1H, dq, J = 7.1, 7.1 Hz, H4), 2.62 (1H, m, H8), 2.05 (1H, m, H12), 1.68-1.75 (2H, m, H10, H12), 1.59 (1H, m, H2), 1.19 (3H, d, J =

6.9 Hz, H15), 1.03 (3H, d, $J = 6.9$ Hz, H14), 0.89 (9H, s, $\text{Si}(\text{CH}_3)_3$), 0.86 (3H, d, $J = 6.9$ Hz, H16), 0.70 (3H, d, $J = 6.7$ Hz, H17), 0.05 (6H, s, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (125.8 MHz, CDCl_3) δ 202.6, 159.9, 148.4, 131.6, 130.2, 127.3, 113.6, 100.9, 85.0, 81.7, 79.6, 73.3, 61.5, 59.2, 58.0, 55.3, 46.7, 39.8, 37.6, 34.1, 30.3, 25.9, 18.3, 17.8, 12.4, 11.8, 9.6, -5.3, -5.4; HRMS calc. for $\text{C}_{33}\text{H}_{56}\text{O}_7\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 615.3693, found 615.3687.

(3R, 4R, 8S, 9S, 10R, 11S, 12S)-1-*t*-Butyldimethylsiloxy-11,13-dihydroxy-3,9-dimethoxy-4,8,10,12-tetramethyltridecan-5-one

R_f: 0.30 (50% EtOAc / hexane); **[α]_D** -17.8 (c 0.23, CHCl_3); **IR** (thin film) 3439, 2931, 1712, 1462, 1255, 1091 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 4.06 (1H, br s, OH), 3.82 (1H, br d, $J = 9.6$ Hz, H11), 3.71 (2H, m, H1), 3.65 (2H, m, H13), 3.59 (1H, ddd, $J = 7.5, 7.5, 3.3$ Hz, H3), 3.51 (3H, s, OCH_3), 3.30 (3H, s, OCH_3), 2.94 (1H, dd, $J = 8.9, 2.2$ Hz, H9), 2.85 (1H, dq, $J = 7.5, 7.0$ Hz, H4), 2.57 (1H, ddd, $J = 17.5, 10.2, 5.3$ Hz, H6), 2.48 (1H, ddd, $J = 17.5, 9.8, 5.7$ Hz, H6), 1.95 (1H, m, H7), 1.88 (2H, m, H10, H12), 1.79 (1H, m, H8), 1.71 (1H, dddd, $J = 14.3, 7.0, 7.0, 3.3$ Hz, H2), 1.60 (1H, m, H2), 1.38 (1H, m, H7), 1.09 (3H, d, $J = 7.0$ Hz, H16), 1.01 (3H, d, $J = 7.0$ Hz, H14), 0.89 (9H, s, $\text{Si}(\text{CH}_3)_3$), 0.82 (3H, d, $J = 6.8$ Hz, H15), 0.72 (3H, d, $J = 6.9$ Hz, H17), 0.06 (3H, s, SiCH_3), 0.06 (3H, s, SiCH_3); ^{13}C NMR (125.8 MHz, CDCl_3) δ 213.4, 93.1, 79.7, 77.2, 69.4, 62.2, 58.9, 57.9, 49.7, 41.1, 37.3, 35.7, 35.0, 33.9, 26.4, 25.9, 18.3, 15.9, 13.3, 12.2, 11.7, -5.3, -5.4; HRMS calc. for $\text{C}_{25}\text{H}_{52}\text{O}_6\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 499.3431, found 499.3431.

The C₂₃-C₃₅ Degradation Fragments **5a** and **5b**

Isolated as a 4:1 mixture of diastereomers (configuration of C₃₁ not determined).

Major diastereomer (**5a**): **R_f**: 0.20 (10% MeOH / CH_2Cl_2); **[α]_D** +3.7 (c 0.08, CHCl_3); **IR** (thin film) 3369, 2964, 2933, 1578, 1422, 1083 cm^{-1} ; ^1H NMR: see Table 1a below; ^{13}C NMR: see Table 2 below; HRMS calc. for $\text{C}_{19}\text{H}_{40}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$ 387.2723, found 387.2715.

Minor diastereomer (**5b**): **R_f**: 0.25 (10% MeOH / CH_2Cl_2); **IR** (thin film) 3408, 2923, 2852, 1462, 1080 cm^{-1} ; ^1H NMR: see Table 1a below; ^{13}C NMR: see Table 2 below; HRMS calc. for $\text{C}_{19}\text{H}_{40}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$ 387.2723, found 387.2715.

(3S, 4S, 7S, 8S, 9S, 10S, 11S, 12S, 1 S)-1-*t*-Butyldimethylsiloxy-3,9-dimethoxy-7-hydroxy-11,13-(*p*-methoxybenzyldioxy)-4,8,10,12-tetramethyltridecan-5-one (**21**) and (3S, 4S, 7R, 8S, 9S, 10S, 11S, 12S, 1 S)-1-*t*-butyldimethylsiloxy-3,9-dimethoxy-7-hydroxy-11,13-(*p*-methoxybenzyldioxy)-4,8,10,12-tetramethyltridecan-5-one (**7-*epi*-21**)

R_f: 0.20 (25% Et₂O / petroleum ether); **IR** (thin film) 3489, 2954, 1706, 1518, 1250, 1095, 834 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃) δ 7.40 (2H, d, *J* = 8.7 Hz), 6.89 (2H, d, *J* = 8.7 Hz), 5.45 (1H, s), 4.21 (1H, m), 4.13 (1H, dd, *J* = 11.0, 4.6 Hz)*, 4.12 (1H, dd, *J* = 11.0, 4.6 Hz), 3.80 (3H, s), 3.56-3.78 (4H, m), 3.52 (1H, br d, *J* = 11.0 Hz), 3.48 (3H, s)*, 3.45 (3H, s), 3.30 (3H, s), 3.29 (3H, s)*, 3.23 (1H, dd, *J* = 10.3, 2.5 Hz), 2.82-2.92 (2H, m), 2.59 (1H, dd, *J* = 17.2, 9.8 Hz), 1.94-2.15 (3H, m), 1.58-1.78 (3H, m), 1.04 (3H, d, *J* = 7.3 Hz), 1.02 (d, *J* = 7.0 Hz), 1.00 (d, *J* = 6.6 Hz)*, 0.95 (d, *J* = 7.0 Hz), 0.72 (d, *J* = 6.7 Hz), 0.71 (d, *J* = 6.8 Hz)*; **¹³C NMR** (125.8 MHz, CDCl₃) δ 215.7, 159.8, 131.6, 127.3, 113.6, (101.0), 100.9, (85.8), 85.7, 81.7, 79.8, (79.2), 73.4, 68.1, 61.7, 58.9, 57.8, 55.3, 50.3, (49.8), 47.0, (39.9), 39.8, (37.6), 37.5, 33.8, 30.3, 25.9, 18.2, 14.4, 12.1, 11.9, 10.1, -5.3, -5.4; **HRMS** calc. for C₃₃H₅₈O₈SiNa [M+Na]⁺ 633.3799, found 633.3781.

(3*S*, 4*S*, 6*E*, 8*S*, 9*S*, 10*S*, 11*S*, 12*S*, 1*S*)-1-*t*-Butyldimethylsiloxy-3,9-dimethoxy-11,13-(*p*-methoxybenzyldioxy)-4,8,10,12-tetramethyltridec-6-en-5-one

R_f: 0.50 (20% EtOAc / hexane); [**α**]_D +37.0 (c 0.12, CHCl₃); **IR** (thin film) 2929, 1693, 1669, 1518, 1384, 1250, 1094, 834 cm⁻¹; **¹H NMR** (500 MHz, CDCl₃) δ 6.81 (2H, d, *J* = 8.7 Hz, H₃), 6.90 (1H, dd, *J* = 15.8, 8.9 Hz, H₇), 6.89 (2H, d, *J* = 8.7 Hz, H₄), 6.15 (1H, d, *J* = 15.8 Hz, H₆), 5.46 (1H, s, H₁), 4.11 (1H, dd, *J* = 11.1, 4.6 Hz, H_{13β}), 3.81 (3H, s, OCH₃), 3.75 (1H, dd, *J* = 10.1, 1.6 Hz, H₁₁), 3.71 (2H, m, H₁), 3.62 (1H, ddd, *J* = 7.7, 7.7, 3.1 Hz, H₃), 3.52 (1H, dd, *J* = 11.1, 11.1 Hz, H_{13α}), 3.48 (3H, s, OCH₃), 3.30 (3H, s, OCH₃), 3.23 (1H, dd, *J* = 10.2, 1.9 Hz, H₉), 3.15 (1H, dq, *J* = 7.1, 7.1 Hz, H₄), 2.62 (1H, m, H₈), 2.04 (1H, m, H₁₂), 1.71 (1H, m, H₁₀), 1.68 (1H, m, H₂), 1.59 (1H, m, H₂), 1.21 (3H, d, *J* = 7.0 Hz, H₁₅), 1.02 (3H, d, *J* = 7.1 Hz, H₁₄), 0.89 (9H, s, SiC(CH₃)₃), 0.87 (3H, d, *J* = 7.0 Hz, H₁₆), 0.69 (3H, d, *J* = 6.7 Hz, H₁₇), 0.05 (6H, s, Si(CH₃)₂); **¹³C NMR** (125.8 MHz, CDCl₃) δ 202.6, 159.9, 148.2, 131.6, 130.3, 127.3, 113.6, 100.9, 85.1, 81.6, 79.4, 73.3, 61.6, 59.2, 58.0, 55.3, 46.6, 39.7, 37.6, 34.1, 30.3, 25.9, 18.2, 17.4, 12.5, 11.8, 9.7, -5.3, -5.4; **HRMS** calc. for C₃₃H₅₆O₇SiNa [M+Na]⁺ 615.3693, found 615.3702.

(3*S*, 4*S*, 8*S*, 9*S*, 10*R*, 11*S*, 12*S*)-1-*t*-Butyldimethylsiloxy-11,13-dihydroxy-3,9-dimethoxy-4,8,10,12-tetramethyltridecan-5-one

R_f: 0.20 (50% EtOAc / hexane); [**α**]_D +7.1 (c 0.065, CHCl₃); **IR** (thin film) 3444, 2930, 1713, 1462, 1255, 1091, 836 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃) δ 4.05 (1H, s), 3.81 (1H, br d, *J* = 9.8 Hz), 3.71 (2H, dd, *J* = 7.0, 5.6 Hz), 3.67 (1H, dd, *J* = 8.3, 8.3 Hz), 3.56-3.63 (3H, m), 3.51 (3H, s), 3.30 (3H, s), 2.95 (1H, dd, *J* = 8.6, 2.4 Hz), 2.85 (1H, dq, *J* = 7.1, 7.1 Hz), 2.57 (1H, ddd, *J* = 17.4, 9.5, 5.7 Hz), 2.50 (1H, ddd, *J* = 17.4, 9.1, 6.3 Hz), 1.75-2.02 (4H, m), 1.55-1.75 (2H, m), 1.35 (1H, m), 1.09 (3H, d, *J* = 7.1 Hz), 1.01 (3H, d, *J* = 6.9 Hz), 0.90 (9H, s), 0.82 (3H, d, *J* = 6.8 Hz), 0.72 (3H, d, *J* = 6.9 Hz); **¹³C NMR** (100.6 MHz, CDCl₃) δ 213.4, 93.1, 79.8, 77.3, 69.4, 62.1, 58.9, 57.8, 49.6, 41.0, 37.3, 35.5, 35.0, 33.9, 26.4, 25.9, 18.2, 15.9, 13.3, 12.2, 11.7, -5.4, -5.4; **HRMS** calc. for C₂₅H₅₂O₆SiNa [M+Na]⁺ 499.3436, found 499.3431.

The C₂₃-C₃₅ Diastereomers **6a** and **6b**

Isolated as a 4:1 mixture of diastereomers (configuration of C₃₁ not determined).

Major diastereomer (**6a**): R_f: 0.20 (10% MeOH / CH₂Cl₂); [α]_D -6.6 (c 0.075, CHCl₃); IR (thin film) 3379, 2961, 2929, 1731, 1460, 1380, 1082, 988, 679 cm⁻¹; ¹H NMR: see Table 1b below; ¹³C NMR: see Table 2 below; HRMS calc. for C₁₉H₄₀O₆Na [M+Na]⁺ 387.2723, found 387.2713.

Minor diastereomer (**6b**): R_f: 0.25 (10% MeOH / CH₂Cl₂); IR (thin film) 3385, 2970, 1566, 1394, 1250, 1078, 661 cm⁻¹; ¹H NMR: see Table 1b below; ¹³C NMR: Insufficient amounts of the minor diastereomer were isolated for ¹³C NMR analysis; HRMS calc. for C₁₉H₄₀O₆Na [M+Na]⁺ 387.2723, found 387.2738.

Tables 1a and 1b. Comparison of ^1H NMR data for the $\text{C}_{23}\text{-C}_{35}$ degradation fragments (recorded at 500 MHz, CD_3OD).

Proton No. ^a	Natural $\text{C}_{23}\text{-C}_{35}$ degradation fragment ^{a,b,c}		5a ^c	5b ^{c,d}
23a	3.77 (dd, 10.3, 5.1)	3.77 (dd, 10.3, 5.1)	3.77 (dd, 10.6, 5.0)	3.76 (dd, 10.6, 5.1)
23b	3.57 (dd, 10.3, 6.0)	3.57 (dd, 10.3, 6.0)	3.57 (dd, 10.6, 6.0)	3.57 (dd, 10.6, 5.9)
24	1.77 (m)	1.77 (m)	1.78 (m)	1.77 (m)
25	3.75 (dd) ^d	3.75 (dd) ^d	3.76 (m)	3.74 (m)
26	1.88 (dd) ^d	1.88 (dd) ^d	1.88 (m)	1.88 (m)
27	3.14 (dd, 6.9, 4.3)	3.14 (dd, 6.9, 4.3)	3.15 (dd, 7.2, 4.6)	3.14 (dd, 6.9, 4.8)
28	1.76 (m)	1.76 (m)	1.79 (m)	1.76 (m)
29a	1.62 (m)	1.72 (m)	1.60 (m)	1.73 (m)
29b	1.39 (m)	1.14 (m)	1.39 (m)	1.15 (m)
30a	1.76 (m)	1.60 (m)	1.76 (m)	n.a.
30b	1.53 (m)	1.40 (m)	1.53 (m)	n.a.
31	3.47 (m)	3.41 (m)	3.47 (ddd, 8.0, 8.0, 3.5)	3.41 (m)
32	1.97 (m)	1.72 (m)	1.95 (m)	1.72 (m)
33	3.63 (m)	3.74 (m)	3.62 (ddd, 9.4, 4.8, 2.6)	3.72 (m)
34a	1.86 (m)	1.86 (m)	1.77 (m)	1.82 (m)
34b	1.65 (m)	1.65 (m)	1.59 (m)	n.a.
35a	3.70 (m)	3.70 (m)	3.68 (m)	3.68 (m)
35b	3.70 (m)	3.70 (m)	3.72 (m)	3.73 (m)
24-Me	0.87 (d, 6.6)	0.87 (d, 6.6)	0.87 (d, 6.8)	0.87 (d, 6.8)
26-Me	0.92 (d, 6.7)	0.92 (d, 6.7)	0.92 (d, 7.1)	0.93 (d, 7.0)
28-Me	1.03 (d, 6.6)	1.03 (d, 6.6)	1.03 (d, 6.9)	1.03 (d, 6.8)
32-Me	0.85 (d, 6.7)	0.92 (d, 6.7)	0.85 (d, 7.0)	0.92 (d, 7.0)
27-OMe	3.54 (s)	3.54 (s)	3.55 (s)	3.54 (s)
33-OMe	3.36 (s)	3.42 (s)	3.36 (s)	3.42 (s)

Proton No. ^a	Natural $\text{C}_{23}\text{-C}_{35}$ degradation fragment ^{a,b,c}		6a ^c	6b ^c
23a	3.77 (dd, 10.3, 5.1)	3.77 (dd, 10.3, 5.1)	3.77 (dd, 10.6, 5.1)	3.76 (dd, 10.6, 5.0)
23b	3.57 (dd, 10.3, 6.0)	3.57 (dd, 10.3, 6.0)	3.57 (dd, 10.6, 5.9)	3.57 (dd, 10.6, 6.0)
24	1.77 (m)	1.77 (m)	1.76 (m)	1.76 (m)
25	3.75 (dd) ^d	3.75 (dd) ^d	3.73 (dd, 9.9, 1.5)	3.75 (dd, 10.0, 1.8)
26	1.88 (dd) ^d	1.88 (dd) ^d	1.88 (dq, 7.1, 7.1, 1.5)	1.87 (m)
27	3.14 (dd, 6.9, 4.3)	3.14 (dd, 6.9, 4.3)	3.15 (dd, 7.1, 4.9)	3.14 (dd, 6.8, 4.6)
28	1.76 (m)	1.76 (m)	1.76 (m)	1.78 (m)
29a	1.62 (m)	1.72 (m)	1.14 (dddd, 15.4, 13.1, 9.6, 3.6)	n.a.
29b	1.39 (m)	1.14 (m)	1.83 (dddd, 15.4, 11.8, 6.7, 3.2)	n.a.
30a	1.76 (m)	1.60 (m)	1.78 (m)	n.a.
30b	1.53 (m)	1.40 (m)	1.24 (16.8, 11.8, 8.2, 3.6)	n.a.
31	3.47 (m)	3.41 (m)	3.43 (ddd, 8.2, 8.2, 2.5)	3.42 (m)
32	1.97 (m)	1.72 (m)	1.95 (dq, 8.2, 6.8, 4.8)	1.73 (m)
33	3.63 (m)	3.74 (m)	3.62 (ddd, 9.2, 4.8, 2.6)	3.69 (m)
34a	1.86 (m)	1.86 (m)	1.78 (m)	n.a.
34b	1.65 (m)	1.65 (m)	1.59 (dddd, 14.4, 9.2, 6.7, 5.1)	1.84 (m)
35a	3.70 (m)	3.70 (m)	3.73 (m)	3.66 (m)
35b	3.70 (m)	3.70 (m)	3.66 (m)	3.71 (m)
24-Me	0.87 (d, 6.6)	0.87 (d, 6.6)	0.87 (d, 6.6)	0.87 (d, 6.8)
26-Me	0.92 (d, 6.7)	0.92 (d, 6.7)	0.93 (d, 7.1)	0.93 (d, 7.0)
28-Me	1.03 (d, 6.6)	1.03 (d, 6.6)	1.04 (d, 6.9)	1.03 (d, 6.8)
32-Me	0.85 (d, 6.7)	0.92 (d, 6.7)	0.86 (d, 6.8)	0.93 (d, 7.0)
27-OMe	3.54 (s)	3.54 (s)	3.54 (s)	3.54 (s)
33-OMe	3.36 (s)	3.42 (s)	3.36 (s)	3.41 (s)

^a See reference 7, reidispongiolide A numbering system is followed. ^b The data reported for the two C_{31} epimers is reported separately. ^c All data is presented in order: chemical shift (multiplicity, coupling constants in Hz). ^d No coupling constants provided. ^e Assignments based on COSY data. n.a. : not assigned.

Table 2. Comparison of ^{13}C NMR data for the $\text{C}_{23}\text{-C}_{35}$ degradation fragments (recorded at 125.8 MHz, CD_3OD).

carbon no.	natural $\text{C}_{23}\text{-C}_{35}$ degradation fragment ^{a,b}	5a ^c	5b ^{d,e}	6a
23	63.5	67.0	67.0	67.0
24	36.4	36.5	36.8	37.0
25	71.0	74.3	74.2	74.3
26	34.4	37.7	37.7	37.7
27	87.0	90.8	90.7	90.7
28	33.5	39.7	39.7	39.7
29	24.9	27.5	n.o.	28.1
30	30.8 [30.0]	33.1	n.o. ^f	33.5 ^g
31	69.0 [70.3]	73.7	72.8	74.4
32	38.4 [38.1]	41.6	41.6	41.8
33	78.2 [77.1]	80.5	81.8	80.5
34	31.4	33.5	34.1 ^f	33.6 ^g
35	56.3	60.4	59.7	60.4
24-Me	10.2	13.8	13.8	13.8
26-Me	6.9	10.3	10.4	10.4
28-Me	14.3	17.5	17.6	17.7
32-Me	6.6 [7.3]	10.6	9.7	10.7
27-OMe	58.8	62.2	62.2	62.1
33-OMe	54.5	57.1	n.o.	57.1

^a See reference 7. ^b The data reported for the minor C_{31} epimer is presented in quotations []. ^c Assignments based on analysis of HMQC data. ^d Carbon chemical shifts were derived from analysis of the mixture of C_{31} epimers. ^e Assignments are based on comparison with data acquired for 5. ^f Assignments may be interchanged. ^g Assignments may be interchanged. n.o. : not observed.