Supplementary Information

Synthesis, Structure Revision and Absolute Configuration of (+)-Didemniserinolipid B, a Serinol Marine Natural Product from a Tunicate *Didemnum* sp.

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General

Melting points are uncorrected. Optical rotations values were measured on PerkinElmer Model 343 polarimeter. ¹H- and ¹³C-NMR spectra were recorded on a Bruker AM400 (400 MHz for ¹H and 100 MHz for ¹³C) or a Bruker DRX600 (600 MHz for ¹H and 125 MHz for ¹³C) spectrometer using the corresponding solvent peak as a reference (CHCl₃: 7.26 ppm). IR spectra were recorded on PerkinElmer SpectrumOne FTIR spectrometer. Mass spectra data were obtained on a Kratos MS890MS Q-TOF spectrometer using electrospray ionization (ESI). Microwave reaction was done with Personal Chemistry Smith Synthesizer. Merck Silica Gel 60 (230-400 mesh) was used for flash column chromatography.

(2*R*,3*R*,5*R*,6*R*,1'*R*)-3-(*tert*-Butyldimethylsilyl)oxymethyl-2-[6'-(*tert*-butyldiphenylsilyl)oxy-1'-hydroxy-2'-hexynyl]-5,6-dimethoxy-5,6-dimethyl-1,4-dioxane (**3**) and its 1'*S*-isomer (**4**)

To a solution of 5-(*tert*-butyldiphenylsilyl)oxy-1-pentyne (7.23 g, 22.5 mmol) in THF (35 ml) was added *n*-BuLi (12.5 ml 1.6 M in hexanes, 20 mmol) at -78°C. The reaction was warmed up to 0°C and left to stir for 10 min. After cooling down to -78°C, a solution of **2** (1.74 g, 4.99 mmol) in THF (4 ml) was added dropwise and this mixture stirred at -78°C for 2.5 hr. The reaction was quenched by the addition of sat. aq. NH₄Cl soln. (20 ml) and diluted with ether (200 ml). The organic layer was washed with water (200 ml) and brine (200 ml), dried (MgSO₄) and concentrated *in vacuo*. The products were separated and purified by flash column chromatography [petrol/ether = 10:1, 5:1, 2:1, 1:1 (+ 1% NEt₃)].

3; colourless oil (2.47 g, 3.69 mmol, 73.9%), *R*_f 0.16 (petrol/ether = 3:1); [α]_D³¹ -43° (*c* 0.20, CHCl₃); $\nu_{\max}$ /cm⁻¹ (film) 3429 (br s), 2952 (w), 2114 (w); δ_{H} (400 MHz, CDCl₃): 7.66-7.62 (4H, m, ArH), 7.45-7.35 (6H, m, ArH), 4.47 (1H, ddt, *J* 7.2, 3.3, 2.0, 1'-H), 4.22 (1H, dd, *J* 10.0, 7.8, CHHOTBS), 4.15 (1H, dd, *J* 3.5, 7.2, 2-H), 3.80 (1H, ddd, *J* 7.8, 4.3, 3.5, 3-H), 3.75 (1H, dd, *J* 4.8, 10.0, CHHOTBS), 3.68 (2H, t, *J* 6.0, 6'-H), 3.29 (3H, s, OMe), 3.27 (3H, s, OMe), 3.18 (1H, d, *J* 3.3, OH), 2.32 (2H, dt, *J* 7.4, 2.0, 4'-H), 1.73 (2H, tt, *J* 7.4, 6.0, 5'-H), 1.32 (3H, s, Me), 1.28 (3H, s, Me), 1.03 (9H, s, *t*-Bu), 0.89 (9H, s, *t*-Bu), 0.069 (3H, s, SiMe), 0.062 (3H, s, SiMe); *m/z* (ESI) 693.3619 (*M*⁺+Na. C₃₇H₅₈O₇Si₂Na requires 693.3619).

4; minor product: colourless oil (0.73 g, 1.1 mmol, 22%), *R*_f 0.33 (petrol/ether = 3:1); [α]_D³¹ -63° (*c* 0.20, CHCl₃); δ_{H} (400 MHz, CDCl₃): 7.67-7.63 (4H, m, ArH), 7.45-7.35 (6H, m, ArH), 4.46 (1H, t, *J* 10.0, CHHOTBS), 4.42 (1H, ddt, *J* 8.8, 5.4, 2.0, 1'-H), 4.16 (1H, ddd, *J* 8.8, 3.5, 1.0, 2-H), 4.08 (1H, d, OH), 3.92 (1H, ddd, *J* 10.0, 3.5, 2.5, 3-H), 3.71 (2H, t, *J* 6.0, 6'-H), 3.62 (1H, ddd, *J* 10.0, 2.5, 1.0, CHHOTBS), 3.27 (3H, s, OMe), 3.23 (3H, s, OMe), 2.36 (2H, dt, *J* 2.0, 7.4, 4'-H), 1.74 (2H, tt, *J* 6.0, 7.4, 5'-H), 1.263 (3H, s, Me), 1.259 (3H, s, Me), 1.03 (9H, s, *t*-Bu), 0.91 (9H, s, *t*-Bu), 0.12 (6H, s, SiMe₂).

(2*R*,3*R*,5*R*,6*R*,1'*R*)-3-(*tert*-Butyldimethylsilyl)oxymethyl-2-[(6'-(*tert*-butyldiphenylsilyl)oxy-1'-methoxymethoxy-2'-hexynyl]-5,6-dimethoxy-5,6-dimethyl-1,4-dioxane (**5**)

To a solution of NaI (1.27 g, 8.48 mmol) in DME (20 ml) was added MOMCl (0.80 ml, 11 mmol). The reaction was left to stir at rt for 1 h before *i*-PrNEt₂ (2.05 ml, 11.7 mmol) and **3** (1.42 g, 2.12 mmol) as a solution in DME (20 ml) were added. The reaction was heated to 60°C and left to stir at that temperature for 25 hr before finally cooling to rt. Sat. Na₂CO₃ soln. (10 ml) was added, followed by DCM (100 ml) and water (50 ml). The organic layer was again washed with water (50 ml), and the combined aqueous layers were re-extracted with DCM (50 ml). The combined organic layers were washed with brine (150 ml), dried (MgSO₄) and concentrated *in vacuo*. Purification by flash column chromatography (petrol/ether = 20:1 + 1% NEt₃) gave **5** as a colourless oil (1.13 g, 1.58 mmol, 74.5%). *R*_f 0.53 (petrol/ether = 5:1); [α]_D³¹ -36° (*c* 0.60, CHCl₃); $\nu_{\max}$ /cm⁻¹ (film) 2953 (m), 2856 (m), 1110 (m), 1034 (m); δ_{H} (400 MHz, CDCl₃): 7.67-7.62 (4H, m, ArH), 7.45-7.35 (6H, m, ArH), 4.83 (1H, d, *J* 6.6, OCHHO), 4.63 (1H, d, *J* 6.6, OCHHO), 4.27 (1H, dd, *J* 9.7, 1.8, CHHOTBS), 4.22 (1H, dt, *J* 9.7, 3.5, CHHOTBS), 4.06 (1H, m), 3.95-3.85 (2H, m), 3.68 (2H, t, *J* 6.0, 6'-H), 3.39 (3H, s, OMe), 3.34 (3H, s, OMe), 3.29 (3H, s, OMe), 2.32 (2H, t, *J* 7.2, 4'-H), 1.74 (2H, tt, *J* 6.0, 7.2, 5'-H), 1.28 (3H, s, Me), 1.27 (3H, s, Me), 1.04 (9H, s, *t*-Bu), 0.89 (9H, s, *t*-Bu), 0.058 (3H, s, SiMe), 0.45 (3H, s, SiMe) *m/z* (ESI) 737.3887 (*M*⁺+Na. C₃₉H₆₂O₈Si₂Na requires 737.3881).

(2*R*,3*R*,5*R*,6*R*,1'*R*)-2-(6'-Hydroxy-1'-methoxymethoxy-2'-hexynyl)-3-hydroxymethyl-5,6-dimethoxy-5,6-dimethyl-1,4-dioxane (6)

To a solution of **5** (1.41 g, 1.98 mmol) in THF (25 ml) at rt was added TBAF (6 ml, 1 M solution in THF, 6 mmol). The reaction was stirred for 20 hr at rt, then after concentration *in vacuo* the resulting residue was purified by flash column chromatography [ether, EtOAc (+ 1% NEt₃)] giving **6** as a colourless oil (0.730 g, 1.98 mmol, quant.). *R*_f 0.08 (ether); [α]_D³¹ -76° (c 0.30, CHCl₃); ν_{max}/cm⁻¹ (film) 3418 (br. s), 2951 (s), 2230 (w), 1108 (m), 1030 (m); δ_H (400 MHz, CDCl₃): 4.86 (1H, d, *J* 6.5, OCHHO), 4.72 (1H, dt, *J* 9.2, 2.0, 1'-H), 4.70 (1H, d, *J* 6.5, CHHO), 4.23 (1H, ddd, *J* 9.2, 4.3, 1.2, 2-H), 3.99 (1H, ddd, *J* 13.5, 10.3, 5.2), 3.9-3.8 (2H, m), 3.75-3.65 (3H, m), 3.41 (3H, s, OCH₃), 3.39 (3H, s, OCH₃), 3.28 (3H, s, CH₂OCH₃), 2.33 (2H, dt, *J* 2.0, 7.0, 4'-H), 1.73 (2H, quint, *J* 6.6, 5'-H), 1.45 (1H, m, OH), 1.35 (3H, s, CH₃), 1.289 (3H, s, CH₃) *m/z* (ESI) 385.1841 (M⁺+Na. C₁₇H₃₀O₈Na requires 385.1839).

(2*R*,3*R*,5*R*,6*R*,1'*R*)-2-[(6'-*tert*-Butyldimethylsilyl)oxy-1'-methoxymethoxy-2'-hexynyl]-3-hydroxymethyl-5,6-dimethoxy-5,6-dimethyl-1,4-dioxane (7)

To a solution of imidazole (0.200 g, 2.97 mmol) in THF (15 ml) was added a solution of **6** (0.730 g, 1.98 mmol) in THF (8 ml), then dropwise a solution of TBSCl in THF (15 ml). After stirring for 36 hr, the reaction mixture was diluted with ether (100 ml), washed with water (100 ml) and brine (100 ml), dried (MgSO₄) and concentrated *in vacuo*. Purification by flash chromatography (petrol/ether = 3:1 + 1% NEt₃) gave **7** as a colourless oil (697 mg, 1.46 mmol, 73.7%). *R*_f 0.7 (EtOAc); [α]_D³¹ -110° (c 2.5, CHCl₃); ν_{max}/cm⁻¹ (film) 3481 (br, m), 2952 (s), 2857 (s), 2229 (w), 1108 (m), 1032 (m); δ_H (400 MHz, CDCl₃): 4.86 (1H, d, *J* 6.5, OCHHO), 4.72 (1H, dt, *J* 9.2, 2.0, 1'-H), 4.70 (1H, d, *J* 6.5, OCHHO), 4.23 (1H, m), 3.9-3.8 (2H, m), 3.77 (1H, dd *J* 11.0, 1.5), 3.63 (2H, t, *J* 6.0, 6'-H), 3.41 (3H, s, OMe), 3.39 (3H, s, OMe), 3.28 (3H, s, CH₂OCH₃), 2.27 (2H, dt, *J* 7.2, 2.0, 4'-H), 1.67 (2H, tt, *J* 6.0, 7.2, 5'-H), 1.31 (3H, s, Me), 1.25 (3H, s, Me), 0.88 (9H, s, *t*-Bu), 0.04 (6H, s, Si₂Me); *m/z* (ESI) 499.2716 (M⁺+Na. C₂₃H₄₄O₈SiNa requires 499.2704).

(2*R*,3*R*,5*R*,6*R*,1'*R*)-3-Formyl-2-[(6'-*tert*-butyldimethylsilyl)oxy-1'-methoxymethoxy-2'-hexynyl]-5,6-dimethoxy-5,6-dimethyl-1,4-dioxane (8)

To a solution of oxalyl chloride (0.25 ml, 2.93 mmol), in DCM (50 ml) at -78°C was added DMSO (0.34 ml, 4.39 mmol). The reaction was stirred for 2 h at -78°C before **7** (696.8 mg, 1.464 mmol) was added dropwise as a solution in DCM over 30 min. Stirring was continued at -78°C for 30 min before NEt₃ (1.22 ml, 8.78 mmol) was added dropwise. The reaction was then allowed to warm up to rt and then diluted with ether (200 ml). The mixture was washed with water (2x200 ml) and brine (200 ml), dried (MgSO₄) and concentrated *in vacuo*. The resulting clear colourless oil **8** (684 mg, 1.44 mmol, 98.5%) was used crude in the next reaction. *R*_f 0.14 (petrol/ether = 1:1); δ_H (400 MHz, CDCl₃): 9.79 (1H, t, *J* 1.4, CHO), 4.93 (1H, dt, *J* 8.1, 2.0, 1'-H), 4.89 (1H, d, *J* 6.6, OCHHO), 4.65 (1H, d, *J* 6.6, OCHHO), 4.25 (1H, ddd, *J* 8.1, 3.3, 1.5, 2-H), 4.02 (1H, dd, *J* 3.3, 1.3, 3-H), 3.61 (2H, t, *J* 6.0, 6'-H), 3.39 (3H, s, OMe), 3.31 (3H, s, OMe), 3.25 (3H, s, OMe), 2.25 (2H, dt, *J* 7.2, 2.0, 4'-H), 1.65 (2H, tt, *J* 6.0, 7.2, 5'-H), 1.35 (3H, s, Me), 1.30 (3H, s, Me), 0.88 (9H, s, *t*-Bu), 0.04 (6H, s, Si₂Me).

(2*R*,3*R*,5*R*,6*R*,1'*E*,4''*S*,1''*R*)-3-[18'-(3''-*tert*-Butoxycarbonyl-2'',2''-dimethyloxazolidin-4''-yl)methoxy-3'-oxo-1'-octadecen-16'-ynyl]-2-[6'''-(*tert*-butyldimethylsilyl)oxy-1'''-methoxymethoxy-2'''-hexynyl]-5,6-dimethyl-5,6-dimethoxy-1,4-dioxane [(4''*S*)-14]

To a suspension of **8** (950 mg, 2.0 mol), LiCl (170 mg, 4.0 mmol) in MeCN (5 ml) was added *i*-Pr₂NEt (0.435 ml, 323 mg, 2.5 mmol) and (*S*)-**13** (1.54 g, 2.50 mol), and the resulting solution was stirred for 12 hr at 20°C. The mixture was diluted with ether and washed with H₂O and brine, dried with MgSO₄ and concentrated *in vacuo*. The residue was purified with flash column chromatography (SiO₂; petrol/EtOAc = 20:1, petrol/ether = 10:1) to give (4''*S*)-**14** (860 mg, 0.918 mmol, 45.9%). *R*_f 0.6 (petrol/ether = 1:1); [α]_D²⁵ -25° (c 0.43, CHCl₃); ν_{max}/cm⁻¹ (film) 1700 (s), 1100 (s), 835 (s), 775 (s); δ_H (400 MHz, CDCl₃): 7.28 (1H, dd, *J* 9.6, 16.2, 1'-H), 6.16 (1H, d, *J* 16.2, 2'-H), 4.83 (1H, d, *J* 6.7, OCHHO), 4.63 (1H, d, *J* 6.7, OCHHO), 4.3-4.2 (2H, m, 2-, 3-H), 4.14 (2H, m, 18'-H), 4.06 (1H, d, *J* 8.9, 1''-H), 4.00 (1H, d, *J* 8.4), 3.91 (1H, m), 4.2-3.9 (total 1H, m), 3.62 (2H, t, *J* 6.9, 6''-H), 3.7-3.6 (1H, m), 3.5-3.2 (total 1H, m), 3.39 (3H, s, OMe), 3.31 (3H, s, OMe), 3.13 (3H, s, OMe), 2.62 (1H, dd, *J* 16.4, 7.2, 2'-H), 2.55 (1H, dd, *J* 16.4, 7.1, 2'-H), 2.25 (2H, m), 2.21 (2H, t, *J* 7.3, 15'-H), 1.66 (2H, q, *J* 6.8), 1.65-1.5 (4H, m), 1.56 (3H, s, 2''-Me), 1.48 (12H, s, 2''-Me, *t*-Bu), 1.33 (3H, s, Me), 1.4-1.2 (19H, m, CH₂, Me), 0.88 (9H, s, *t*-BuSi), 0.04 (6H, s, SiMe₂); *m/z* (ESI) 958.6067 (M⁺+Na. C₅₁H₈₉NO₁₂SiNa requires 958.6052).

(4''*R*)-14

To a stirred solution of NaH (80 mg, 60% suspension in mineral oil, 2.0 mmol) in THF (8 ml) was added phosphonate (*R*)-**13** (1.32 g, 2.15 mmol) as a solution in THF (5 ml) at 0°C. This mixture was stirred at this temperature for 30 min. After cooling to -10°C,

aldehyde **8** (372 mg, 0.784 mmol) was added dropwise as solution in THF (5 ml). Stirring was maintained for 21 hr at -10°C . The reaction was quenched with sat. aq. NH_4Cl soln. and diluted with ether. The organic layer was washed with water and brine, dried (MgSO_4) and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2 , petrol/ether = 20:1 + 1% NEt_3) to yield (4''*R*)-**33** as a colourless oil (481 mg, 0.513 mmol, 65.5%). R_f 0.6 (petrol/ether = 1:1); $[\alpha]_D^{31} -38^{\circ}$ (c 0.70, CHCl_3); $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 1694 (s), 1100 (s), 835 (s), 775 (s); δ_H (400 MHz, CDCl_3): 7.28 (1H, dd, J 9.6, 16.2, 1'-H), 6.16 (1H, d, J 16.2, 2'-H), 4.84 (1H, d, J 6.6, OCHHO), 4.63 (1H, d, J 6.6, OCHHO), 4.3-4.2 (2H, m, 2-, 3-H), 4.14 (2H, m, 18'-H), 4.06 (1H, dt, J 8.9, 2.0, 1'''-H), 4.00 (1H, d, J 8.9), 3.91 (1H, m), 4.2-3.9 (total 1H, m), 3.63 (2H, t, J 6.9, 6''-H), 3.7-3.6 (1H, m), 3.5-3.2 (total 1H, m), 3.39 (3H, s, OMe), 3.31 (3H, s, OMe), 3.13 (3H, s, OMe), 2.62 (1H, dd, J 16.4, 6.9, 2'-H), 2.55 (1H, dd, J 16.4, 7.1, 2'-H), 2.25 (2H, m), 2.21 (2H, m, 15'-H), 1.66 (2H, q, J 6.8), 1.65-1.5 (4H, m), 1.56 (3H, s, 2''-Me), 1.48 (12H, s, 2''-Me, *t*-Bu), 1.33 (3H, s, Me), 1.4-1.2 (19H, m, CH_2 , Me), 0.88 (9H, s, *t*-BuSi), 0.04 (6H, s, SiMe_2); m/z (ESI) 958.6052 ($\text{M}^+ + \text{Na}$). $\text{C}_{51}\text{H}_{89}\text{NO}_{12}\text{SiNa}$ requires 958.6052).

(2*R*,3*R*,5*R*,6*R*,4''*S*,1'''*R*)-3-[18'-(3''-tert-Butoxycarbonyl-2'',2''-dimethyloxazolidin-4''-yl)methoxy-3'-oxooctadecyl]-2-[6'''-(tert-butyldimethylsilyl)oxy-1'''-(methoxymethoxy)hexyl]-5,6-dimethyl-5,6-dimethoxy-1,4-dioxane [(4''*S*)-15**]**

To Raney nickel (3 g, 50% suspension in H_2O) was added EtOH (3 ml) after washing twice with EtOH (6 ml). (4''*S*)-**14** (670 mg, 0.704 mmol) in EtOH (6 ml) was added and the resulting suspension was stirred for 2 days under a hydrogen atmosphere. The mixture was filtered through a short pad of silica gel and concentrated *in vacuo*. The residue was chromatographed on silica gel (petrol/ether = 10:1 - 5:1) to give (4''*S*)-**15** (484 mg, 0.511 mmol, 72.6%) as a colourless oil. R_f 0.60 (toluene/EtOAc = 4:1), 0.25 (petrol/ether = 1:1); $[\alpha]_D^{25} +12^{\circ}$ (c 0.30, CHCl_3); ν_{max} (film)/ cm^{-1} 1701 (s, C=O), 1102 (s), 1033 (s), 835 (s), 774 (s); δ_H (400 MHz, CDCl_3): 4.93 (1H, d, J 6.7, OCHHO), 4.71 (1H, d, J 6.7, OCHHO), 4.03 (1H, dd, J 5.8, 9.4, 2-H), 4.00 (1H, m), 3.92 (1H, dd, J 9.0, 4.4), 4.1-3.9 (total 1H, m), 3.60 (4H, t, J 6.6, 18'-, 6'''-H), 3.55-3.25 (4H, m), 3.41 (3H, s, OMe), 3.27 (3H, s, OMe), 3.26 (3H, s, OMe), 2.65 (2H, t, J 6.4, 2'-H), 2.39 (2H, t, J 7.6, 4'-H), 2.32 (1H, m, 1'-H), 1.53 (12H, s, Me, *t*BuO), 1.48 (3H, s, Me), 1.65-1.35 (17H, m), 1.35-1.20 (24H, m), 0.89 (9H, s, *t*-BuSi), 0.04 (6H, s, Me_2Si); m/z (ESI) 968.6845 ($\text{M}^+ + \text{Na}$). $\text{C}_{51}\text{H}_{99}\text{NO}_{12}\text{SiNa}$ requires 968.6835)

(4''*R*)-15****

Similarly, (4''*R*)-**14** (206 mg, 0.220 mmol) gave (4''*R*)-**15** a colourless oil (203 mg, 0.214 mmol, 97.3%). R_f 0.60 (toluene/EtOAc = 4:1), 0.25 (petrol/ether = 1:1); $[\alpha]_D^{31} -43^{\circ}$ (c 0.20, CHCl_3); ν_{max} (film)/ cm^{-1} 1698 (s, C=O), 1106 (m), 838 (m), 776 (m); δ_H (400 MHz, CDCl_3): 4.92 (1H, d, J 6.7, OCHHO), 4.70 (1H, d, J 6.7, OCHHO), 4.02 (1H, dd, J 3.8, 9.4, 2-H), 4.00 (1H, d, J 9.4), 3.91 (1H, dd, J 9.0, 4.5), 4.1-3.9 (total 1H, m), 3.60 (4H, t, J 6.6, 18'-, 6'''-H), 3.55-3.25 (4H, m), 3.41 (3H, s, OMe), 3.27 (3H, s, OMe), 3.26 (3H, s, OMe), 2.65 (2H, t, J 6.7, 2'-H), 2.39 (2H, t, J 7.6, 4'-H), 2.32 (1H, m, 1'-H), 1.54 (12H, s, Me, *t*BuO), 1.48 (3H, s, Me), 1.65-1.35 (17H, m), 1.35-1.20 (24H, m), 0.89 (9H, s, *t*-BuSi), 0.04 (6H, s, Me_2Si); m/z (ESI) 968.6850 ($\text{M}^+ + \text{Na}$). $\text{C}_{51}\text{H}_{99}\text{NO}_{12}\text{SiNa}$ requires 968.6835)

(2*R*,3*R*,5*R*,6*R*,4''*S*,1'''*R*)-3-[18'-(3''-tert-Butoxycarbonyl-2'',2''-dimethyloxazolidin-4''-yl)methoxy-3'-oxooctadecyl]-2-[6'''-hydroxy-1'''-(methoxymethoxy)hexyl]-5,6-dimethyl-5,6-dimethoxy-1,4-dioxane [(4''*S*)-16**]**

To a suspension of (4''*S*)-**15** (372 mg, 0.393 mmol) in THF (1 ml) TBAF (0.5 ml, 1 M in THF, 0.5 mmol) was added. After stirring for 12 hr, the mixture was passed through a pad of silica gel and florisil. After washing this pad with ether (+ 1% NEt_3), the combined solutions were concentrated *in vacuo* and purified by flash column chromatography (petrol/ether = 4:1 - 0:1), yielding (4''*S*)-**16** (310 mg, 0.373 mmol, 94.9%) as a colourless oil. R_f 0.66 (petrol/EtOAc = 1:1), 0.30 (petrol/EtOAc = 2:1); $[\alpha]_D^{25} +12^{\circ}$ (c 0.92, CHCl_3); ν_{max} (film)/ cm^{-1} 3495 (w, OH), 1700 (s, C=O), 1105 (s), 1033 (s); δ_H (400 MHz, CDCl_3): 4.94 (1H, d, J 6.7, OCHHO), 4.70 (1H, d, J 6.7, OCHHO), 4.03 (1H, dd, J 3.9, 9.3, 2-H), 4.00 (1H, d, J 9.7), 4.1-3.85 (total 1H, m), 3.92 (1H, dd, J 9.3, 4.4), 3.65-3.55 (4H, m, 18'-, 6'''-H), 3.55-3.25 (4H, m), 3.41 (3H, s, OCH_2CH_3), 3.28 (3H, s, OMe), 3.26 (3H, s, OMe), 2.75-2.55 (2H, m, 2'-H), 2.40 (2H, t, J 7.5, H-4'), 2.29 (1H, ddt, J 14.2, 12.1, 5.7, H-1'), 1.48 (9H, s, *t*-Bu), 1.65-1.35 (21H, m), 1.35-1.2 (28H, m); m/z (ESI): 854.5970 ($\text{M} + \text{Na}^+$). $\text{C}_{45}\text{H}_{85}\text{NO}_{12}\text{Na}$ requires 854.5970).

(4''*R*)-16****

Similarly, (4''*R*)-**15** (17.5 mg, 0.0185 mmol) gave (4''*R*)-**16** (13.6 mg, 0.0164 mmol, 88.6%) as a colourless oil. R_f 0.66 (petrol/EtOAc = 1:1), 0.30 (petrol/EtOAc = 2:1); $[\alpha]_D^{25} -11.0^{\circ}$ (c 1.71, CHCl_3); ν_{max} (film)/ cm^{-1} 3525 (w), 1699 (s), 1105 (s), 1033 (s); δ_H (400 MHz, CDCl_3): 4.94 (1H, d, J 6.7, OCHHO), 4.70 (1H, d, J 6.7, OCHHO), 3.99 (1H, d, J 9.7), 4.1-3.95 (total 1H, m), 4.02 (1H, dd, J 8.7, 3.8), 3.92 (1H, dd, J 8.9, 4.3), 3.64 (2H, t, J 6.6, 6'''-H), 3.60 (1H, m), 3.55-3.25 (4H, m), 3.40 (3H, s, OCH_2OCH_3), 3.27 (3H, s, OMe), 3.26 (3H, s, OMe), 2.71 (1H, ddd, J 18.1, 8.5, 5.7, H-2'), 2.62 (1H, dt, J 18.1, 5.6, H-2'), 2.40

(2H, t, *J* 7.5, H-4'), 2.30 (1H, ddt, *J* 14.1, 11.1, 5.4, H-1'), 1.80 (1H, br. s, OH), 1.47 (9H, s, *t*-Bu), 1.42 (3H, s, Me), 1.65-1.35 (17H, m), 1.35-1.2 (28H, m); *m/z* (ESI): 854.5961 (M+Na⁺. C₄₅H₈₅NO₁₂Na requires 854.5970).

(2*R*,3*R*,5*R*,6*R*,4''*S*,1'''*R*)-3-[18'-(3''-*tert*-Butoxycarbonyl-2'',2''-dimethyloxazolidin-4''-yl)methoxy-3'-oxooctadecyl]-2-[5'''-formyl-1'''-(methoxymethoxy)pentyl]-5,6-dimethyl-5,6-dimethoxy-1,4-dioxane [(4''*S*)-17]

A suspension of (4''*S*)-**16** (297 mg, 0.357 mmol), Dess-Martin periodinane (424 mg, 1.00 mmol) and pyridine (79 mg, 1.0 mmol) in DCM (4 ml) was stirred at 20°C for 12 hr. The mixture was diluted with ether and washed with sat. aq. Na₂S₂O₃ soln., H₂O, sat. aq. NaHCO₃ soln. and brine, dried with MgSO₄ and concentrated *in vacuo*. The residue was purified with flash column chromatography (petrol/ether = 10:1, petrol/EtOAc = 10:1) to give (4''*S*)-**17** (233 mg, 0.281 mmol, 78.7%). *R*_f 0.60 (petrol/EtOAc = 2:1), 0.27 (petrol/EtOAc = 3:1); [α]_D²⁵ +10° (c 0.86, CHCl₃); *v*_{max}(film)/cm⁻¹ 2716 (w), 1701 (s), 1134 (s), 1107 (s), 1036 (s); δ_H (400 MHz, CDCl₃): 9.75 (1H, t, *J* 1.6, CHO), 4.93 (1H, d, *J* 6.7, OCHHO), 4.68 (1H, d, *J* 6.7, OCHHO), 4.01 (1H, dd, *J* 9.4, 3.9, 2-H), 3.98 (1H, d, *J* 7.9), 3.91 (1H dd, *J* 4.3, 8.8), 4.1-3.85 (total 1H, m), 3.58 (2H, m, 18'-H), 3.5-3.25 (4H, m), 3.39 (3H, s, OCH₂OCH₃), 3.25 (3H, s, OMe), 2.71 (3H, s, OMe), 2.61 (1H, ddd, *J* 18.1, 8.9, 5.5, H-2'), 2.61 (1H, dt, *J* 18.1, 5.4, H-2'), 2.46 (2H, pseudo t, *J* 7.2, H-5'''), 2.39 (2H, t, *J* 7.4, H-4'), 2.28 (1H, ddt, *J* 14.1, 12.2, 5.4, H-1'), 1.47 (9H, s, *t*-Bu), 1.8-1.35 (17H, m), 1.35-1.2 (28H, m); *m/z* (ESI): 852.5812 (M+Na⁺. C₄₅H₈₃NO₁₂Na requires 854.5813).

(4''*R*)-17

Similarly, (4''*R*)-**16** (139 mg, 0.167 mmol) gave (4''*R*)-**17** (104 mg, 0.125 mmol, 74.8%) as a colourless oil. *R*_f 0.60 (2:1 petrol/EtOAc), 0.27 (petrol/EtOAc = 3:1); [α]_D²⁵ -4.8° (c 0.80, CHCl₃); *v*_{max}(film)/cm⁻¹ 2716 (w), 1698 (s), 1132 (s), 1105 (s), 1035 (s); δ_H (400 MHz, CDCl₃): 9.77 (1H, t, *J* 1.6, CHO), 4.94 (1H, d, *J* 6.7, OCHHO), 4.69 (1H, d, *J* 6.7, OCHHO), 4.02 (1H, dd, *J* 9.4, 3.9, 2-H), 3.99 (1H, d, *J* 7.9), 4.1-3.85 (total 1H, m), 3.92 (1H, d, *J* 9.2, 4.5), 3.61 (2H, m, 18'-H), 3.55-3.25 (4H, m), 3.40 (3H, s, OCH₂OCH₃), 3.28 (3H, s, OMe), 3.26 (3H, s, OMe), 2.72 (1H, ddd, *J* 18.1, 8.9, 5.6, H-2'), 2.61 (1H, dt, *J* 18.1, 4.5, H-2'), 2.46 (2H, m, H-5'''), 2.40 (2H, t, *J* 3.9, H-4'), 2.29 (1H, ddt, *J* 14.2, 12.2, 6.0, H-1'), 1.47 (9H, s, *t*-Bu), 1.8-1.4 (17H, m), 1.35-1.2 (28H, m); *m/z* (ESI): 852.5801 (M+Na⁺. C₄₅H₈₃NO₁₂Na requires 854.5813).

(2*R*,3*R*,5*R*,6*R*,4''*S*,1'''*R*,6'''*E*)-3-[18'-(3''-*tert*-Butoxycarbonyl-2'',2''-dimethyloxazolidin-4''-yl)methoxy-3'-oxooctadecyl]-2-(7'''-ethoxycarbonyl-1'''-methoxymethoxy-6'''-heptenyl)-5,6-dimethyl-5,6-dimethoxy-1,4-dioxane [(4''*S*)-18]

To a suspension of (4''*S*)-**17** (204 mg, 1.246 mmol), LiCl (224 mg, 5.28 mmol) in MeCN (8 ml) was added *i*-Pr₂NEt (0.91 ml, 5.2 mmol) and triethyl phosphonoacetate (1.04 ml, 1.11 g, 4.39 mol), and the resulting solution was stirred for 2 hr at 20°C. The mixture was diluted with ether and washed with H₂O and brine, dried with MgSO₄ and concentrated *in vacuo*. The residue was purified with flash column chromatography (SiO₂, petrol/EtOAc = 10:1) to give (4''*S*)-**18** (212 mg, 0.236 mmol, 95.9%) as a colourless oil. *R*_f 0.50 (petrol/EtOAc = 3:1) [α]_D²⁵ +9.5° (c 0.68, CHCl₃); *v*_{max}(film)/cm⁻¹ 1699 (s, C=O), 1655 (w, C=C), 1105 (s), 1031 (s); δ_H (400 MHz, CDCl₃): 6.96 (1H, dt, *J* 15.6, 7.2, H-6'''), 5.82 (1H, d, *J* 15.6, H-7'''), 4.94 (1H, d, *J* 6.7, OCHHO), 4.69 (1H, d, *J* 6.7, OCHHO), 4.17 (2H, q, *J* 7.1, CH₂CH₃), 4.02 (1H, dd, *J* 9.2, 3.9), 3.99 (1H, d, *J* 7.6), 4.1-3.9 (total 1H, m), 3.92 (1H, dd, *J* 4.3, 9.2), 3.61 (2H, t, *J* 7.5, 18'-H), 3.55-3.25 (total 4H, m), 3.40 (3H, s, OCH₂OCH₃), 3.28 (1H, m), 3.26 (3H, s, OMe), 3.26 (3H, s, OMe), 2.70 (1H, ddd, *J* 18.1, 9.7, 5.7, H-2'), 2.61 (1H, dd, *J* 18.1, 5.8, H-2'), 2.40 (2H, t, *J* 7.6, H-4'), 2.30 (1H, m, H-1'), 2.23 (2H, m, H-5'''), 1.54 (9H, s, *t*-Bu), 1.65-1.4 (17H, m), 1.28 (3H, t, *J* 7.1, CH₂CH₃), 1.35-1.2 (28H, m); *m/z* (ESI): 922.6228 (M+Na⁺. C₄₉H₈₉NO₁₃Na requires 922.6232).

(4*R*'')-18

Similarly, (4''*R*)-**17** (49.4 mg, 59.5 μmol) gave (4''*R*)-**18** (53.4 mg, 59.4 μmol, 99.8%) as a colourless oil. *R*_f 0.50 (petrol/EtOAc = 3:1) [α]_D²⁵ -12.2° (c 2.58, CHCl₃); *v*_{max}(film)/cm⁻¹ 1717 (m, C=O), 1702 (s, C=O), 1655 (w, C=C), 1110 (s), 1036 (s); δ_H (400 MHz, CDCl₃): 6.95 (1H, dt, *J* 15.6, 6.8, H-6'''), 5.81 (1H, d, *J* 15.6, H-7'''), 4.93 (1H, d, *J* 6.7, OCHHO), 4.69 (1H, d, *J* 6.7, OCHHO), 4.17 (2H, q, *J* 7.1, CH₂CH₃), 4.1-3.9 (total 1H, m), 4.01 (1H, dd, *J* 9.5, 3.8), 3.99 (1H, d, *J* 7.7), 3.92 (1H, dd, *J* 8.8, 4.3), 3.60 (1H, pseudo t, *J* 8), 3.5-3.25 (4H, m), 3.40 (3H, s, OCH₂OCH₃), 3.30 (1H, m), 3.27 (3H, s, OMe), 3.25 (3H, s, OMe), 2.70 (1H, ddd, *J* 18.0, 8.5, 5.7, H-2'), 2.61 (1H, dt, *J* 18.0, 5.7, H-2'), 2.39 (2H, t, *J* 7.5, H-4'), 2.29 (1H, m, H-1'), 2.23 (2H, m, H-5'''), 1.47 (9H, s, *t*-Bu), 1.65-1.45 (16H, m), 1.35 (3H, t, *J* 7.1, CH₂CH₃), 1.35-1.2 (29H, m); *m/z* (ESI): 922.6228 (M+Na⁺. C₄₉H₈₉NO₁₃Na requires 922.6232).

Ethyl (8*R*,9*R*,10*R*,13*S*,2'*R*)-28-[(2'-amino-3'-hydroxy)propyl]oxy-8,13:9,13-diepoxy-10-hydroxy-2-octacocenoate [proposed (30*R*)-didemserinolipid B (1)]

A solution of (4''*S*)-**18** (254.4 mg, 0.276 mmol) in EtOH (5 ml) and 1 N HCl (1 ml) was stirred at 45°C for 12 hr. The mixture was concentrated *in vacuo* to give a crude oil. This oil was chromatographed on silica gel (DCM/MeOH = 20:1 – 5:1) to give (30*R*)-**1** (116.9 mg, 0.200 mmol, 72.5%) as amorphous solid. *R*_f 0.60 (DCM/MeOH = 5:1); [α]_D²⁵ +21° (*c* 0.29, CHCl₃); *v*_{max}(film)/cm⁻¹ 3350 (br m, OH), 2922 (s), 2852 (s), 1720 (s, C=O), 1654 (m, C=C), 1464 (m), 1367 (s), 1265 (m), 1179 (s), 1111 (s), 1039 (s), 981 (s), 913 (w), 721 (m); δ_H and δ_C: see tables 1 and 2; *m/z* (ESI): 584.4526 (M+H⁺. C₃₃H₆₂NO₇ requires 584.4526).

Ethyl (8*R*,9*R*,10*R*,13*S*,2'*S*)-28-[(2'-amino-3'-hydroxy)propyl]oxy-8,13:9,13-diepoxy-10-hydroxy-2-octacocenoate [proposed (30*S*)-didemniserinolipid B (1)]

Similarly, (4''*R*)-**18** (18.3 mg, 20.3 μmol) gave (30*S*)-**1** (9.6 mg, 16 μmol, 80%) as amorphous solid. *R*_f 0.60 (DCM/MeOH = 5:1); [α]_D²⁵ +16° (*c* 0.28, CHCl₃); *v*_{max}(film)/cm⁻¹ 3370 (br m, OH), 2922 (s), 2852 (s), 1719 (s, C=O), 1653 (m, C=C), 1466 (m), 1368 (s), 1263 (m), 1178 (s), 1109 (s), 1037 (s), 980 (s), 914 (w), 720 (m); δ_H and δ_C: see tables 1 and 2; *m/z* (ESI): 584.4520 (M+H⁺. C₃₃H₆₂NO₇ requires 584.4526).

Ethyl (8*R*,9*R*,10*R*,13*S*,2'*R*)-8,13:9,13-diepoxy-28-[[2'-(9''-fluorenylmethoxycarbonyl)-amino-3'-hydroxy]propyl]oxy-10-hydroxy-2-octacocenoate [(30*R*)-19**]**

A solution of (30*R*)-**1** (116.9 mg, 0.200 mmol), FmocCl (300 mg, 1.16 mmol) and K₂CO₃ (150 mg, 1.09 mmol) in 1,4-dioxane-H₂O (1:1, 3 ml) was stirred for 2.5 hr at 20°C. The mixture was extracted with DCM and washed with sat. aq. NH₄Cl soln. and brine, dried with MgSO₄ and concentrated *in vacuo*. The residue was purified with flash chromatography (DCM/MeOH = 50:1; and petrol/EtOAc = 10:1, 1:1) to give (30*R*)-**19** as amorphous solid (102.1 mg, 0.127 mmol, 63.4%). *R*_f 0.40 (DCM/MeOH = 10:1), 0.67 (EtOAc); [α]_D²⁵ +20° (*c* 0.79, CHCl₃); *v*_{max}(film)/cm⁻¹ 3400 (br m), 2924 (s), 2853 (s), 1717 (s), 1653 (w), 1525 (m), 1290 (s), 1041 (m), 984 (w), 741 (m); δ_H 7.76 (2H, d, *J* 7.5, ArH), 7.60 (2H, d, *J* 7.5, ArH), 7.40 (2H, t, *J* 7.5, ArH), 7.31 (2H, t, *J* 7.5, ArH), 6.94 (1H, dt, *J* 15.7, 6.9, 3-H), 5.81 (1H, dd, *J* 15.7, 1.5, 2-H), 5.44 (1H, br s, NH), 4.41 (2H, br d, *J* 6.5, ArCH₂CH), 4.23 (1H, t, *J* 6.7, ArCH₂CH), 4.18 (2H, q, *J* 7.2, CH₂CH₃), 4.05 (1H, s, 9-H), 3.88 (1H, dd, *J* 7.6, 5.0, 8-H), 3.84 (1H, br s, 31-H), 3.72 (1H, br s, 30-H), 3.61 (1H, br s, 10-H), 3.47 (2H, m, 28-H), 2.63 (1H, m, 31-OH), 2.40 (1H, d, *J* 9.7, 10-OH), 2.21 (2H, ddt, *J* 1.5, 7.2, 7.2, 5-H), 1.96 (1H, m, 11ax-H), 1.78 (1H, ddd, 12.3, 12.3, 5.5, 12ax-H), 1.7-1.6 (2H, m), 1.6-1.4 (9H, m), 1.35-1.1 (26H, m), 1.28 (3H, t, *J* 7.2, CH₃); *m/z*: (ESI) 828.5024 (M+Na⁺. C₄₈H₇₁NO₉Na requires 828.5027).

(30*S*)-19****

Similarly, (30*S*)-**1** (11.5 mg, 0.0197 mmol) gave (30*S*)-**19** as amorphous solid (10.4 mg, 0.0129 mmol, 65.4%). *R*_f 0.40 (DCM/MeOH = 10:1), 0.67 (EtOAc); [α]_D²⁵ +9.0° (*c* 0.25, CHCl₃); *v*_{max}(film)/cm⁻¹ 3400 (br m), 2926 (s), 2853 (s), 1718 (s), 1653 (w), 1531 (m), 1246 (s), 1041 (m), 984 (w), 741 (m); δ_H 7.77 (2H, d, *J* 7.4, ArH), 7.60 (2H, d, *J* 7.4, ArH), 7.40 (2H, t, *J* 7.4, ArH), 7.32 (2H, t, *J* 7.4, ArH), 6.93 (1H, dt, *J* 15.6, 8.2, 3-H), 5.81 (1H, d, *J* 15.6, 2-H), 5.42 (1H, br s, NH), 4.40 (2H, m, ArCH₂CH), 4.23 (1H, t, *J* 6.8, ArCH₂CH), 4.18 (2H, q, *J* 7.1, CH₂CH₃), 4.05 (1H, s, 9-H), 3.9-3.8 (3H, m, 8, 31-H), 3.74 (1H, m, 30-H), 3.7-3.55 (3H, m, 10, 29-H), 3.45 (2H, m, 31-OH), 2.21 (2H, dt, *J* 6.9, 7.0, 5-H), 2.1-1.9 (2H, m, 10-OH, 11ax-H), 1.78 (1H, ddd, 12.5, 12.5, 5.5, 12ax-H), 1.7-1.6 (2H, m), 1.6-1.4 (9H, m), 1.35-1.1 (26H, m), 1.28 (3H, t, *J* 7.1, CH₃); *m/z*: (ESI) 828.5062 (M+Na⁺. C₄₈H₇₁NO₉Na requires 828.5027).

Ethyl (8*R*,9*R*,10*R*,13*S*,2'*S*)-8,13:9,13-diepoxy-28-[(2'-amino-3'-hydroxy)propyl]oxy-10-hydroxy-2-octacocenoate 2'-sulfate sodium salt [(30*S*)-20**, revised didemniserinolipid B]**

A suspension of (30*R*)-**19** (6.8 mg, 8.4 μmol) SO₃•Py (1.6 mg, 10 μmol) and Na₂SO₄ (10 mg) in dry DMF (0.2 ml) was stirred under microwave irradiation at 110°C for 2 hr. The reaction mixture was concentrated *in vacuo*. The crude yellow oil was dissolved in DMF-piperidine (4:1, 0.5 ml) and the resulting solution was stirred at 20°C for 2 hr. The mixture was concentrated *in vacuo* and the residue was purified with flash chromatography (DCM/MeOH = 20:1 – 5:1) to give (30*S*)-**20** (2.8 mg, 4.1 μmol, 49%) as an amorphous solid. *R*_f 0.7 (DCM/MeOH = 3:1); [α]_D²⁵ +11° (*c* 0.12, CHCl₃); *v*_{max}(film)/cm⁻¹ 3450 (br m, OH), 2921 (s), 2852 (s), 1720 (s, C=O), 1655 (m, C=C), 1514 (w), 1465 (m), 1368 (m), 1259 (s), 1231 (s), 1096 (m), 1017 (s), 982 (s), 795 (m), 756 (w); δ_H and δ_C: see tables 1 and 2; *m/z*: (ESI)

708.3766 ($M+Na^+$. $C_{33}H_{60}NO_{10}SNa_2$ requires 708.3278); 588.4251 ($M-NaHSO_4+Na^+$. $C_{33}H_{59}NO_6SNa$ requires 588.4235).

(30R)-20

Similarly, (30S)-**19** gave (30R)-**20** (trace amount). R_f 0.7 (DCM/MeOH = 3:1); δ_H 6.95 (1H, dt, J 15.4, 6.7, 3-H), 5.73 (1H, d, J 15.4, 2-H), 4.39 (1H, m, 31-H), 4.26 (1H, m, 31-H), 4.18 (2H, q, J 7.2, CH_2CH_3), 4.06 (1H, m, 9-H), 3.88 (1H, m, 8-H), 3.80 (1H, m, 30-H), 3.7-3.55 (3H, m), 3.5-3.35 (2H, m), 2.21 (2H, m, 4-H), 1.98 (1H, m, 11ax-H), 1.70-1.0 (37H, m), 1.29 (3H, t, J 7.2, CH_2CH_3).

Ethyl (8R,9R,10R,13S,2'S)-8,13:9,13-diepoxy-28-[(2'-amino-3'-hydroxy)propyl]oxy-10-hydroxy-2-octacocenoate 10,2'-disulfate disodium salt [(30S)-21]

A suspension of (30R)-**19** (18.1 mg, 22.5 μ mol), $SO_3 \cdot Py$ (13.5 mg, 94 μ mol), Na_2SO_4 (10 mg) and pyridine (50 ml, 0.6 mmol) in dry DMF (0.5 ml) was stirred under microwave irradiation at 110°C for 1 hr. The reaction mixture was concentrated *in vacuo*. The crude yellow oil was dissolved in DMF-piperidine (9:1, 1 ml) and the resulting solution was stirred at 20°C for 24 hr. The mixture was concentrated *in vacuo* and the residue was purified with flash chromatography (SiO_2 , DCM/MeOH = 20:1 – 5:1) to give (30R)-**21** (14.9 mg, 18.9 μ mol, 84.0%) as amorphous solid. R_f 0.25

(DCM/MeOH = 3:1); $[\alpha]_D^{25} +17^\circ$ (c 0.34, MeOH); ν_{max} (film)/ cm^{-1} 3450 (br m, OH), 2921 (s), 2852 (s), 1722 (s, C=O), 1654 (m, C=C), 1467 (m), 1368 (m), 1217 (s), 1114 (m), 1071 (s), 1015 (s), 951 (s), 846 (m), 773 (m), 719 (w); δ_H 6.87 (1H, dt, J 15.6, 6.9, 3-H), 5.73 (1H, d, J 15.6, 2-H), 4.29 (2H, br s, 9, 10-H), 4.19 (1H, br d, J 11.3, 31-H), 4.09 (2H, q, J 7.1, CH_2CH_3), 4.05 (1H, m, 31-H), 3.84 (1H, m, 8-H), 3.55-3.25 (5H, m, overlapped with MeOH), 2.13 (2H, m, 4-H), 1.95 (1H, m, 11ax-H), 1.70 (1H, m, 12ax-H), 1.55-1.0 (39H, m); m/z : (ESI) 788.3322 ($M+H^+$. $C_{33}H_{60}NO_{13}S_2Na_2$ requires 788.3301).

Table 1. ¹H NMR spectra of the natural and synthetic compounds.

Position	Natural 1 (500 MHz)	(30 <i>S</i>)- 20 (600 MHz)	(30 <i>R</i>)- 1 (600 MHz)	(30 <i>S</i>)- 1 (600 MHz)
2	5.80 d	5.80	5.81 d	5.81 d
3	6.95 dt	6.94 dt	6.95 dt	6.95 dt
4	2.20 q	2.21 q	2.21 q	2.21 q
5	1.47 m	1.48 m	1.49 m	1.50 m
6	1.26 m	1.55 m	1.55 m	1.56 m
7	1.54 m	1.55 m	1.56 m	1.57 m
	1.43 m	1.43 m	1.43 m	1.43 m
8	3.87 m	3.88 dd	3.88 dd	3.87 dd
9	4.06 br s	4.06 s	4.06 s	4.06 s
10	3.61 s	3.61 s	3.62 s	3.61 s
11	1.96 m	1.97 ax m	1.97 ax m	1.98 ax m
	1.69 m	1.69 eq m	1.70 eq m	1.70 eq m
12	1.79 dt	1.79 ax dt	1.80 ax dt	1.79 ax dt
	1.53 m	1.53 eq m	1.53 eq m	1.52 eq m
14	1.66 m	1.66 m	1.66 m	1.66 m
	1.41 m			
15 – 26	1.2–1.3	1.2–1.3	1.2–1.3	1.2–1.3
27	1.60 m	1.56 m	1.57 m	1.56 m
28	3.47 m	3.47 m	3.47 m	3.42 m
29*	4.26 m	3.65 m	3.64 m	3.50 m
	4.34 m			
30	3.81 m	3.80 m	3.60 m	3.07 m
31*	3.65 m	4.28 m	3.94 m	3.62 m
		4.35 m	3.85 m	3.52 m
CH ₂ CH ₃	4.18 q	4.18 q	4.18 q	4.18 q
CH ₂ CH ₃	1.27 t	1.29 t	1.27 t	1.27 t

* Reassignment of the H-29 and H-31 signals in the ¹H NMR spectrum requires reassignment of the corresponding ¹³C NMR signals in reference 2.

Table 2. ¹³C NMR spectra of the natural and synthetic compounds.

Position	Natural 1 (125 MHz)	(30 <i>S</i>)- 20 (125 MHz [†])	(30 <i>R</i>)- 1 (150 MHz)	(30 <i>S</i>)- 1 (150 MHz)
1	166.7	166.7	166.7	166.7
2	121.4	121.5	121.5	121.5
3	149.1	148.9	148.9	148.8
4	32.0	32.1	32.1	32.1
5	27.9	27.8	27.9	27.9
6	25.3	25.1	25.1	25.1
7	35.1	35.0	35.1	35.1
8	77.8	77.7	77.7	77.7
9	82.4	82.3	82.4	82.4
10	66.2	66.2	66.2	66.3
11	37.5	25.0	25.0	25.1
12	30.1	30.1	30.1	30.1
13	109.5	109.6	109.6	109.7
14	23.0	37.5	37.5	37.5
15	25.0 – 29.8	23.1	23.0	23.0
16 – 27	25.0 – 29.8	25.9 – 29.8	26.0 – 30.3	26.1 – 29.8
28	72.0	71.9	71.9	71.8
29	65.2 [‡]	66.7	68.3	74.0
30	51.6	51.4	53.4	52.1
31	66.8 [‡]	65.2	60.5	65.3
CH ₂ CH ₃	60.1	60.2	60.2	60.1
CH ₂ CH ₃	14.3	14.3	14.3	14.3

[†] Recorded on a Bruker 500 Ultrashield spectrometer fitted with a Cryo-probe.

[‡] Reassignment of the H-29 and H-31 signals in the ¹H NMR spectrum requires reassignment of the corresponding ¹³C NMR signals in reference 2.