Supplementary Information

(2*R*,3*R*,4*E*)-3-Benzyl-[(1'*R*)-1'-phenyl-ethyl]-amino-2-(benzoyl carbonate)-hex-4-enoic acid methyl ester 6

n-Butyllithium (1.38 M, 0.57 mL, 0.79 mmol) was added dropwise to a solution of hexamethyl disilazane (0.18 mL, 0.83 mmol) in THF (1 mL) at 0 ºC and stirred for 30 min. The solution was added dropwise *via* cannula to a solution of the β-amino ester[1] **5** (176 mg, 0.520 mmol) in THF (2 mL) at 0 ºC, stirred for 60 min and cooled to −78 ºC. Dibenzyl peroxydicarbonate[2] (157 mg, 0.520 mmol) in THF (1.5 mL) was then added dropwise *via* cannula and stirring continued at −78 ºC for 1.75 h. The mixture was warmed to 0 ºC and quenched with saturated ammonium chloride solution (15 mL), water (20 mL) was then added and the mixture extracted with ether (3 × 15 mL) and CH_2Cl_2 (2 × 15 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. Purification by flash chromatography, eluting with 95 : 5 petrol−ethyl acetate, gave the *β-amino ester* **6** (109 mg, 27%) as a colourless oil, R_f 0.15 (20% EtOAc in petrol); $[\alpha]_D^{20}$ −14.6 (*c.* 0.41 in $CHCl_3$); υ_{max}/cm^{-1} (film) 2953, 1751, 1452 and 698; δ_H (300 MHz, $CDCl_3$) 7.36-7.18 (15 H, m, 3 × Ph), 5.68-5.62 (2 H, m, 4-H and 5-H), 5.09 (2 H, s, PhCH_2O), 4.98 (1 H, d, *J* 5.0, 2-H), 4.06 (1 H, q, *J* 6.8, 1'-H), 3.95 (1 H, d, ^2J, 14.3, PhCH_AN), 3.73 (1 H d, ^2J, 14.3, PhCH_BN), 3.73 (1 H, dd *J* 8.1 and 5.0, 3-H), 3.53 (3 H, s, CO_2Me), 1.68 (3 H, d, *J* 5.0, 6-H_3) and 1.33 (3 H, d, *J* 6.8, 2'-H_3); δ_C (75 MHz, $CDCl_3$) 169.2, 154.9, 144.0, 141.2, 135.4, 131.4, 130.4, 129.5, 129.0, 128.9, 128.9, 128.7, 128.6, 128.5, 128.5, 128.4, 128.3, 127.2, 127.0, 126.7, 79.2, 70.4, 61.4, 57.2, 52.6, 52.4, 18.6 and 14.4; *m/z* (ES) 488 (100%, MH^+), 384 (17) and 338 (9). (Found: MH^+, 488.2441. $C_{30}H_{33}NO_5$ requires *MH*, 488.2437).

(2*R*, 3*S*, 5*R*, 6*R*)-5,6-Dimethoxy-5,6-dimethyl-[1,4]-dioxane-2-pyrrolidinamide-3-methylcarboxylate 13

Trimethylaluminium (2.0 M in pentanes, 0.61 mL, 1.23 mmol) was added slowly to pyrrolidine (0.10 mL, 1.25 mmol) in toluene (0.45 mL) at room temperature. After stirring for 15 min, the diester[3] **9** (91 mg, 0.311 mmol) was added in one portion. The solution was stirred at room temperature for 96 h, cooled to −78 ºC and quenched by the cautious addition of

methanol (0.1 mL). The solid residues were removed by filtration through of Celite and the filtrate evaporated under reduced pressure. Purification by flash chromatography, eluting with 70 : 30 petrol−ethyl acetate followed by neat ethyl acetate, gave the amide[3] **13** (6.3 mg, 6%) as a pale yellow oil, R_f 0.43 (EtOAc); $[\alpha]_D^{20}$ −171 (*c*. 0.63 in $CDCl_3$); ν_{max}/cm^{-1} (film) 2952, 1746 and 1622; δ_H (300 MHz, $CDCl_3$) 4.80 (1 H, d, *J* 3.9, 2- or 3-H), 4.68 (1 H, d, *J* 3.9, 3- or 2-H), 4.09 (1 H, dt , ^2J 11.2 and *J* 7.2, NCH_A), 3.75 (3 H, s, ester OMe), 3.65 (1 H, dt, ^2J 11.2 and *J* 7.2, NCH_B), 3.50 (2 H, t, *J* 6.9, NCH_2), 3.31 (3 H, s, 5- or 6-OMe), 3.22 (3 H, s, 6- or 5-OMe), 2.01-1.86 (2 H, m, NCH_2CH_2), 1.85-1.73 (2 H, m, NCH_2CH_2), 1.35 (3 H, s, 5- or 6-Me) and 1.34 (3 H, s, 6- or 5-Me); δ_C (75 MHz, $CDCl_3$) 170.6, 167.7, 100.8, 99.7, 70.1, 69.7, 52.2, 50.3, 49.0, 47.9, 47.4, 27.2, 23.6, 18.3, and 18.2; *m/z* (ES) 354 (43%, MNa^+), 332 (62, MH^+) and 300 (100, M^+−OMe).

(2*R*, 3*S*, 5*R*, 6*R*)-5,6-Dimethoxy-[1,4]-dioxane-3-methylcarboxylate-2-carboxylic acid 10
1,8-Diazabicyclo[5.4.0]undec-7-ene (2.4 mL, 17 mmol) was added to a suspension of the diester[3] **9** (2.41 g, 8.25 mmol) in water (30 mL) and stirred for 16 h at room temperature. The mixture was adjusted to pH 2 with an aqueous hydrochloric acid solution (2 M), extracted with ethyl acetate (5 × 50 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Purification by flash chromatography, eluting with 97 : 2 : 1 dichloromethane−methanol−acetic acid, gave the *mono-acid* **10** (1.52 g, 66%) as a colourless foam, R_f 0.36 (4% MeOH in CH_2Cl_2 + 2% AcOH); $[\alpha]_D^{20}$ −130 (*c*. 1.05 in $CDCl_3$); ν_{max}/cm^{-1} (film) 3214 (br.), 2953 and 1745; δ_H (300 MHz, $CDCl_3$) 4.71 (1 H, d, *J* 4.1, 2- or 3-H), 4.58 (1 H, d, *J* 4.1, 3- or 2-H), 3.78 (3 H, s, CO_2Me), 3.32 (3 H, s, 5- or 6-OMe), 3.24 (3 H s, 6- or 5-OMe), 1.41 (3 H, s, 5- or 6-Me) and 1.36 (3 H, s, 6- or 5-Me); δ_C (75 MHz, $CDCl_3$) 170.5, 169.9, 101.6, 99.9, 69.2, 66.7, 52.6, 50.6, 49.2, 18.3 and 17.9; *m/z* (ES) 301 (67%, MNa^+) and 247 (45, M^+−OMe). (Found: MNa^+, 301.0916. $C_{11}H_{18}O_8$ requires *MNa,* 301.0899).

(2*R*, 3*S*, 5*R*, 6*R*)-5,6-Dimethoxy-[1,4]-dioxane-3-methylcarboxylate-2-dipropylamide 11
1-[3-(Dimethylamino)propyl]-3-ethyl carbodiimide hydrochloride (1.24 g, 6.50 mmol) was added to a solution of 1-hydroxybenzatriazole hydrate (0.88 g, 6.50 mmol), dipropylamine

(0.90 mL, 6.5 mmol) and the acid **10** (1.50 g, 5.40 mmol) in ethyl acetate (85 mL) and the solution stirred for 18 h at room temperature. Water (100 mL) and ethyl acetate (100 mL) were added, the organic layer separated and the aqueous layer extracted with ethyl acetate (3 × 75 mL), the combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. Purification by flash chromatography, eluting with 80 : 20 petrol−ethyl acetate, gave the *amide* **11** (1.40 g, 72%) as a colourless oil which crystallised on standing to colourless needles, m.p. 56.8-59.0 ˚C (from Et_2O−petrol); R_f 0.12 (20% EtOAc in petrol); $[\alpha]_D^{20}$ −107 (*c*. 1.07 in $CHCl_3$); (Found: C, 56.5; H, 8.70; N, 3.7; $C_{17}H_{31}NO_7$ requires: C, 56.5; H, 8.65; N, 3.9); ν_{max}/cm^{-1} (film) 2961, 1747 and 1625; δ_H (500 MHz, $CDCl_3$) 4.85 (1 H, d, *J* 4.0, 2-H), 4.71 (1 H, d, *J* 4.0, 3-H), 3.86 (1 H, ddd, ^2J 14.1, *J* 10.7 and 5.5, NC_AH_A), 3.73 (3 H, s, CO_2Me), 3.41 (1 H, dt, ^2J 13.2 and *J* 7.7, NC_BH_A), 3.31 (3 H, s, 6-OMe), 3.26 (1 H, ddd, ^2J 14.1, *J* 10.7 and 5.5, NC_AH_B), 3.22 (3 H, s, 5-OMe), 3.04 (1 H, dt, ^2J 13.2 and *J* 7.7, NC_BH_B), 1.80-1.69 (2 H, m, NCH_2CH_2), 1.68-1.57 (2 H, m, NCH_2CH_2), 1.33 (3 H, s, 5-Me), 0.91 (3 H, t, *J* 7.7, CH_2CH_3) and 0.88 (3 H, t, *J* 7.7, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 170.5, 168.3, 100.8, 99.6, 70.2, 70.2, 52.1, 50.2, 49.9, 49.8, 49.2, 23.4, 20.8, 18.4, 18.3, 11.9 and 11.56; *m/z* (ES) 384 (16%, MNa^+), 362 (83, MH^+) and 330 (100, M^+−OMe). (Found: MNa^+, 384.1996. $C_{17}H_{31}NO_7$ requires *MNa*, 384.1998).

Also obtained was (2*R*, 3R, 5*R*, 6*R*)-5,6-Dimethoxy-[1,4]-dioxane-3-methylcarboxylate-2-dipropylamide **16** (76 mg, 4%) as a colourless oil, R_f 0.42 (20% EtOAc in petrol); $[\alpha]_D^{20}$ −61.3 (*c*. 2.20 in CH_2Cl_2); ν_{max}/cm^{-1}(film) 2927, 1745 and 1650; δ_H (500 MHz, $CDCl_3$) 4.99 (1 H, d, *J* 10.1, 2- or 3-H), 4.96 (1 H, d, *J* 10.1, 3- or 2-H), 3.74 (3 H, s, CO_2Me), 3.38-3.23 (4 H, m, 2 × NCH_2) 3.35 (3 H, s, 5- or 6-OMe), 3.31 (3 H, s, 6- or 5-OMe), 1.66 (2 H, m, NCH_2CH_2), 1.55 (2 H, m, NCH_2CH_2), 1.41 (3 H, m, 5- or 6-Me), 1.37 (3 H, m, 5- or 6-Me), 0.94 (3 H, t, *J* 7.4, CH_2CH_3) and 0.87 (3 H, t, *J* 7.4, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 170.4, 168.1, 101.3, 101.1, 71.6, 68.8, 52.7, 49.6, 49.1, 49.1, 47.8, 30.1, 22.8, 21.1, 18.5, 11.7 and 11.6; *m/z* (ES) 362 (56%, MH^+) and 330 (100, M^+−OMe). (Found: MNa^+ 384.2002. $C_{17}H_{31}NO_7$ requires *MNa*, 384.1998).

(2*R*, 3R, 5*R*, 6*R*)-5,6-Dimethoxy-[1,4]-dioxane-2,3-bis(dipropylamide) 15

Lithium hydroxide (286 mg, 6.80 mmol) was added to a solution of the diester[3] **9** (200 mg, 0.68 mmol) and hydrogen peroxide (30% in water, 1.50 L, 13.6 mmol) in tetrahydrafuran−water (3 : 1, 3 mL) at 0 ˚C. The solution was warmed to room temperature, stirred for 3 days, quenched with an aqueous sodium thiosulfate solution (1.5 M, 10 mL), adjusted to pH 2 with dilute aqueous hydrochloric acid, extracted with ethyl acetate (3 × 25 mL) dried ($MgSO_4$) and evaporated under reduced pressure. The residue was redissolved in ethyl actetate (10 mL) cooled to 0 ˚C, dipropylamine (123 μL, 0.90 mmol), 1-hydroxybenzatriazole hydrate (135 mg, 0.90 mmol) and 1-[3-(Dimethylamino)propyl]-3-ethyl carbodiimide hydrochloride (173 mg, 0.90) were added, the mixture was warmed to room temperature and stirred for 20 h. Water (15 mL) and ethyl acetate (10 mL) were added, the organic layer separated, the aqueous layer extracted with ethyl acetate (2 × 20 mL), the combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. Purification by flash chromatography, eluting with 90 : 10 petrol−ethyl acetate, gave the *diamide* **15** (17 mg, 6%) as a colourless oil, R_f 0.48 (30% EtOAC in petrol); $[\alpha]_D^{20}$ −63.8 (*c*. 0.79 in $CHCl_3$); ν_{max}/cm^{-1} (film) 2964 and 1650; δ_H (500 MHz, $CDCl_3$) 5.09 (2 H, s, 2- and 3-H), 3.38-3.15 (8 H, m, 4 × NCH_2), 3.33 (6 H, s, 5- and 6-OMe), 1.76-1.63 (4 H, m, 2 × NCH_2CH_2), 1.59-1.43 (4 H, m, 2 × NCH_2CH_2), 1.40 (6 H, s, 5- and 6-Me), 0.94 (6 H, t, *J* 7.4, CH_2CH_3) and 0.85 (6 H, t, *J* 7.4, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 168.4, 101.1, 69.3, 49.6, 49.0, 47.7, 22.8, 21.1, 17.83, 11.8 and 11.6; *m/z* (ES) 431 (50, MH^+) and 399 (100, M^+−OMe). (Found: M^+–OMe, 399.2845. $C_{22}H_{42}NO_6$ requires *M−OMe*, 399.2859).

(2*R*, 3*S*)-1-Dipropylamide-4-methylcarboxylate-2,3-hydroxy-butane 12

A trifluoroacetic acid−water solution (9 : 1, 5 mL) was added to the diacetal **11** (200 mg, 0.55 mmol) and the resulting mixture swirled for 2 min at room temperature and evaporated under reduced pressure. Purification by flash chromatography, eluting with 50 : 50 petrol−ethyl acetate, to give the *amide* **12** (105 mg, 77%) as a colourless oil; R_f 0.18 (50% EtOAc in petrol); $[\alpha]_D^{20}$ +60.3 (*c*. 1.24 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3391, 2964, 2877, 1748 and 1633; δ_H (500 MHz, $CDCl_3$) 4.64 (1 H, d, *J* 3.2, 2- or 3-H), 4.34 (1 H, d, *J* 3.2, 3- or 2-H), 3.74 (3 H, s, CO_2Me), 3.50 (1 H, dt, ^2J 13.7 and *J* 7.7, NCH_2), 3.33 (1 H, dt, ^2J 15.0 and *J* 7.7 NCH_2), 3.26

(1 H, dt, ^2J 15.0 and J 7.7, NCH_2), 3.12 (1 H, dt, ^2J 13.7 and J 7.7, NCH_2), 1.65 (2 H, sx, J 7.7, NCH_2CH_2), 1.58 (2 H, sx, J 7.7, NCH_2CH_2), 0.95 (3 H, t, J 7.7, CH_2CH_3) and 0.91 (3 H, t, J 7.7, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 171.8, 170.5, 73.1, 70.4, 52.8, 49.3, 48.2, 22.4, 20.9, 11.7 and 11.5; *m/z* (ES) 248 (100%, MH^+). (Found: MH^+, 248.1495. $C_{11}H_{21}NO_5$ requires *MH*, 248.1498).

(2*R*, 3*R*)-*N,N*-Dimethyl-2,3-*O*-isopropylidene-4-hydroxybutyramide 23a

Dimethylamine (2 M in MeOH, 20 mL, 40 mmol) was added slowly to the lactone[4] **22** (2.50 g, 15.8 mmol) at 0 ˚C under N_2. The resulting solution was stirred for 15 min, allowed to warm to room temperature, stirred for a further 1 h and evaporated under reduced pressure. Purification by flash chromatography, eluting with 95 : 5 ethyl acetate−methanol, and recrystallisation from petrol−diethyl ether gave the *amide* **23a** (2.85 g, 89%), as colourless needles, m.p. 69.2-72.4 ºC (from petrol−Et_2O); R_f 0.08 (EtOAc); $[\alpha]_D^{20}$ +33.5 (*c*. 1.42 in $CDCl_3$); (Found: C, 53.3; H, 8.30; N, 6.8; $C_9H_{17}NO_4$ requires: C, 53.2; H, 8.45; N, 6.9); ν_{max}/cm^{-1} (film) 3400, 2937 and 1652; δ_H (500 MHz, $CDCl_3$) 4.93 (1 H, d, J 6.1, 2-H), 4.40 (1 H, q, J 6.1, 3-H), 3.72 (1 H, dt, ^2J 12.3 and J 6.1, 4-H_A), 3.58 (1 H, dt, ^2J 12.3 and J 6.1, 4-H_B), 3.39 (1 H, t, J 6.1, OH), 3.12 (3 H, s, NMe), 2.99 (3 H, s, NMe), 1.56 (3 H, s, CMe) and 1.40 (3 H, s, CMe); δ_C (75 MHz, $CDCl_3$) 168.5, 110.0, 78.2, 75.5, 62.7, 37.6, 36.6, 27.7 and 25.9; *m/z* (ES) 226 (63 %, MNa^+) and 204 (35, MH^+).

(2*R*, 3*R*)-*N,N*-Dipropyl-2,3-*O*-isopropylidene-4-hydroxybutyramide 23b

Dipropylamine (47 mL, 340 mmol) in methanol (123 mL) was added slowly to the lactone **22** (5.38 g, 34.0 mmol) at 0 ˚C under N_2, the resulting solution allowed to warm to room temperature and stirred at room temperature for 72 h. Toluene (120 mL) was added and the mixture evaporated under reduced pressure. Purification by flash chromatography, eluting with 70 : 30 petrol−ethyl acetate, and recrystallisation from petrol−diethyl ether gave the *amide* **23b** (5.76 g, 65%) as colourless needles, m.p. 64.1-67.8 ºC (from petrol−Et_2O); R_f 0.41 (50% EtOAc in petrol); $[\alpha]_D^{20}$ +18.8 (*c*. 1.45 in $CDCl_3$); (Found: C, 60.3; H, 9.60; N, 5.2; $C_{13}H_{25}NO_4$ requires: C, 60.2; H, 9.75; N, 5.4); ν_{max}/cm^{-1} (film) 3400, 2937 and 1647; δ_H (500

MHz, $CDCl_3$) 4.89 (1 H, d, *J* 6.2, 2-H), 4.37 (1 H, dt , *J* 10.2 and 6.2, 3-H), 3.74-3.67 (1 H, m, 4-H_A), 3.60-3.54 (1 H, m, 4-H_B), 3.39-3.20 (5 H, m, 2 × NCH_2 and OH), 1.67-1.54 (4 H, m, 2 × NCH_2CH_2), 1.57 (3 H, s, Me), 1.40 (3 H, s, Me), 0.93 (3 H, t, *J* 7.4, $NCH_2CH_2CH_3$) and 0.91 (3 H, t, *J* 7.4, $NCH_2CH_2CH_3$); δ_C (75 MHz, $CDCl_3$) 168.2, 110.2, 78.5, 75.3, 62.9, 50.0, 49.0, 27.5, 25.9, 22.9, 21.0, 11.8 and 11.6; *m/z* (ES) 282 (28 %, MNa^+) and 260 (64, MH^+).

(4*R*,5*R*, 6*R*)- and (4*S*,5*R*, 6*R*)-6-Dipropylcarbamoyl-2-methylidene-4-hydroxy-5,6-*O*-isopropylidene-hexanoic acid ethyl ester 25 and 26

Oxalyl chloride (3.7 mL, 43 mmol) was added slowly to a stirred solution of dimethyl sulfoxide (6.1 mL, 86 mmol) in dichloromethane (170 mL) under N_2 at −78 ˚C and the resulting solution stirred for 45 min at −78 ˚C. A solution of the alcohol **23b** (5.56 g, 21.5 mmol) in dichloromethane (125 mL) was added dropwise *via* cannula and the mixture stirred for 3.5 h at −78 ˚C. Triethylamine (48 mL, 344 mmol) was added and the solution allowed to warm to room temperature over 1 h. Water (300 mL) was added, the organic layer separated and the aqueous layer extracted with dichloromethane (2 × 300 mL). The combined organic extracts were washed with brine (500 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude aldehyde which was used immediately without purification. To the crude aldehyde in tetrahydrafuran−water (1 : 1, 300 mL) was added indium powder (2.72 g, 23.7 mmol) and ethyl α–(bromomethyl)acrylate[5] (3.6 mL, 26 mmol), the resulting suspension was stirred for 40 h at room temperature and filtered through Celite. Ethyl acetate (150 mL) was added, the organic layer separated and the aqueous layer extracted with ethyl acetate (2 × 150 mL). The combined organic extracts were washed with brine (300 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Purification by column chromatography (gradient elution : 20% → 45% EtOAc in Petrol) and recrystallisation from petrol−diethyl ether) gave the (4*R*)-*amide* **25** (3.57 g, 45%) as colourless plates, m.p. 54.7-57.5 ºC (from petrol−Et_2O); R_f 0.45 (50% EtOAc in petrol); $[\alpha]_D^{20}$ +52.2 (*c*. 1.64 in $CHCl_3$); (Found: C, 61.3; H, 8.90; N, 4.0; $C_{19}H_{33}NO_6$ requires: C, 61.4; H, 8.95; N, 3.8); ν_{max}/cm^{-1} (film) 3367, 2963, 1710 and 1639; δ_H (500 MHz, $CDCl_3$) 6.26 (1 H, s, C=CH_A), 5.73 (1 H, s, C=CH_B), 4.88 (1 H, d, *J* 6.1, 6-H), 4.21 (2 H, q, *J* 7.1 OC$H_2$$CH_3$), 4.07 (1 H, dd, *J* 8.1 and 6.1, 5-H), 3.96-3.91 (1 H, m, 4-

H), 3.74 (1 H, d, *J* 4.2, O*H*), 3.44-3.34 (2 H, m, NCH_2), 3.19-3.09 (2 H, m, NCH_2), 2.87 (1 H, dd, ^2J 14.3 and *J* 2.0, 3-H_A), 2.34 (1 H, dd, ^2J 14.3 and *J* 8.7, 3-H_B), 1.66-1.53 (4 H, m, 2 × NCH_2CH_2), 1.60 (3 H, s, CMe), 1.38 (3 H, s, CMe), 1.30 (3 H, t, *J* 7.1, OCH_2CH_3), 0.92 (3 H, t, *J* 7.4, $NCH_2CH_2CH_3$) and 0.88 (3 H, t, *J* 7.4, $NCH_2CH_2CH_3$); δ_C (75 MHz, $CDCl_3$) 168.8, 168.6, 137.5, 128.6, 110.3, 80.8, 74.8, 69.4, 61.5, 50.0, 49.0, 37.0, 27.5, 26.2, 22.9, 21.0, 14.6, 11.8 and 11.7; *m/z* (ES) 394 (20%, MNa^+) and 372 (100, MH^+).

Also obtained by column chromatography (gradient elution : 5% → 20% EtOAc in Petrol) of the supernatant was the (4*S*)-*amide* **26** (1.00 g, 13%) as a colourless oil, R_f 0.53 (50% EtOAc in petrol); $[\alpha]_D^{20}$ +17.2 (*c*. 6.82 in $CHCl_3$); ν_{max}/cm^{-1}(film) 3408, 2967, 1715 and 1639; δ_H (500 MHz, $CDCl_3$) 6.25 (1 H, d, ^2J 1.0, C=CH_A), 5.73 (1 H, d, ^2J 1.0, C=CH_B), 4.92 (1 H, d, *J* 6.7, 6-H), 4.18 (3 H, m, CO_2CH_2 and 5-H), 4.00 (1 H, d, *J* 2.6, O*H*), 3.72 (1 H, dddd, *J* 7.7, 5.4, 2.6 and 1.5, 4-H), 3.42 (1 H, ddd, ^2J 13.8, *J* 13.3 and 7.7, NCH_A), 3.30-3.18 (3 H, m, NCH_2 and CH_B), 2.59 (1 H, dd, ^2J 14.3 and *J* 7.7, 3-H_A), 2.50 (1 H, dd, ^2J 14.3 and *J* 5.4, 3-H_B), 1.69-1.52 (4 H, m, NCH_2CH_2), 1.67 (3 H, s, CMe), 1.40 (3 H, s, CMe), 1.29 (3 H, t, *J* 7.1, OCH_2CH_3), 0.94 (3 H, t, *J* 7.3, $NCH_2CH_2CH_3$) and 0.90 (3 H, t, *J* 7.5, $NCH_2CH_2CH_3$); δ_C (75 MHz, $CDCl_3$) 168.7, 167.6, 137.5, 128.0, 110.8, 79.7, 74.7, 69.3, 61.0, 49.9, 49.1, 36.8, 26.5, 26.2, 22.9, 21.0, 14.6, 11.8 and 11.6; *m/z* (ES) 394 (17%, MNa^+) and 372 (100, MH^+). (Found: MNa^+, 394.2202. $C_{19}H_{33}NO_6$ requires *MNa,* 394.2206).

(2*R*, 3*R*)-*N,N*-Dipropyl-2,3,4-trihydroxybutyramide 21b

A solution of trifluoroacetic acid−water (9 : 1, 25 mL) was added to the amide **23b**(759 mg, 2.93 mmol), the mixture swirled for 2 min and evaporated under reduced pressure. Purification by flash chromatography, eluting with 96 : 4 dichloromethane−methanol containing a small amount of triethylamine, followed by recrystallisation from ethyl acetate−petrol, gave the *amide* **21b** (424 mg, 66%) as colourless needles, m.p. 100.4-102.7 ºC (from petrol−EtOAc); R_f 0.50 (10% MeOH in CH_2Cl_2); $[\alpha]_D^{20}$ −39.2 (*c*. 1.02 in MeOH); ν_{max}/cm^{-1} (film) 3307, 2955, 2875, and 1617; δ_H (500 MHz, d_4-MeOD) 4.45 (1 H, d, *J* 6.3, 2-H), 3.77-3.70 (3 H, m, 3-H, 4-H_A and 4-H_B), 3.58 (1 H, ddd, ^2J 15.4, *J* 9.8 and 6.3, NCH_A), 3.49 (1 H, ddd, ^2J 15.0, *J* 8.7 and 6.5, NCH_A), 3.27-3.18 (2 H, m, 2 × NCH_B), 1.73-1.59 (4 H,

m, 2 × NCH_2CH_2), 0.97 (3 H, t, *J* 7.4, CH_2CH_3) and 0.94 (3 H, t, *J* 7.5, CH_2CH_3); δ_C (75 MHz, d_4-MeOD) 175.0, 75.0, 69.5, 64.4, 50.8, 49.6, 23.7, 22.1, 12.0 and 11.7; *m/z* (ES) 220 (100, MH^+). (Found: MH^+, 220.1547. $C_{10}H_{21}NO_4$ requires *MH,* 220.1549).

(2*R*, 2'*R*, 3'*R*)-2'-Hydroxy-2-(3'-hydroxy-5'-oxo-tetrahydro-furan-2'-yl)-*N*,*N*-dipropyl-acetamide 49

A solution of the amide **25** (371 mg, 1.00 mmol) in methanol (25 mL) was subjected to ozonolysis at −78˚C. Following addition of hydrogen peroxide (30% in water, 2.5 mL), water (5 mL) and formic acid (1 mL), the solution was warmed to room temperature stirred for 3 h and evaporated under reduced pressure. The residue was redissolved in formic acid−water (1 : 1, 20 mL), stirred for 18 h and evaporated under reduced pressure. Column chromatography (gradient elution : 50 → 70% ethyl acetate in petrol) gave a crude product which was redissolved in methanol−water (1 : 5, 15 mL), barium hydroxide monohydrate (52 mg, 0.274 mmol) was added, the solution stirred for 21 h and evaporated under reduced pressure. The residue was redissolved in water (10 mL), ammonium sulphate (36 mg, 0.274 mmol) was added, the solution stirred for 2 h, passed through a 4 μm filter and evaporated under reduced pressure. The residue was partitioned between ethyl acetate (20 mL) and water (20 mL), the organic layer separated and the aqueous layer extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give the *lactone* **49** (68 mg, 26%) as a colourless oil, R_f 0.69 (EtOAc); $[\alpha]_D^{20}$ +0.9 (*c*. 1.35 in MeOH); ν_{max}/cm^{-1} (film) 3391, 2966, 1783, 1631 and 1360; δ_H (500 MHz, $CDCl_3$) 4.59 (2 H, m, 2-H and 3'-H), 4.29 (1 H, t, *J* 3.5, 2'-H), 3.47-3.06 (4 H, m, 2 × NCH_2), 2.87 (1 H, dd, ^2J 18.0 and *J* 7.7, 4'-H_A), 2.50 (1 H, dd, ^2J 18.0 and *J* 5.2, 4'-H_B), 1.61-1.48 (4 H, m, 2 × NCH_2CH_2), 0.88 (3 H, t, *J* 7.3, $NCH_2CH_2CH_3$) and 0.83 (3 H, t, *J* 7.4, $NCH_2CH_2CH_3$); δ_C (75 MHz, $CDCl_3$) 175.2, 170.4, 87.2, 68.7, 67.7, 49.5, 48.3, 38.1, 22.4, 21.0, 11.7 and 11.5; *m/z* (ES) 260 (100%, MH^+). (Found: MH^+, 260.1487. $C_{12}H_{21}NO_5$ requires *MH*, 260.1487).

(2*R*, 3*R*)-2,3-*O*-Isopropylidene-pent-4-enoic acid dipropylamide 35

Oxalyl chloride (120 μL, 1.40 mmol) was added slowly to a stirred solution of dimethyl sulfoxide (200 μL, 2.80 mmol) in dichloromethane (5 mL) under N_2 at −78 ˚C and the resulting solution stirred for 35 min at −78 ˚C. A solution of the alcohol **23b** (200 mg, 0.77 mmol) in dichloromethane (4 mL) was added dropwise *via* cannula and the mixture stirred for 3 h at −78 ˚C. Triethylamine (48 mL, 344 mmol) was added and the solution allowed to warm to room temperature over 1 h. Water (10 mL) was added, the organic layer separated and the aqueous layer extracted with dichloromethane (2 × 15 mL). The combined organic extracts were washed with brine (30 mL), dried ($MgSO_4$) and evaporated under reduced pressure to give the crude aldehyde. *n*-Butyllithium (1.43 M in hexane, 1.15 mL, 1.64 mmol) was added slowly to a soltuition of methyl triphenylphosphonium bromide (607 mg, 1.70 mmol) in tetrahydrafuran (4 mL) at −12 ˚C. The solution was warmed to room temperature, stirred for 30 min, cooling to −12 ˚C, the crude aldehyde in tetrahydrafuran (2 mL) was added dropwise *via* cannula, the mixture warmed to room temperature and stirred for 18 h. The reaction was quenched by addition of a saturated aqueous ammonium chloride solution (10 mL), extracted with diethyl ether (3 × 15 mL). The combined organic extracts were washed with saturated aqueous ammonium chloride solution (20 mL), water (20 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Purification by flash chromatography, eluting with 85 : 15 petrol−ethyl acetate, gave the *amide* **35** (33 mg, 16%) as a colourless oil, R_f 0.42 (40% EtOAc in petrol); $[\alpha]_D^{20}$ −28.6 (*c.* 0.91 in $CHCl_3$); υ_{max}/cm^{-1} (film) 2965, 2875, 1660 and 1455; δ_H (500 MHz, $CDCl_3$) 5.80 (1 H, ddd, *J* 17.1, 10.3 and 7.7, 4-H), 5.40 (1 H, d, *J* 17.1, 5-H_{trans}), 5.24 (1 H, d, *J* 10.3, 5-H_{cis}), 4.94 (1 H, d, *J* 7.7, 2-H), 4.78 (1 H, t, *J* 7.7, 3-H), 3.49 (1 H, dt, ^2J 13.3 and *J* 7.7, NCH_A), 3.15-3.00 (3 H, m, 3 × NC*H*), 1.66 (3 H, s, CMe), 1.65-1.47 (4 H, m, 2 × NCH_2CH_2), 1.41 (3 H, s, CMe), 0.91 (3 H, t, *J* 7.3, CH_2CH_3) and 0.88 (3 H, t, *J* 7.3, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 167.9, 134.2, 120.2, 111.1, 79.8, 76.1, 49.4, 48.6, 27.3, 25.9, 22.6, 21.1, 11.9 and 11.6; *m/z* (ES) 256 (100%, MH^+). (Found: MH^+, 256.1903. $C_{14}H_{25}NO_3$ requires *MH*, 256.1913).

(4*R*, 3*R*, 2*S*)-2'-(3,4-*O*-Isopropylidene-5-oxo-tetrahydro-furan-2-ylmethyl)-acrylic acid ethyl ester 27 and (2*R*, 3*R*, 2'*S*)-2,3-*O*-Isopropylidene-3-(4'-methylene-5'-oxo-tetrahydro-furan-2'-yl)-*N*,*N*-dipropyl-propionamide 28

In a separate experiment on a 4.86 mmol scale, the crude product was purified by preparative HPLC to give the (4*R*)-*amide* **25** (676 mg, 37%) spectroscopically identically to that obtained previously. Further purification by column chromatography (gradient elution : 20% → 35% EtOAc in Petrol) gave the (4*S*)-*amide* **26** (202 mg, 3%) as a colourless oil, spectroscopically identical to that obtained previously.

Also obtained was the lactone **28** (173 mg, 3%) as a colourless oil, R_f 0.35 (50% EtOAc in petrol); $[\alpha]_D^{20}$ +93.5 (*c*. 4.9 in $CHCl_3$); ν_{max}/cm^{-1}(film) 2966, 1765, 1650, 1622 and 1465; δ_H (500 MHz, $CDCl_3$) 6.19 (1 H, t, ^4J 2.6, C=CH_A), 5.60 (1 H, t, ^4J 2.6, C=CH_B), 4.98 (1 H, ddd, *J* 8.7, 5.1 and 3.1, 2'-H), 4.96 (1 H, d, *J* 7.7, 2-H), 4.42 (1 H, dd, *J* 7.7 and 3.1, 3-H), 3.75 (1 H, ddd, ^2J 14.8, *J* 10.4 and 5.6, NCH_A), 3.46 (1 H, dt, ^2J 13.3 and *J* 7.7, NCH_A), 3.25 (1 H, ddd, ^2J 14.3, *J* 10.4 and 5.6, NCH_B), 3.09 (1 H, dt, ^2J 13.3 and *J* 7.7, NCH_B), 2.96 (1 H, ddt, ^2J 17.2, *J* 8.7 and ^4J 2.6, 3'-H_A), 2.82 (1 H, ddt, ^2J 17.2, *J* 5.1 and ^4J 2.6, 3'-H_B), 1.75-1.54 (4 H, m, NCH_2CH_2), 1.47 (3 H, s, CMe), 1.36 (3 H, s, CMe), 0.91 (3 H, t, *J* 6.6, $NCH_2CH_2CH_3$) and 0.90 (3 H, t, *J* 6.9, $NCH_2CH_2CH_3$); δ_C (75 MHz, $CDCl_3$) 170.5, 167.6, 134.7, 121.7, 110.9, 80.2, 76.9, 74.9, 49.9, 49.8, 30.2, 26.6, 25.1, 23.1, 20.9, 11.8, and 11.5; *m/z* (ES) 326 (100, MH^+). (Found: MH^+, 326.1981; $C_{17}H_{27}NO_5$ requires *MH,* 326.1967).

Also obtained was the *lactone* **27** (142 mg, 3%) as a colourless oil, R_f 0.67 (50% EtOAc in petrol); $[\alpha]_D^{20}$ −78.1 (*c*. 1.25 in $CHCl_3$); ν_{max}/cm^{-1}(film) 2988, 1788 and 1713; δ_H (500 MHz, $CDCl_3$) 6.35 (1 H, d, ^2J 0.8, C=CH_A), 5.83 (1 H, d, ^2J 0.8, C=CH_B), 4.81 (1 H, d, *J* 4.6, 4-H), 4.74 (2 H, m, 3- and 2-H), 4.23 (2 H, q, *J* 7.1, CO_2CH_2), 2.89 (1 H, dd, ^2J 14.5 and *J* 5.6, 4'-H_A), 2.81 (1 H, dd, ^2J 14.5 and *J* 7.7, 4'-H_B), 1.50 (3 H, s, CMe), 1.40 (1 H, s, CMe) and 1.32 (3 H, t, *J* 7.1, OCH_2CH_3); δ_C (75 MHz, $CDCl_3$) 173.8, 166.6, 134.7, 129,4, 114.1, 77.4, 76.8, 76.4, 61.1, 32.3, 26.9, 26.0 and 14.2; *m/z* (ES) 288 (32, MNH_4^+) and 271 (100, MH^+). (Found: MH^+, 271.1182; $C_{13}H_{18}O_6$ requires *MH*, 271.1182).

(4*R*, 5*R*, 6*R*)-6-Dipropylcarbamoyl-2-oxo-4-hydroxy-5,6-*O*-isopropylidene-hexanoic acid ethyl ester 40

The ester **25** (508 mg, 1.37mmol) in methanol (40 mL) was divided in to ten equal portions and O_2 (4 min), O_3 (4 min) then O_2 (4 min) bubbled through the solutions at −78 ˚C. Dimethyl sulfide (0.8 mL / portion) was added and the solutions warmed to room temperature, stirred for 4 h, all the portions recombined and evaporated under reduced pressure. Water (30 mL) was added and extracted with ethyl acetate (3 × 50 mL), the combined organic extracts were washed with brine (75 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Purification by flash chromatography, eluting with 50 : 50 ethyl acetate−petrol, gave the *ketone* **40** (412 mg, 81%) as a pale yellow oil, R_f 0.36 (40% EtOAc in petrol); $[\alpha]_D^{20}$ +15.8 (*c*. 1.37 in $CDCl_3$); ν_{max}/cm^{-1} (film) 3391, 2966, 1780, 1728 and 1642; δ_H (500 MHz, $CDCl_3$) 4.90 (1 H, d, *J* 6.3, 6-H), 4.37 (1 H, app. tt, *J* 8.7 and 3.9, 4-H), 4.32 (2 H, q, *J* 7.1 OCH_2CH_3), 4.14 (1 H, dd, *J* 8.7 and 6.3, 5-H), 3.94 (1 H, d, *J* 3.9, O*H*), 3.42-3.16 (4 H, m, 2 × NCH_2), 3.28 (1 H, dd, ^2J 16.9 and *J* 3.2, 3-H_A), 2.97 (1 H, dd, ^2J 16.9 and *J* 8.6, 3-H_B), 1.67-1.56 (4 H, m, 2 × NCH_2CH_2), 1.51 (3 H, s, CMe), 1.37 (3 H, t, *J* 7.1, OCH_2CH_3), 1.36 (3 H, s, CMe), 0.93 (3 H, t, *J* 7.5, $NCH_2CH_2CH_3$) and 0.91 (3 H, t, *J* 7.5, $NCH_2CH_2CH_3$); δ_C (75 MHz, $CDCl_3$) 193.8, 168.2, 161.2, 110.3, 80.4, 75.1, 67.1, 62.9, 50.1, 49.2, 43.9, 27.4, 25.7, 22.9, 21.0, 14.4, 11.8, and 11.6; *m/z* (ES) 747 (24, $[2M]H^+$), 406 (90, $[M+MeOH]H^+$) and 374 (100, MH^+). (Found: MH^+ 374.2176. $C_{18}H_{31}NO_7$ requires *MH*, 374.2179).

(4*R*, 5*R*, 6*R*)-6-Dipropylcarbamoyl-2-oxo-4,5,6-trihydroxy-hexanoic acid ethyl ester 41

The amide **40** (49 mg, 0.130 mmol) was treated with trifluoroacetic acid−water (1 : 1, 2.0 mL), the mixture stirred for 19 h and evaporated under reduced pressure. Purification by column chromatography (gradient elution: 30%→70% EtOAc in petrol) gave the *amide* **41** (22 mg, 51%) as a colourless oil, R_f 0.39 (EtOAc); $[\alpha]_D^{20}$ −8.6 (*c*. 0.42 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3368, 2966, 1745 and 1630;δ_H (500 MHz, $CDCl_3$) 4.74-4.66 (1 $H_{fur(maj)}$ and 1 H_{pyr}, m, 4-$H_{fur(maj)}$ and 5-H_{pyr}), 4.62-4.58 (1 $H_{fur(maj)}$ and 1 $H_{fur(min)}$, m, 6-$H_{fur(maj)}$ and 4-$H_{fur(min)}$), 4.40 (1 H, d, *J* 4.8, 6-$H_{fur(min)}$), 4.38 (1 H, m, 4-H_{pyr}), 4.31-4.24 (2 H_{pyr}, 2 $H_{fur(maj)}$ and 2 $H_{fur(min)}$, m, 3 × OCH_2), 4.20 (1 H, t, *J* 4.8, 5-$H_{fur(min)}$), 4.13-4.04 (1 $H_{fur(maj)}$ and 1 H_{pyr}, m, 5-$H_{fur(maj)}$ and 6-

H_{pyr}), 4.25-3.75 (3 H_{pyr}, 3 $H_{fur(maj)}$ and 3 $H_{fur(min)}$, br. s, 9 × OH), 3.66-3.11 (4 H_{pyr}, 4 $H_{fur(maj)}$ and 4 $H_{fur(min)}$, m, 6 × NCH_2), 2.72 (1 H, dd, ^2J 13.7 and J 6.8, 3-$H_{A\ fur(min)}$), 2.56 (1 H, dd, ^2J 13.5 and J 7.3, 3-$H_{A\ fur(maj)}$), 2.45 (1 H, dd, ^2J 13.5 and J 7.3, 3-$H_{B\ fur(maj)}$), 2.28 (1 H, dd, ^2J 10.7 and J 3.2, 3-$H_{A\ pyr}$), 2.23 (1 H, dd, ^2J 13.7 and J 4.3, 3-$H_{B\ fur(min)}$), 2.21 (1 H, dd, ^2J 10.7 and J 7.3, 3-$H_{B\ pyr}$), 1.64-1.56 (4 H_{pyr}, 4 $H_{fur(maj)}$ and 4 $H_{fur(min)}$, m, 6 × NCH_2CH_2), 1.37-1.29 (3 H_{pyr}, 3 $H_{fur(maj)}$ and 3 $H_{fur(min)}$, m, 3 × OCH_2CH_3) and 0.96-0.88 (6 H_{pyr}, 6 $H_{fur(maj)}$ and 6 $H_{fur(min)}$, m, 6 × $NCH_2CH_2CH_3$); δ_C (75 MHz, $CDCl_3$) 171.7 (7-$C_{fur(min)}$), 171.3 (7-$C_{fur(maj)}$), 170.9 (1-$C_{fur(maj)}$), 170.1 (1-$C_{fur(min)}$), 169.5 (1-C_{pyr}), 168.7 (7-C_{pyr}), 102.7 (2-$C_{fur(maj)}$), 102.2 (2-$C_{fur(min)}$), 96.2 (2-C_{pyr}), 88.3 (5-$C_{fur(maj)}$), 88.2 (5-$C_{fur(min)}$), 72.4 (4-$C_{fur(min)}$), 71.0 (4-$C_{fur(maj)}$), 69.5 (6-$C_{fur(maj)}$), 69.0 (6-$C_{fur(min)}$), 68.5 (4-C_{pyr}), 68.2 (6-C_{pyr}), 67.1 (5-C_{pyr}), 63.4 (OEt), 63.0 (OEt), 62.6 (OEt), 49.7 (NPr_2), 49.5 (NPr_2), 49.4 (NPr_2), 48.4 (NPr_2), 48.2 (NPr_2), 48.1 (NPr_2), 43.9 (3-$C_{fur(maj)}$), 43.2 (3-$C_{fur(min)}$), 35.9 (3-C_{pyr}), 22.5 (NPr_2), 22.5 (NPr_2), 22.3 (NPr_2), 21.0 (NPr_2), 21.0 (NPr_2), 20.9 (NPr_2), 14.6 (OEt), 14.5 (OEt), 14.4 (OEt), 11.8 (NPr_2), 11.8 (NPr_2), 11.6 (NPr_2), 11.5 (NPr_2), 11.5 (NPr_2) and 11.5 (NPr_2); *m/z* (ES) 356 (18, MNa^+) and 334 (100, MH^+). (Found: MNa^+, 356.1693. $C_{15}H_{27}NO_7$ requires *MNa*, 356.1685). Analysis by 500 MHz ^{1}H NMR revealed a 41 : 39 : 20 mixture of two furanose and one pyranose forms.

(4*R*, 5*R*, 6*R*)-6-Dipropylcarbamoyl-2-oxo-4,5,6-trihydroxy-hexanoic acid ammonium salt 42

Barium hydroxide monohydrate (88 mg, 0.46 mmol) in water (21 mL) was added slowly to a solution of the ester **41**(309 mg, 0.93 mmol) in methanol (4.3 mL) and the mixture stirred at room temperature for 16 h. The mixture was evaporated under reduced pressure, the residue dissolved in water (15 mL) and ammonium sulfate (61 mg, 0.46 mmol) added. The mixture was stirred for 2 h at room temperature, the precipitate removed by filtration through a 4 μm filter and the filtrate evaporated under reduced pressure to give the *ammonium salt* **42**(289 mg, 97%) as a pale yellow foam, R_f 0.58 (5 : 2 : 2 EtOAc−AcOH−H_2O); $[\alpha]_D^{20}$ −31.0 (*c*. 1.11 in H_2O); ν_{max}/cm^{-1} (solid) 3600−2500 (br.) and 1618; δ_H (500 MHz, D_2O) 4.70 (1 H, d, J 9.9, 6-H_{pyr}), 4.38 (1 H, d, J 5.6, 6-$H_{fur(maj)}$), 4.31 (1 H, d, J 6.8, 6-$H_{fur(min)}$), 4.33-4.25 (1 $H_{fur(maj)}$ and

1 $H_{fur(min)}$, m, 4-$H_{fur(maj)}$ and 4-$H_{fur(min)}$), 3.99-3.94 (1 $H_{fur(maj)}$ and 1 H_{pyr}, m, 5-$H_{fur(maj)}$ and 4-H_{pyr}), 3.84 (1 H, dd, *J* 6.8 and 3.9, 5-$H_{fur(min)}$), 3.64 (1 H, dd, *J* 9.9 and 3.2, 5-H_{pyr}), 3.33-2.79 (4 H_{pyr}, 4 $H_{fur(maj)}$ and 4 $H_{fur(min)}$, m, 6 × NCH_2), 2.31 (1 H, dd, ^2J 14.1 and *J* 7.3, 3-$H_{A\ fur(maj)}$), 2.11 (1 H, dd, ^2J 14.1 and *J* 6.8, 3-$H_{A\ fur(min)}$), 2.03 (1 H, dd, ^2J 14.1 and *J* 5.6, 3-$H_{B\ fur(min)}$), 1.88 (1 H, dd, ^2J 15.0 and *J* 3.4, 3-$H_{A\ pyr}$), 1.82 (1 H, dd, ^2J 15.0 and *J* 3.4, 3-$H_{B\ pyr}$), 1.77 (1 H, dd, ^2J 14.1 and *J* 2.6, 3-$H_{B\ fur(maj)}$), 1.45-1.19 (4 H_{pyr}, 4 $H_{fur(maj)}$ and 4 $H_{fur(min)}$, m, 6 × NCH_2CH_2), and 0.66-0.53 (6 H_{pyr}, 6 $H_{fur(maj)}$ and 6 $H_{fur(min)}$, m, 6 × $NCH_2CH_2CH_3$); δ_C (75 MHz, D_2O) 176.9 (1-$C_{fur(min)}$), 176.4 (1-$C_{fur(maj)}$), 176.4 (1-C_{pyr}), 171.9 (7-$C_{fur(min)}$), 171.4 (7-$C_{fur(maj)}$), 171.3 (7-C_{pyr}), 104.7 (2-$C_{fur(maj)}$), 104.3 (2-$C_{fur(min)}$), 96.7 (2-C_{pyr}), 87.3 (5-$C_{fur(maj)}$), 87.0 (5-$C_{fur(min)}$), 72.2 (4-$C_{fur(min)}$), 71.7 (4-$C_{fur(maj)}$), 68.7 (5-C_{pyr}), 68.6 (6-$C_{fur(min)}$), 68.4 (6-$C_{fur(maj)}$), 67.6 (4-C_{pyr}), 65.8 (6-C_{pyr}), 50.5 (Pr), 49.8 (Pr), 49.7 (Pr), 49.3 (Pr), 48.6 (Pr), 48.4 (Pr), 44.7 (3-$C_{fur(maj)}$), 43.7 (3-$C_{fur(min)}$), 37.1 (3-C_{pyr}), 22.4 (Pr), 22.4 (Pr), 22.0 (Pr), 20.6 (Pr), 20.5 (Pr), 20.5 (Pr), 10.9 (Pr), 10.9 (Pr), 10.9 (Pr), 10.8 (Pr), 10.6 (Pr) and 10.6 (Pr); *m/z* (ES) 306 (100%, $[M-NH_3]H^+$). (Found: $[M-NH_3]Na^+$, 328.1382. $C_{13}H_{23}NO_7 \cdot NH_3$ requires *[M−NH₃]Na*, 328.1372).

Analysis by 500 MHz ^{1}H NMR revealed a 38 : 33 : 29 mixture of two fuanose and one pyranose forms.

(4*R*, 5*R*, 6*R*)-6-Dipropylcarbamoyl-2-oxo-4,5,6-trihydroxy-hexanoic acid 43

Ion-exchange chromatography (Dowex 1X8−100, formate form, gradient elution: 0 → 1.0 M formic acid) of the ammonium salt **42**(100 mg, 0.31 mmol) gave the *acid* **43**(68 mg, 72%; 97 : 3, 4*R* : 4*S*) as a colourless foam, R_f 0.58 (5 : 2 : 2 EtOAc−AcOH−H_2O); $[\alpha]_D^{20}$ −35.4 (*c*. 1.30 in H_2O); ν_{max}/cm^{-1} (solid) 3392 (br.), 2967, 2877, 1736 and 1621; δ_H (500 MHz, D_2O) 4.95 (1 H, d, *J* 9.8, 6-$H_{pyr(maj)}$), 4.93 (1 H, d, *J* 9.0, 6-$H_{pyr(min)}$), 4.57 (1 H, ddd, *J* 6.4, 5.8 and 3.9, 4-$H_{fur(min)}$) 4.54 (1 H, d, *J* 6.8, 6-$H_{fur(min)}$), 4.52 (1 H, app. dt, *J* 7.0 and 2.6, 4-$H_{fur(maj)}$), 4.46 (1 H, d, *J* 7.3, 6-$H_{fur(maj)}$), 4.25 (1 H, dd, *J* 7.3 and 2.6, 5-$H_{fur(maj)}$), 4.20 (1 H, q, *J* 3.4, 4-$H_{pyr(maj)}$), 4.16 (1 H, ddd, *J* 5.1, 3.0 and 2.6, 4-$H_{pyr(min)}$), 4.10 (1 H, dd, *J* 6.8 and 3.9, 5-$H_{fur(min)}$), 3.93 (1 H, dd, *J* 9.0 and 3.0, 5-$H_{pyr(min)}$), 3.86 (1 H, dd, *J* 9.8 and 3.4, 5-$H_{pyr(maj)}$), 3.60-3.05 (4 $H_{fur(maj)}$, 4 $H_{fur(min)}$, 4 $H_{pyr(maj)}$ and 4 $H_{pyr(min)}$, m, 2 × $NCH_{2\ fur(maj)}$, 2 × $NCH_{2\ fur(min)}$, 2 × $NCH_{2\ pyr(maj)}$ and

2 × NC$H_{2\ pyr(min)}$), 2.64 (1 H, dd, ^{2}J 14.5 and J 6.8, 3-$H_{A\ fur(maj)}$), 2.54 (1 H, dd, ^{2}J 14.1 and J 5.1, 3-$H_{A\ pyr(min)}$), 2.42 (1 H, dd, ^{2}J 15.0 and J 5.8, 3-$H_{A\ fur(min)}$), 2.39 (1 H, dd, ^{2}J 15.0 and J 6.4, 3-$H_{B\ fur(min)}$), 2.15 (1 H, dd, ^{2}J 15.0 and J 3.4, 3-$H_{A\ pyr(maj)}$), 2.11 (1 H, dd, ^{2}J 15.0 and J 3.4, 3-$H_{B\ pyr(maj)}$), 2.09 (1 H, dd, ^{2}J 14.5 and J 2.6, 3-$H_{B\ fur(maj)}$), 1.90 (1 H, dd, ^{2}J 14.1 and J 2.6, 3-$H_{B\ pyr(min)}$), 1.67-1.35 (4 $H_{fur(maj)}$, 4 $H_{fur(min)}$, 4 $H_{pyr(maj)}$ and 4 $H_{pyr(min)}$, m, 2 × NCH_2CH_2 $_{fur(maj)}$, 2 × NCH_2CH_2 $_{fur(min)}$, 2 × NCH_2CH_2 $_{pyr(maj)}$ and 2 × NCH_2CH_2 $_{pyr(min)}$) and 0.87-0.35 (6 $H_{fur(maj)}$, 6 $H_{fur(min)}$, 6 $H_{pyr(maj)}$ and 6 $H_{pyr(min)}$, m, 2 × $NCH_2CH_2CH_3$ $_{fur(maj)}$, 2 × $NCH_2CH_2CH_3$ $_{fur(min)}$, 2 × $NCH_2CH_2CH_3$ $_{pyr(maj)}$ and 2 × $NCH_2CH_2CH_3$ $_{pyr(min)}$); δ_C (75 MHz, D_2O) 173.5 (1-$C_{fur(min)}$), 173.2 (1-$C_{pyr(min)}$), 172.9 (1-$C_{fur(maj)}$), 172.9 (1-$C_{pyr(maj)}$), 172.2 (7-$C_{fur(min)}$), 172.1 (7-$C_{fur(maj)}$), 170.5 (7-$C_{pyr(maj)}$), 170.2 (7-$C_{pyr(min)}$), 103.2 (2-$C_{fur(maj)}$), 102.9 (2-$C_{fur(min)}$), 95.5 (2-$C_{pyr(maj)}$), 88.1 (5-$C_{fur(min)}$), 87.3 (5-$C_{fur(min)}$), 72.1 (4-$C_{fur(maj)}$), 71.5 (4-$C_{fur(min)}$), 71.7 (5-$C_{pyr(min)}$), 70.3 (5-$H_{pyr(maj)}$), 68.2 (6-$C_{fur(min)}$), 67.7 (6-$C_{fur(maj)}$), 67.0 (4-$H_{pyr(maj)}$), 66.6 (4-$C_{pyr(min)}$), 65.7 (6-$C_{pyr(maj)}$), 65.6 (6-$C_{pyr(min)}$), 50.3 (Pr), 50.0 (Pr), 49.8 (Pr), 49.8 (Pr), 49.2 (Pr), 48.9 (Pr), 48.6 (Pr), 48.4 (Pr), 44.2 (3-$C_{fur(min)}$), 43.7 (3-$C_{fur(maj)}$), 38.8 (3-$C_{pyr(min)}$), 36.7 (3-$C_{pyr(maj)}$), 22.4 (Pr), 22.3 (Pr), 22.1 (Pr), 22.1 (Pr), 20.6 (Pr), 20.5 (Pr), 20.5 (Pr), 20.5 (Pr), 10.9 (Pr), 10.9 (Pr), 10.8 (Pr), 10.7 (Pr), 10.7 (Pr), 10.6 (Pr), 10.6 (Pr) and 10.6 (Pr), (1 peak missing); *m/z* (ES) 328 (70%, MNa^+), 306 (45, MH^+). (Found: MNa^+, 328.1382. $C_{13}H_{23}NO_7$ requires *MNa*, 328.1372).

Analysis by 500 MHz ^{1}H NMR revealed that the *R*-isomer existed as a 44 : 32 : 16 : 8 mixture of two furanose and two pyranose forms.

(4*S*, 5*R*, 6*R*)-6-Dipropylcarbamoyl-2-oxo-4-hydroxy-5,6-*O*-isopropylidene-hexanoic acid ethyl ester 44

A solution of the amide **26** (48 mg, 0.13 mmol) in methanol (4 mL) at −78 ˚C was subjected to ozonolysis, following addition of dimethylsulfide (0.8 mL), the mixture was warmed to room temperature, stirred for 2.5 h and evaporated under reduced pressure. Purification by flash chromatography, eluting with 70 : 30 petrol−ethyl acetate gave the *ketone* **44**(21 mg, 42%) as a pale yellow oil, R_f 0.36 (50% EtOAc in petrol); $[\alpha]_D^{20}$ +23.0 (*c*. 2.1 in $CDCl_3$); ν_{max}/cm^{-1} (film) 3369, 2966, 1783, 1729 and 1639; δ_H (500 MHz, $CDCl_3$) 4.96 (1 H, d, J 6.6,

6-H), 4.31 (2 H, q, *J* 7.2, OCH_2), 4.26 (2 H, m, 5-H and OH), 4.02 (1 H, m, 4-H), 3.52-3.20 (4 H, m, 2 × NCH_2), 3.21 (1 H, dd, ^2J 18.1 and *J* 5.9, 3-H_A), 3.07 (1 H, dd, ^2J 18.1 and *J* 7.0, 3-H_B), 1.74-1.55 (4 H, m, 2 × NCH_2CH_2), 1.65 (3 H, s, CMe), 1.39 (3 H, s, CMe), 1.36 (3 H, t, *J* 7.2, OCH_2CH_3), 0.97 (3 H, t, *J* 7.3, $NCH_2CH_2CH_3$) and 0.92 (3 H, t, *J* 7.4, $NCH_2CH_2CH_3$); δ_C (75 MHz, $CDCl_3$) 193.6, 168.7, 161.1, 111.2, 79.0, 74.7, 67.5, 63.1, 50.2, 49.4, 43.2, 26.5, 26.4, 23.2, 21.2, 14.5, 11.9 and 11.8; *m/z* (ES) 406 (30, M+$MeOH_2^+$) and 374 (100, MH^+). (Found: MH^+, 374.2174. $C_{18}H_{31}NO_7$ requires *MH*, 374.2179).

(4*S*, 5*R*, 6*R*)-6-Dipropylcarbamoyl-2-oxo-4,5,6-trihydroxy-hexanoic acid ethyl ester 45

The amide **44** (20 mg, 0.054 mmol) was treated with trifluoroacetic acid−water (1:1, 2 mL), the mixture swirled for 2 min and evaporated under reduced pressure. The process was repeated, purification by flash chromatography, eluting with ethyl acetate, gave the *amide* **45** (9.2 mg, 51%) as a colourless oil, R_f 0.40 (EtOAc); $[\alpha]_D^{20}$ −43.3 (*c*. 4.43 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3368, 2967, 1742 and 1636; δ_H (500 MHz, $CDCl_3$) 4.81 (1 H, d, *J* 8.5, 6-$H_{fur(maj)}$), 4.74 (1 H, d, *J* 8.4, 6-$H_{fur(min)}$), 4.67 (1 H, ddd, *J* 5.8, 3.4 and 1.9, 4-$H_{fur(min)}$), 4.64 (1 H, m, 4-$H_{fur(maj)}$), 4.41 (1 H, d, *J* 9.3, 6-H_{pyr}), 4.32-4.23 (2 H_{pyr}, 2 $H_{fur(maj)}$ and 2 $H_{fur(min)}$, m, 3 × OCH_2), 4.12-4.07 (1 H, m, 5-$H_{fur(min)}$), 4.10 (1 H, ddd, *J* 16.7, 9.3 and 6.5, 4-H_{pyr}), 3.94 (1 H, dd, *J* 8.5 and 3.4, 5-$H_{fur(maj)}$), 3.91 (1 H, t, *J* 9.3, 5-H_{pyr}), 3.32-3.00 (4 H_{pyr}, 4 $H_{fur(maj)}$ and 4 $H_{fur(min)}$, m, 6 × NCH_2), 2.64 (1 H, dd, ^2J 14.0 and *J* 5.1, 3-$H_{A\ fur(maj)}$), 2.60 (1 H, dd, ^2J 14.7 and *J* 1.9, 3-$H_{A\ fur(min)}$), 2.41 (1 H, dd, ^2J 14.7 and *J* 5.8, 3-$H_{B\ fur(min)}$), 2.27 (1 H, d, ^2J 14.0, 3-$H_{B\ fur(maj)}$), 2.16 (1 H, dd *J* 16.7 and ^2J 12.8, 3-$H_{A\ pyr}$), 2.12 (1 H, dd, ^2J 12.8 and *J* 6.5, 3-$H_{B\ pyr}$), 1.60-1.54 (4 H_{pyr}, 4 $H_{fur(maj)}$ and 4 $H_{fur(min)}$, m, 6 × NCH_2CH_2), 1.35-1.28 (3 H_{pyr}, 3 $H_{fur(maj)}$ and 3 $H_{fur(min)}$, m, 3 × OCH_2CH_3) and 0.93-0.85 (6 H_{pyr}, 6 $H_{fur(maj)}$ and 6 $H_{fur(min)}$, m, 6 × $NCH_2CH_2CH_3$); δ_C (75 MHz, $CDCl_3$) 172.8 (7-$C_{fur(maj)}$), 172.8 (7-$C_{fur(min)}$), 170.9 (1-$C_{fur(min)}$), 170.2 (1-C_{pyr}), 170.1 (1-$C_{fur(maj)}$), 168.7 (7- C_{pyr}), 103.3 (2-$C_{fur(maj)}$), 102.8 (2-$C_{fur(min)}$), 95.8 (2-C_{pyr}), 86.8 (5-$C_{fur(maj)}$), 85.4 (5-$C_{fur(min)}$), 73.4 (4-C_{pyr}), 73.1 (4-$C_{fur(min)}$), 72.4 (4-$C_{fur(maj)}$), 70.9 (6-C_{pyr}), 68.2 (5- C_{pyr}), 66.8 (6-$C_{fur(maj)}$), 66.0 (6-$C_{fur(min)}$), 63.6 (Et), 63.2 (Et), 62.8 (Et), 49.6 (Pr), 49.3 (Pr), 49.2 (Pr), 48.4 (Pr), 48.1 (Pr), 48.0 (Pr), 44.4 (3-$C_{fur(min)}$), 43.2 (3-$C_{fur(maj)}$), 37.7 (3-C_{pyr}), 22.4 (Pr), 22.4 (Pr), 22.3 (Pr), 21.0 (Pr), 20.9 (Pr), 20.9 (Pr), 14.5 (Et_t), 14.4 (Et), 14.3 (Et), 11.7 (Pr),

11.6 (Pr), 11.5 (Pr), 11.5 (Pr), 11.5 (Pr) and 11.5 (Pr); *m/z* (ES) 356 (48%, MNa^+) and 334 (100, MH^+). (Found: MH^+, 334.1859. $C_{15}H_{27}NO_7$ requires *MH*, 334.1866).
Analysis by 500 MHz ^{1}H NMR revealed an initial mixture of 72 : 14 : 14 one pyranose and two furanose forms, which equilibrated over 9 days in $CDCl_3$ to a 53 : 29 : 18 mixture of one pyranose and two furanose forms forms.

(4*S*, 5*R*, 6*R*)-6-Dipropylcarbamoyl-2-oxo-4,5,6-trihydroxy-hexanoic acid ammonium salt 46

Barium hydroxide monohydrate (140 mg, 0.74 mmol) in water (34 mL) was added slowly to a solution of the ester **45** (493 mg, 1.48 mmol) in methanol (7 mL) and the mixture stirred at room temperature for 23 h and evaporated under reduced pressure. The residue was dissolved in water (23 mL), ammonium sulphate (98 mg, 0.74 mmol) added, the mixture stirred for 2 h at room temperature, the precipitate removed by filtration through Celite and the filtrate evaporated under reduced pressure to give the *ammonium salt* **46** (474 mg, quantitative) as a colourless foam, R_f 0.58 (5 : 2 : 2 EtOAc−AcOH−H_2O); $[\alpha]_D^{20}$ −20.2 (*c*. 1.04 in H_2O); ν_{max}/cm^{-1} (solid) 3310 (br.), 2968, 2877 and 1621; δ_H (500 MHz, D_2O) 4.78 (1 H, d, *J* 9.0, 6-H_{fur}), 4.56 (1 H, d, *J* 9.4, 6-$H_{pyr(maj)}$), 4.45 (1 H, d, *J* 9.4, 6-$H_{pyr(min)}$), 4.40 (1 H, dd, *J* 4.7 and 2.8, 4-H_{fur}), 4.12 (1 H, dd, *J* 9.0 and 2.8, 5-H_{fur}), 3.92 (1 H, ddd, *J* 11.7, 9.4 and 5.1, 4-$H_{pyr(maj)}$), 3.84 (1 H, ddd, *J* 12.0, 9.4 and 5.1, 4-$H_{pyr(min)}$), 3.62 (1 H, t, *J* 9.4, 5-$H_{pyr(maj)}$), 3.60 (1 H, t, *J* 9.4, 5-$H_{pyr(min)}$), 3.45 (1 H, dt, ^2J 15.0 and *J* 7.7, NC$H_{A\ pyr(maj)}$), 3.37 (1 H, ddd, ^2J 15.0, *J* 8.6 and 6.4, NC$H_{A\ pyr(maj)}$), 3.25 (1 H, dt, ^2J 15.0 and *J* 7.7, NC$H_{B\ pyr(maj)}$), 3.18 (1 H, ddd, ^2J 15.0, *J* 8.6 and 6.4, NC$H_{B\ pyr(maj)}$), 3.51-3.05 (4 $H_{pyr(min)}$, and 4 H_{fur}, m, 2 × NC$H_{2\ fur}$ and 2 × NC$H_{2\ pyr(min)}$), 2.50 (1 H, dd, ^2J 12.8 and *J* 5.1, 3-$H_{A\ pyr(min)}$), 2.37 (1 H, d, ^2J 14.5, 3-$H_{A\ fur}$), 2.27 (1 H, dd, ^2J 14.5 and *J* 4.7, 3-$H_{B\ fur}$), 2.11 (1 H, dd ^2J 13.1 and *J* 5.1, 3-$H_{A\ pyr(maj)}$), 2.11 (1 H, m, 3-$H_{B\ pyr(min)}$), 1.84 (1 H, app. t, *J* 12.4, 3-$H_{B\ pyr(maj)}$), 1.64-1.44 (4 $H_{pyr(maj)}$, 4 $H_{pyr(min)}$ and 4 H_{fur}, m, 2 × $NCH_2CH_{2\ pyr(maj)}$, 2 × $NCH_2CH_{2\ pyr(min)}$ and 2 × $NCH_2CH_{2\ fur}$), 0.83 (3 H, t, *J* 7.3, $NCH_2CH_2CH_{3\ pyr(maj)}$), 0.81 (3 H, t, *J* 7.3, $NCH_2CH_2CH_{3\ pyr(maj)}$) and 0.86-0.78 (6 $H_{pyr(min)}$, and 6 H_{fur}, m, 2 × $NCH_2CH_2CH_{3\ pyr(min)}$ and 2 × $NCH_2CH_2CH_{3\ fur}$); δ_C (75 MHz, D_2O, major pyranose anomer only) 175.9, 170.6, 97.6, 73.1, 69.9, 68.9, 50.4, 49.3, 39.5, 22.4, 20.6, 10.9

and 10.7; *m/z* (ES) 306 (100, $[M-NH_3]H^+$). (Found: $(M-NH_3)H^+$, 306.1542. $C_{13}H_{23}NO_7{\cdot}NH_3$ requires *(M−NH₃)H*, 306.1553).

Analysis by 500 MHz ^{1}H NMR revealed a 84 : 7 : 9 mixture of two pyranose and one furanose forms.

(4*S*, 5*R*, 6*R*)-6-Dipropylcarbamoyl-2-oxo-4,5,6-trihydroxy-hexanoic acid 47

Ion-exchange chromatography (Dowex 1X8−100, formate form, gradient elution: 0 → 1.0 M formic acid) of the ammonium salt **46** (100 mg, 0.31 mmol) gave the *acid* **47** (74 mg, 79%) as a colourless foam, R_f 0.58 (5 : 2 : 2 EtOAc−AcOH−H_2O); $[\alpha]_D^{20}$ −30.6 (*c*. 1.24 in H_2O); ν_{max}/cm^{-1} (solid) 3392 (br.) 2968, 2878, 1737 and 1621; δ_H (500 MHz, D_2O) 4.87 (1 H, d, *J* 9.0, 6-$H_{fur(min)}$), 4.80 (1 H, d, *J* 9.0, 6-$H_{fur(maj)}$), 4.61 (1 H, d, *J* 9.4, 6-$H_{pyr(maj)}$), 4.58-4.53 (1 $H_{fur(maj)}$ and 1 $H_{fur(min)}$, m, 4-$H_{fur(maj)}$ and 4-$H_{fur(min)}$), 4.33 (1 H, d, *J* 9.4, 6-$H_{pyr(min)}$), 4.16 (1 H, dd, *J* 9.0 and 3.4, 5-$H_{fur(maj)}$), 4.10 (1 H, dd, *J* 9.0 and 3.4, 5-$H_{fur(min)}$), 3.95 (1 H, ddd, *J* 11.5, 9.4 and 5.1, 4-$H_{pyr(maj)}$), 3.79 (1 H, ddd, *J* 12.0, 9.4 and 5.1, 4-$H_{pyr(min)}$), 3.64 (1 H, t, *J* 9.4, 5-$H_{pyr(maj)}$), 3.67-3.62 (1 H, m, 5-$H_{pyr(min)}$), 3.44 (1 H, dt, ^2J 15.0 and *J* 7.7, NC$H_{A\ pyr(maj)}$), 3.35 (1 H, ddd, ^2J 13.7, *J* 8.6 and 6.4, NC$H_{A\ pyr(maj)}$), 3.25 (1 H, dt, ^2J 15.0 and *J* 7.7, NC$H_{B\ pyr(maj)}$), 3.19 (1 H, ddd, ^2J 13.7, *J* 8.6 and 6.4, NC$H_{B\ pyr(maj)}$), 3.60-3.00 (4 $H_{fur(maj)}$, 4 $H_{fur(min)}$ and 4 $H_{pyr(min)}$, m, 2 × NC$H_{2\ fur(maj)}$, 2 × NC$H_{2\ fur(maj)}$and 2 × NC$H_{2\ pyr(min)}$), 2.61-2.55 (1 $H_{fur(maj)}$, 1 $H_{fur(min)}$ and 1 $H_{pyr(min)}$, m, , 3-$H_{A\ fur(min)}$ 3-$H_{A\ fur(min)}$ and 3-$H_{A\ pyr(min)}$), 2.34 (1 H, dd, ^2J 15.0 and *J* 5.6, 3-$H_{B\ fur(maj)}$), 2.23 (1 H, dd ^2J 13.3 and *J* 5.1, 3-$H_{A\ pyr(maj)}$), 2.17 (1 H, d, ^2J 14.5, 3-$H_{B\ fur(min)}$), 1.84 (1 H, dd, ^2J 13.3 and *J* 11.5, 3-$H_{B\ pyr(maj)}$), 1.68 (1 H, dd, ^2J 12.8 and *J* 12.0, 3-$H_{B\ pyr(min)}$), 1.60-1.40 (4 $H_{pyr(maj)}$, 4 $H_{pyr(min)}$, 4 $H_{fur(maj)}$ and 4 $H_{fur(min)}$, m, 2 × $NCH_2CH_{2\ pyr(maj)}$, 2 × $NCH_2CH_{2\ pyr(min)}$, 2 × $NCH_2CH_{2\ fur(maj)}$ and 2 × $NCH_2CH_{2\ fur(min)}$), 0.82 (3 H, t, *J* 7.3, $NCH_2CH_2CH_{3\ pyr(maj)}$), 0.80 (3 H, t, *J* 7.3, $NCH_2CH_2CH_{3\ pyr(maj)}$) and 0.85-0.76 (6 $H_{pyr(min)}$, 6 $H_{fur(maj)}$ and 6 $H_{fur(min)}$, m, 2 × $NCH_2CH_2CH_{3\ pyr(min)}$, 2 × $NCH_2CH_2CH_{3\ fur(maj)}$ and 2 × $NCH_2CH_2CH_{3\ fur(min)}$); δ_C (75 MHz, D_2O, major pyranose anomer only) 172.6, 169.9, 96.4, 72.7, 69.7, 68.3, 50.3, 49.2, 39.0, 22.4, 20.5, 10.9 and 10.7; *m/z* (ES) 328 (100%, MNa^+), 306 (85, MH^+) and 288 (100, M^+−OH). (Found: MNa^+, 328.1377. $C_{13}H_{23}NO_7$ requires *MNa*, 328.1372).

Analysis by 500 MHz ^{1}H NMR revealed a 79 : 8 : 7 : 6 mixture of two pyranose and two furanose forms.

(2*R*, 3*R*)-2,3-*O*-Isopropylidene-pent-4-enoic acid dipropylamide 35

Dipropylamine (103 μl, 0.75 mmol), 1-hydroxybenzotriazole (101 mg, 0.75 mmol), and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (144 mg, 0.75 mmol) were added to a solution of the acid[6] **34** (86 mg, 0.50 mmol) in ethyl acetate (8 mL). The solution was stirred under N_2 for 18 h, water (10 mL) and ethyl acetate (10 mL) added, the aqueous layer extracted with ethyl acetate (3 × 10 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Purification by flash chromatography, eluting with 80 : 20 petrol−ethyl acetate, gave the *dipropylamide* **35** (99 mg, 77%) as a colourless oil, R_f 0.42 (40% EtOAc in petrol); $[\alpha]_D^{20}$ −28.6 (*c.* 0.91 in $CHCl_3$); υ_{max}/cm^{-1} (film) 2965, 2875, 1660 and 1455; δ_H (500 MHz, $CDCl_3$) 5.80 (1 H, ddd, *J* 17.1, 10.3 and 7.7, 4-H), 5.40 (1 H, d, *J* 17.1, 5-H_{trans}), 5.24 (1 H, d, *J* 10.3, 5-H_{cis}), 4.94 (1 H, d, *J* 7.7, 2-H), 4.78 (1 H, t, *J* 7.7, 3-H), 3.49 (1 H, dt, ^2J 13.3 and *J* 7.7, NCH_A), 3.15-3.00 (3 H, m, 3 × NC*H*), 1.66 (3 H, s, CMe), 1.65-1.47 (4 H, m, 2 × NCH_2CH_2), 1.41 (3 H, s, CMe), 0.91 (3 H, t, *J* 7.3, CH_2CH_3) and 0.88 (3 H, t, *J* 7.3, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 167.9, 134.2, 120.2, 111.1, 79.8, 76.1, 49.4, 48.6, 27.3, 25.9, 22.6, 21.1, 11.9 and 11.6; *m/z* (ES) 256 (100%, MH^+). (Found: MH^+, 256.1903. $C_{14}H_{25}NO_3$ requires *MH*, 256.1913).

(2*R*, 3*R*)-2,3-Dihydroxy-pent-4-enoic acid dipropylamide 36

Trifluoroacetic acid−water (9 : 1, 2 mL) was added to the amide **35** (26 mg, 0.10 mmol), the mixture swirled for 2 min and evaporated under reduced pressure. Purification by flash chromatography, eluting with 60 : 40 petrol−ethyl acetate gave the *dipropylamide* **36** (16 mg, 74%) as colourless needles; m.p. 77.4-79.1 ˚C (from CH_2Cl_2); R_f 0.27 (50% EtOAc in petrol); $[\alpha]_D^{20}$ +17.1 (*c.* 0.84 in $CHCl_3$); (Found: C, 61.4; H, 9.80; N, 6.5; $C_{11}H_{21}NO_3$ requires: C, 61.5; H, 9.75; N, 6.5); υ_{max}/cm^{-1} (film) 3324, 2967, 2875, 1620 and 1475; δ_H (500 MHz, $CDCl_3$) 5.81 (1 H, ddd, *J* 16.9, 10.5 and 6.0, 4-H), 5.34 (1 H, d, *J* 16.9, 5-H_{trans}), 5.25 (1 H, d, *J* 10.5, 5-H_{cis}), 4.44 (1 H, dd, *J* 8.6 and 4.3, 2-H), 4.23 (1 H, ddd, *J* 9.4, 6.0 and 4.3, 3-H), 3.66

(1 H, d, *J* 8.6, 2-OH), 3.58 (1 H, ddd, ^2J 15.0, *J* 8.6 and 6.8, NC_AH_A), 3.36 (1 H, ddd, ^2J 15.4, *J* 9.0 and 7.3, NC_BH_A), 3.16 (1 H, ddd, ^2J 15.4, *J* 8.6 and 6.8, NC_AH_B), 3.05 (1 H, ddd, ^2J 15.0, *J* 8.5 and 6.8, NC_BH_B) 2.98 (1 H, d, *J* 9.4, 3-OH), 1.68-1.50 (4 H, m, 2 × NCH_2CH_2), 0.93 (3 H, t, *J* 7.5, CH_2CH_3) and 0.90 (3 H, t, *J* 7.5, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 171.5, 135.6, 118.1, 74.3, 70.9, 49.2, 48.0, 22.6, 21.1, 11.8 and 11.5; *m/z* (ES) 238 (30%, MNa^+), 216 (100, MH^+). (Found: MH^+ 216.1609, $C_{11}H_{21}NO_3$ requires *MH*, 216.1600).

(6*R*, 5*R*, 4*S*)-6-Dipropylcarbamoyl-2-methylidene-4,5,6-trihydroxy-hexanoic acid ethyl ester 37

A solution of the amide **36** (1.50 g, 6.98 mmol) in methanol (70 mL) at −78 ˚C was subjected to ozonolysis, following addition of dimethylsulfide (7 mL), the mixture was warmed to room temperature, stirred for 3 h and evaporated under reduced pressure. The residue was redissolved in tetrahydrofuran−water (1 : 1, 100 mL), ethyl α-bromomethyl acrylate[5] (1.2 mL, 8.4 mmol), and indium (882 mg, 7.68 mmol) were added and the mixture stirred for 15 h. After filtration through Celite, ethyl acetate (75 mL) was added, the organic layer separated and the aqueous layer extracted with ethyl acetate (2 × 50 mL). The combined organic extracts were washed with brine (100 mL), dried ($MgSO_4$) and evaporated under reduced pressure. Purification by flash chromatography, eluting with 60 : 40 petrol−ethyl acetate gave the amide (0.99 g, 43%; 86 : 14 *syn*−*anti*). Recrystallisation from diethyl ether gave the diastereomerically pure *syn amide* **37** (0.56g, 24%) as colourless needles, m.p. 96.9-97.5 (from Et_2O); R_f 0.23 (70% EtOAc in petrol); $[\alpha]_D^{20}$ +16.0 (*c.* 0.60 in $CDCl_3$); (Found: C, 58.0; H, 8.85; N, 4.0; $C_{16}H_{29}NO_6$ requires: C, 58.0; H, 8.80; N, 4.2); υ_{max}/cm^{-1} (film) 3441, 3340, 2970, 1705 and 1628; δ_H (300 MHz, $CDCl_3$) 6.27 (1 H, d, ^2J 1.3, $C{=}CH_A$), 5.73 (1 H, dt, ^2J 1.3 and ^4J 0.9, $C{=}CH_B$), 4.53 (1 H, dd, *J* 8.7 and 6.6, 6-H), 4.21 (2 H, q, *J* 7.0, OCH_2), 4.00 (1 H, dddd, *J* 7.5, 6.1, 5.7 and 1.8, 4-H), 3.66-3.49 (2 H, m, NCH_2), 3.57 (1 H, d, *J* 8.7, 6-OH), 3.46 (1 H, ddd, *J* 7.9, 6.6 and 1.8, 5-H), 3.19 (1 H, d, *J* 7.9, 5-OH), 3.15-3.03 (2 H, m, NCH_2), 3.00 (1 H, d, *J* 5.7, 4-OH), 2.62 (1 H, ddd, ^2J 14.1, *J* 7.5 and ^4J 0.9, 3-H_A), 2.57 (1 H, ddd, ^2J 14.1, *J* 6.1 and ^4J 0.9, 3-H_B), 1.67-1.51 (4 H, m, NCH_2CH_2), 0.92 (3 H, t, *J* 7.5, CH_2CH_3) and 0.91 (3 H, t, *J* 7.5, CH_2CH_3); δ_C (75 MHz, $CDCl_3$); 173.1, 168.4, 137.3, 128.8, 74.8, 70.5,

69.6, 61.6, 49.3, 48.2, 37.1, 22.4, 21.1, 14.5, 11.7 and 11.5; *m/z* (ES) 254 (30%, MNa^+), 332 (100, MH^+).

Also obtained by preparative HPLC of the supernatant was **(**2*R,* 3*R,* 2'*S*)-2,3-dihydroxy-3-(4'-methylene-5'-oxo-tetrahydro-furan-2'-yl)-*N,N*-dipropyl-propionamide **38** (125 mg, 7%) as colourless needles, m.p. 137.1-139.8 (from CH_2Cl_2); R_f 0.23 (80% EtOAc in petrol); $[\alpha]_D^{20}$ +46.4 (*c.* 1.12 in $CDCl_3$); υ_{max}/cm^{-1} (film) 3349, 2960, 1759 and 1619; δ_H (500 MHz, $CDCl_3$) 6.21 (1 H, t, ^4J 2.6, C=CH_A), 5.64 (1 H, t, ^4J 2.6, C=CH_B), 4.89 (1 H, ddd, *J* 8.1, 5.6 and 2.1, 2'-H), 4.57 (1 H, d, *J* 7.7, 2-H), 3.64 (1 H, dd, *J* 7.7 and 2.1, 3-H), 3.60-3.47 (2 H, m, NCH_2), 3.50-3.35 (2 H, br. s, 2- and 3-O*H*), 3.19-3.07 (2 H, m, NCH_2), 3.04 (1 H, ddt, ^2J 17.1, *J* 8.1 and ^4J 2.6, 3'-H_A), 2.97 (1 H, ddt, ^2J 17.1, *J* 5.6 and ^4J 2.6, 3'-H_B), 1.71-1.48 (4 H, m, NCH_2CH_2), 0.94 (3 H, t, *J* 7.7, CH_2CH_3) and 0.90 (3 H, t, *J* 7.7, CH_2CH_3); δ_C (75 MHz, $CDCl_3$) 172.3, 170.3, 134.2, 121.9, 76.0, 75.2, 68.1, 49.1, 48.0, 29.8, 22.1, 20.7, 11.4 and 11.1; *m/z* (ES) 308 (55%, MNa^+), 286 (100, MH^+). (Found: MH^+ 286.1642, $C_{14}H_{23}NO_5$ requires *MH*, 286.1654).

(4*S,* 5*R,* 6*R*)-6-Dipropylcarbamoyl-2-oxo-4,5,6-trihydroxy-hexanoic acid ethyl ester 45

A solution of the amide **37** (538 mg, 1.63 mmol) in methanol (16 mL) at −78 ˚C was subjected to ozonolysis, following addition of dimethylsulfide (1.6 mL), the mixture was warmed to room temperature, stirred for 2.5 h and evaporated under reduced pressure. Purification by flash chromatography, eluting with 10% ethyl acetate in petrol gave the *amide* **45** (545 mg, quantitative) as a colourless, spectroscopically identical to that obtained previously.

References

1. S.G. Davies, G.D. Smyth and A.M. Chippindale, *J. Chem. Soc., Perkin Trans. 1* 1999, 3089.
2. M.P. Gore and J.C. Vederas, *J. Org. Chem.* 1986, **51**, 3700.
3. D.J. Dixon, A.C. Foster, S.V. Ley and D.J. Reynolds, *J. Chem. Soc., Perkin Trans. 1* 1999, 1631.

4. N. Cohen, B.L. Banner, A.J. Laurenzano and L. Carozza, *Org. Synth.* 1985, **63**, 127.
5. J. Villieras and M. Rambaud, *Org. Synth.* 1988, **66**, 220.
6. D.H.R. Barton, J. Camara, X. Cheng, S.D. Gero, Jaszberenyi, Joseph Cs. and Quiclet-Sire, Beatrice, *Tetrahedron* 1992, **48**, 9261.