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Carbohydrate Research 338 (2003) 1115–1119
CARBOHYDRATE RESEARCH
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Note

New derivatives of D-mannaric and galactaric acids. Synthesis of a new stereoregular Nylon 66 analog from carbohydrate-based monomers having the D-*manno* configuration

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Received 8 January 2003; received in revised form 18 February 2003; accepted 22 February 2003

Abstract

2,3,4,5-Tetra-*O*-methyl-D-mannaric and galactaric acids and their bis(pentachlorophenyl) esters have been prepared as crystalline compounds, in good yields, from D-mannitol and galactitol, respectively. A new stereoregular polyamide, analogous to Nylon 66, has been prepared by polycondensation of bis(pentachlorophenyl) 2,3,4,5-tetra-*O*-methyl-D-mannarate with 1,6-diamino-1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-D-mannitol dihydrochloride. The polymer has a M_w of 31,100 with a polydispersity of 1.5 (GPC). It was highly hygroscopic and soluble in ethanol, acetone, dimethyl sulfoxide, *N*,*N*-dimethylformamide and chloroform, but only slightly soluble in water.

Keywords: Stereoregular polyamides; Regioregular polyamides; D-Mannaric acid, protected; Galactaric acid, protected; Carbohydrate-based monomers; Polycondensation

1. Introduction

In the last few years, efforts have been devoted to preparing linear polyamides, analogous to the industrial Nylons, but more hydrophilic and degradable, in order to extend their applications to new fields demanding materials either with lower environmental impact or displaying biodegradable and biocompatible properties.[1] The use of monomers derived from carbohydrates in the design of polyamides with enhanced hydrophilicity and biodegradability constitutes an interesting strategy that is being intensively explored.[2–4] We have recently reported carbohydrate-based monomers which have been used for the preparation of new regio- and stereoregular AABB-type polyamides derived from D-mannitol and L-iditol.[5,6] In this paper we describe the preparation of 2,3,4,5-tetra-*O*-methyl-D-mannaric acid (**9**) and 2,3,4,5-tetra-*O*-methylgalactaric acid (**10**), as well as their bis(pentachlorophenyl) esters **11** and **12**, respectively. We also describe the synthesis and properties of a stereo- and regioregular polyamide, analogous to Nylon 66, by polycondensation of **11** with 1,6-diamino-1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-D-mannitol dihydrochloride (**13**).[5]

2. Results and discussion

The synthesis of esters **11** and **12** was carried out by protection of the primary hydroxyl groups of D-mannitol (**1**) and galactitol (**2**) as their triphenylmethyl derivatives (**3**)[7] and (**4**)[8] (Scheme 1). O-Methylation of the secondary hydroxyl groups of **3** and **4** with methyl iodide and potassium hydroxide in dimethyl sulfoxide gave **5** and **6**, respectively. These compounds could be easily detritylated by hydrogenation in the presence of palladium to give the corresponding tetra-*O*-methyl alcohols **7** and **8**. After oxidation of the terminal carbons with nitric acid at 70–80 °C, the tetra-*O*-methyl-D-mannaric (**9**) and tetra-*O*-methylgalactaric acids (**10**) were obtained. The active bis(pentachlorophenyl) esters **11** and **12** were obtained in good yield as crystalline compounds from the corresponding aldaric acids with

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0008-6215/03/$ - see front matter
doi:10.1016/S0008-6215(03)00093-4

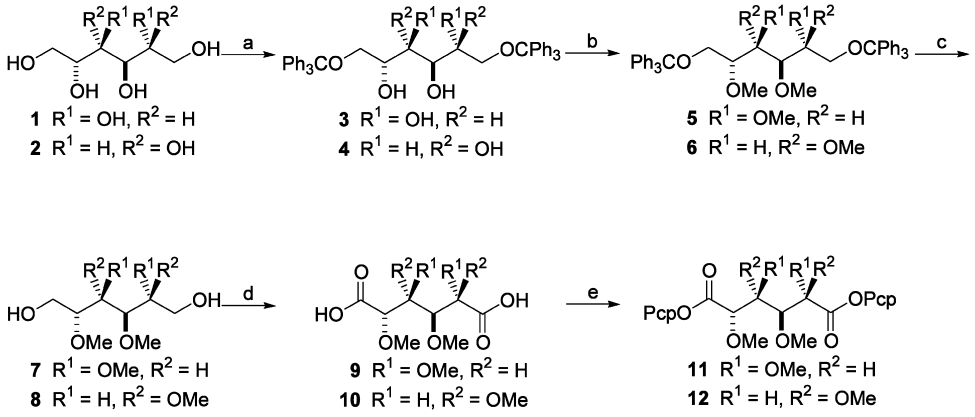
pentachlorophenol and dicyclohexylcarbodiimide in dichloromethane. Their structure was confirmed by IR and NMR spectroscopies, mass spectrometry and microanalytical data. The ^{1}H and ^{13}C NMR data were in agreement with the expected symmetry in both diastereomers.

Polycondensation of the active ester **11** with the diamine **13** was conducted in *N*-methylpyrrolidinone (NMP) as solvent at 45 °C for 7 days (Scheme 2). The polyamide **14** was obtained as a solid compound which was purified by repeatedly pouring a dichloromethane solution of the polymer into diethyl ether and filtration of the precipitate. The presence of eight methoxyl groups in the repeating unit makes this polyamide markedly hygroscopic, an effect that increases with the number of such groups in the polymer chains.[9] Complete removal of the moisture was not possible even under severe conditions of drying, as seen by microanalytical data. The presence of the amide functional group was confirmed by the characteristic IR absorptions for the N–H stretching and the amide I and II bands (3433, 1669, and 1537 cm^{-1}, respectively).

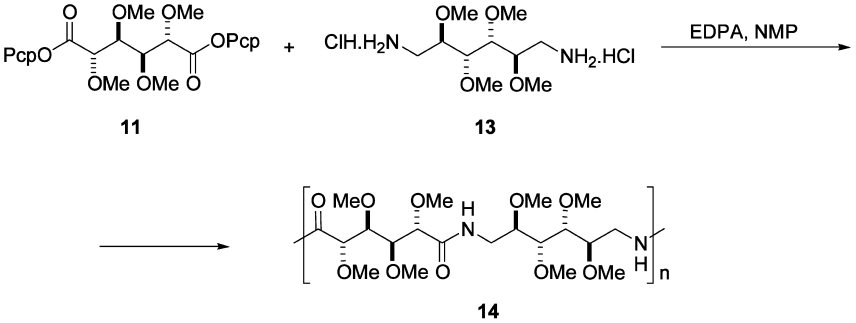
The synthesized polyamide was optically active, and was soluble in ethanol, acetone, dimethyl sulfoxide, *N*,*N*-dimethylformamide, and chloroform. The solubility in chloroform is worth mentioning, because while such behavior is unusual in conventional polyamides, it is quite common in stereoregular polyamides containing stereocenters in the main chain.[10] This is currently interpreted as being a consequence of the occurrence of ordered helical conformations stabilized by intramolecular hydrogen bonds.[11] On the other hand, this polyamide is only slightly soluble in water, although it displays elevated hydrophilicity due to the presence in the chain of the hydrophilic methoxyl groups.

The molecular-weight distribution of the polyamide was studied by gel permeation chromatography (GPC) using Styragel columns with chloroform as the mobile phase. The M_w value is 31,100 with a polydispersity ratio (M_w/M_n) of 1.5. The thermal behavior of the polyamide was examined by differential scanning calorimetry (DSC). During the first heating cycle (-10 to 230 °C), it showed a very sharp endotherm of melting ($T_{mI} = 204$ °C, $\Delta H_{mI} = 65.9$ j g^{-1}) preceded by a broader exotherm peak (193 °C) due to crystallization. From 235 °C, decomposition started. A second heating cycle of a rapidly quenched sample after melting showed the glass-transition ($T_g = 67$ °C) and a broad endotherm of melting ($T_{mII} = 228$ °C, ΔH_{mII} 16.9 j g^{-1}).

Since the two monomers possess a C_2 symmetry axis, the D-*manno*-polyamide **14** was regio- and stereoregu-



Scheme 1. (a) Ph_3CCl, pyridine; (b) MeI, KOH, DMSO; (c) H_2, Pd–C, MeOH; (d) 60% HNO_3; (e) PcpOH, DCC, NMP. Pcp: pentachlorophenyl; DCC: dicyclohexylcarbodiimide; NMP: *N*-methylpyrrolidinone.



Scheme 2. Pcp: pentachlorophenyl; DCC: dicyclohexylcarbodiimide; NMP: *N*-methylpyrrolidinone.

lar, as was confirmed by its NMR spectra. The absence of 1,3-dipolar interactions between the methoxyl groups allows an extended planar zigzag conformation as the preponderant of both monomers in solution.[12,13] However, the preponderant conformation of the polyamide in chloroform solution must be different, as revealed by the value of $J \sim 0$ Hz (7.2 Hz in the monomer **11**) between H-3/4 and H-2/5, which appear as singlets, indicating a rotation around the $C_{2(5)}$–$C_{3(4)}$ bonds, resulting preferentially in a 'bent' or 'sickle' conformation. This rotation may be a consequence of the regular helical conformation stabilized by intramolecular hydrogen bonds that, as was pointed out above, such polyamides can adopt in chloroform solution.[11]

3. Experimental

3.1. General methods

Chemicals were all used as purchased from Aldrich Chemical Co. Solvents were dried and purified, when necessary, by appropriate standard procedures. Melting points are uncorrected. Thin layer chromatography (TLC) was performed on Silica Gel 60 F_{254} (E. Merck) with detection by UV light or charring with H_2SO_4. Flash-column chromatography was performed using Silica Gel 60 (230–400 mesh, E. Merck). Elemental analyses were determined in the Microanalysis Laboratories of the CSIC, Isla de la Cartuja, Sevilla. IR spectra (films or KBr discs) were recorded with a JASCO FT/IR-410 spectrometer. NMR spectra were recorded on a Bruker 200 AC-P. Optical rotations were measured at 20 ± 5 °C with a Bellingham and Standley Inc., P20 polarimeter. FABMS analyses were performed on a double-focusing Kratos MS 80RFA mass spectrometer equipped with the standard FAB source. Argon was used as the bombarding gas. Spectra were obtained using nitrobenzene–NaI as a matrix. Differential scanning calorimetry (DSC) was studied on a calorimeter Perkin–Elmer DSC series 7, calibrated with indium. Samples of about 2–3 mg were heated under N_2 at a rate of 20 °C min^{-1}. Gel permeation chromatography (GPC) was performed in a Waters apparatus equipped with a Waters 2414 refractive index detector and two styragel® HR columns (7.8 × 300 mm) linked in series, thermostated at 35 °C, using chloroform as the mobile phase at a flow rate of 1 mL min^{-1}. Molecular weight were estimated against polystyrene standards.

3.2. 1,6-Di-*O*-trityl-D-mannitol (3)

To a solution of **1** (18.2 g, 0.1 mol) in dry pyridine (150 mL) was added trityl chloride (55.7 mg, 0.2 mol). The mixture was shaken intermittently for 10 days, and poured into ice and water (2.5 L). The precipitated mass was removed by filtration and dried on P_2O_5 to give **3** as a solid (62.9 g, 91%): m.p. 90–93 °C (lit.[7]: 97–103 °C); $[\alpha]_D$ −10° (*c* 1, $CHCl_3$); IR: *v* 3409 (OH), 3088, 3030 (Ph) cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.47 (s, 4 H, 4 OH), 3.23 (dd, 2 H, $J_{1,2\ (5,6)}$ 4.9, $J_{1,1'\ (6,6')}$ 9.6 Hz, H-1/6), 3.28 (dd, 2 H, $J_{1',2\ (5,6')}$ 5.7 Hz, H-1′/6′), 3.77 (d, 2 H, $J_{2,3\ (4,5)}$ 6.3 Hz, H-3/4), 3.92 (m, 2 H, H-2/5), 7.15-7.42 (m, 30 H, Ph); ^{13}C NMR (50 MHz): δ 64.9 (C-1/6), 70.3 (C-3/4), 71.7 (C-2/5), 86.7 (*C*–Ph), 126.9, 127.7, 128,4, 143.5 (Ph). HRMS (FAB): $[M + Na]^+$ found 689.2860; requires 689.2879. Anal. Calcd for $C_{44}H_{42}O_6$: C, 79.28; H, 6.31. Found: C, 79.10; H, 6.10.

3.3. 1,6-Di-*O*-trityl-galactitol (4)

To a solution of **2** (10 g, 54.9 mmol) in dry pyridine (200 mL) was added trityl chloride (30.6 mg, 109.8 mmol). The mixture was stirred at room temperature (rt) for 7 days, crystallized on standing for 1 day. The precipitated mass was removed by filtration and washed with pyridine and water, yield 32.4 g (89%): m.p. 183–184 °C (lit.[8]: 183–184 °C); IR: *v* 3303 (OH), 3088, 3030 (Ph) cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.43 (bs, 4 H, 4 OH), 3.24 (dd, 1 H, $J_{1,2\ (5,6)}$ 5.8, $J_{1,1'\ (6,6')}$ 9.6 Hz, H-1/6), 3.38 (dd, 1 H, $J_{1',2}$ 4.3 Hz, H-1′/6′), 3.57 (s, 2 H, $J_{2,3\ (4,5)}$ 0.0 Hz, H-3/4), 4.00 (t, 2 H, H-2/5,), 7.21–8.62 (m 30 H, Ph); ^{13}C NMR (50 MHz): δ 65.8 (C-1/6), 68.4 (C-3/4), 69.9 (C-2/5), 85.7 (*C*–Ph), 126.8, 127.5, 127.8, 144.2 (Ph). HRMS (FAB): $[M + Na]^+$ found 689.2892; requires 689.2879. Anal. Calcd for $C_{44}H_{42}O_6$: C, 79.28; H, 6.31. Found: C, 79.08; H, 6.15.

3.4. 2,3,4,5-Tetra-*O*-methyl-1,6-di-*O*-trityl-D-mannitol (5)

To a solution of **3** (30 g, 45 mmol) in dry Me_2SO (450 mL) were added KOH (60.6 g, 1.080 mol) and MeI (33.6 mL, 540 mmol). The mixture was stirred at rt for 14 h and the resulting suspension was cooled and treated with CH_2Cl_2 (500 mL). The salts were filtered off, and the filtrate was washed with water (9 × 200 mL). The organic layer was dried (anhyd Na_2SO_4) and concentrated to give an oily residue, which crystallized after treatment with MeOH (20.0 g, 61%): mp 158–160 °C; $[\alpha]_D$ +2.0° (*c* 1, $CHCl_3$); IR: *v* 3051, 2929 (Ph), 1592, 1486, 1443, 1101, 765, 704, 634 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 3.07 (dd, 2 H, $J_{1,2\ (5,6)}$ 4.2, $J_{1,1'}$ (6,6′) 10.2 Hz, H-1/6), 3.17 (s, 6 H, OMe-3/4), 3.40 (m, 2 H, $J_{2,3\ (4,5)}$ 8.3, $J_{1',2\ (5,6')}$ 2.0 Hz, H-2/5) 3.47 (s, 6 H, OMe-2/5), 3.52 (dd, 2 H, H-1′/6′), 3.71 (d, 2 H, H-3/4), 7.21–7.54 (m, 30 H, Ph); ^{13}C NMR (50 MHz): δ 57.7 (OMe-2/5), 60.4 (OMe-3/4), 61.8 (C-1/6), 79.0 (C-3/4), 79.9 (C-2/5), 86.7 (*C*–Ph), 126.8, 127.6, 128.7, 144.0 (Ph). HRMS (FAB): $[M + Na]^+$ found 745.3508; re-

quires 745.3505. Anal. Calcd for $C_{48}H_{50}O_6$: C, 79.75; H, 6.97. Found: C, 79.80; H, 6.99.

3.5. 2,3,4,5-Tetra-*O*-methyl-1,6-di-*O*-trityl-galactitol (6)

To a solution of **4** (10 g, 15 mmol) in dry Me_2SO (150 mL) was added KOH (20.2 g, 360 mmol) and IMe (11.2 mL, 180 mmol). The reaction mixture was stirred at rt for 36 h, poured into an ice–water mixture and extracted with dichloromethane. The organic phase was concentrated under reduced pressure to a residue that was washed with MeOH to give **6** as a solid (8 g, 75%): mp 180–182 °C; IR (KBr): ν 3050, 2930 (Ph) cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 3.18 (s, 6 H, 2 OMe), 3.37 (s, 6 H, 2 OMe), 3.46–3.56 (m, 8 H, H-2/5, H-3/4, H-1/6, H-1′/6′), 7.20–7.47 (m, 30 H, Ph); ^{13}C NMR (50 MHz): δ 58.3 (OMe-2/5), 60.5 (OMe-3/4), 62.5 (C-1/6), 78.8 (C-3/4), 79.1 (C-2/5), 87.0 (*C*–Ph), 126.9, 127.7, 128.6, 143.9 (Ph). HRMS (FAB): $[M+Na]^+$ found 745.3547; requires 745.3505. Anal. Calcd for $C_{48}H_{50}O_6$: C, 79.75; H, 6.97. Found: C, 79.85; H, 7.00.

3.6. 2,3,4,5-Tetra-*O*-methyl-D-mannitol (7)

To a solution of **5** (10 g, 13.83 mmol) in a mixture of Cl_2H_2–MeOH (30 mL) was added 10% Pd–C (3.3 g) and the mixture was treated with H_2 (45 psi) for 24 h. The catalyst was filtered off and washed with MeOH, and the filtrate was concentrated to a white syrup that was purified by flash-column chromatography (20:1 Cl_2H_2–MeOH). The title compound was isolated as a colorless syrup that crystallized on standing in the refrigerator (3 g, 91%): mp 67–69 °C; $[\alpha]_D$ +12° (*c* 1, $CHCl_3$); IR:ν 3442 cm^{-1} (OH). ^1H NMR ($CDCl_3$, 200 MHz): δ 2.34 (s, 2 H, 2 OH), 3.30 (dt, 2 H, $J_{1,2\ (5,6)}$ 2.5, $J_{1',2\ (5,6')}$ 3.2, $J_{2,3\ (4,5)}$ 7.7 Hz, H-2/5), 3.36 (s, 6 H, OMe-3/4), 3.45 (s, 6 H, OMe-2/5), 3.49 (d, 2 H, H-3/4), 3.65 (dd, 2 H, $J_{1,1'}$ 12.1 Hz, H-1/6), 3.92 (dd, 2 H, H-1′/6′); ^{13}C NMR (50 MHz): δ 56.6 (OMe-2/5), 58.6 (C-1/6), 60.6 (OMe-3/4), 78.4 (C-3/4), 80.7 (C-2/5). HRMS (EI): $[M]^{+\cdot}$ found 239.1499; requires 239.1495. Anal. Calcd for $C_{10}H_{22}O_6$: C, 50.41; H, 9.31. Found: C, 50.18; H, 9.09.

3.7. 2,3,4,5-Tetra-*O*-methyl-galactitol (8)

This was prepared from **6** (13.3 mg, 18.4 mmol) as described for **7**. Compound **8** was obtained as an white solid (3 g, 69%): mp 60–62 °C; IR: ν 3436 (OH) cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.53 (s, 2 H, 2 OH), 3.44 (s, 6 H, 2 OMe), 3.47 (s, 6 H, 2 OMe), 3.43–3.52 (m, 4 H, H-2/5, H-3/4), 3.77 (dd, 2 H, $J_{1,2\ (5,6)}$ 3.7, $J_{1,1'}$ (6,6′) 11.7 Hz, H-1/6), 3.86 (dd, 2 H, $J_{1',2\ (5,6')}$ 4.9 Hz, H-1′/6′); ^{13}C NMR (50 MHz): δ 57.7 (OMe-2/5), 60.1 (OMe-3/4), 60.6 (C-1/6), 79.9 (C-3/4) 80.3 (C-2/5). HRMS (EI): $[M]^{+\cdot}$ found 239.1494; requires 239.1495. Anal. Calcd for $C_{10}H_{22}O_6$: C, 50.41; H, 9.31. Found: C, 50.19; H, 9.20.

3.8. 2,3,4,5-Tetra-*O*-methyl-D-mannaric acid (9)

To a solution of **7** (8.8 g, 37 mmol) in water (7 mL) was added HNO_3 (60%, 14 mL) and the mixture was heated at 70–80 °C with stirring for 24 h. The reaction was diluted with water (280 mL) and the residue co-evaporated several times with water and finally with toluene. Flash-column chromatography (20:1 Cl_2H_2–MeOH) of the residue afforded the title compound as a semi-solid that crystallized on standing (8.8 g, 90%): mp 98–100 °C; $[\alpha]_D$ +4° (*c* 1, $CHCl_3$); IR: ν 1730 cm^{-1} (CO). ^1H NMR ($CDCl_3$, 200 MHz): δ 3.52 (s, 6 H, OMe-3/4), 3.62 (s, 6 H, OMe-2/5), 3.98 (d, 2 H, $J_{2,3\ (4,5)}$ 7.4 Hz, H-3/4), 4.36 (d, 2 H, H-2/5), 9.67 (bs, 2 H, 2 COOH); ^{13}C NMR (50 MHz): δ 58.5 (OMe-2/5), 60.6 (OMe-3/4), 80.2 (C-3/4), 81.5 (C-2/5), 174.5 (C-1/6). Anal. Calcd for $C_{10}H_{18}O_8$: C, 45.11; H, 6.81. Found: C, 44.99; H, 6.53.

3.9. 2,3,4,5-Tetra-*O*-methylgalactaric acid (10)

This was prepared from **8** (1.12 g, 4.70 mmol) as described for **9**. Compound **10** was obtained as a white solid (0.9 g, 72%): mp 151–153 °C; IR: ν 3066 (OH), 1745 (CO) cm^{-1}. ^1H NMR (Me_2SO, 200 MHz): δ 3.23 (s, 6 H, 2 OMe), 3.32 (s, 6 H, 2 OMe), 3.63 (s, 2 H, $J_{2,3}$ (4,5) 0.0 Hz, H-2/5), 3.78 (s, 2 H, H-3/4), 12.65 (bs, 2 H, 2 COOH); ^{13}C NMR (50 MHz): δ 57.8 (OMe-2/5), 59.1 (OMe-3/4), 78.1 (C-3/4), 79.9 (C-2/5), 172.5 (C-1/6). HRMS (FAB): $[M+Na]^+$ found 289.0881; requires 289.0899. Anal. Calcd for $C_{10}H_{18}O_8$: C, 45.11; H, 6.81. Found: C, 44.93; H, 6.61.

3.10. Bis(pentachlorophenyl) 2,3,4,5-tetra-*O*-methyl-D-mannarate (11)

To a cold (0–5 °C) solution of **9** (7.2 g, 27 mmol) in dry Cl_2H_2 (69 mL) were added pentachlorophenol (14.38 g, 54 mmol), *N*,*N*-dicyclohexylcarbodiimide (11.14 g, 54 mmol) and *N*,*N*-dimethylaminopyridine (87 mg). The mixture was stirred at rt overnight, then diluted with Cl_2H_2 (290 mL) and the dicyclohexylurea formed was filtered through diatomaceus earth. The filtrate was washed with 5% aq solution of AcOH, then with water, dried (anhyd $MgSO_4$) and concentrated to a white solid, which was washed with MeOH (18.77 g, 91%): mp 176–178 °C; $[\alpha]_D$ +6° (*c* 1, $CHCl_3$); IR: ν 1781 cm^{-1} (CO). ^1H NMR ($CDCl_3$, 200 MHz): δ 3.52 (s, 6 H, OMe-3/4), 3.62 (s, 6 H, OMe-2/5), 3.98 (d, 2 H, $J_{2,3}$ (4,5) 7.2 Hz, H-2/5), 4.36 (d, 2 H, H-3/4); ^{13}C NMR (50 MHz): δ 58.9 (OMe-2/5), 60.8 (OMe-3/4), 79.6 (C-3/4), 79.8 (C-2/5), 127.4–143.8 (C_6Cl_5), 167.5 (C-1/6). HRMS (FAB): $[M+Na]^+$ found 784.7617; requires

784.7569. Anal. Calcd for $C_{22}H_{16}O_8Cl_{10}$: C, 34.63; H, 2.11. Found: C, 34.67; H, 2.20.

3.11. Bis(pentachlorophenyl) 2,3,4,5-tetra-*O*-methyl-galactarate (12)

This was prepared from **10** (0.5 g, 1.88 mmol) as described for **11**. Compound **12** was obtained as a white solid (0.8 g, 52%): mp 160–162 °C; IR: ν 1794 (CO) cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 3.54 (s, 6 H, OMe-3/4), 3.65 (s, 6 H, OMe-2/5), 4.19 (s, 2 H, $J_{2,3\ (4,5)}$ 0.0 Hz, H-2/5), 4.42 (s, 2 H, H-3/4); ^{13}C NMR (50 MHz): δ 59.4 (OMe-2/5), 60.6 (OMe-3/4), 79.1 (C-3/4), 79.7 (C-2/5), 127.4–143.8 (C_6Cl_5), 167.8 (C-1/6). Anal. Calcd for $C_{22}H_{16}O_8Cl_{10}$: C, 34.63; H, 2.11. Found: C, 34.61; H, 2.23.

3.12. Poly[*N*,*N*′-(1′,6′-dideoxy-2′,3′,4′,5′-tetra-*O*-methyl-D-mannitol-1′,6′-ylidene)-2,3,4,5-tetra-*O*-methyl-D-mannaramide] (14)

To a mixture of **11** (132 mg, 0.17 mmol) and 1,6-diamino-1,6-dideoxy-2,3,4,5-tetra-*O*-methyl-D-mannitol dihydrochloride[5] (**13**; 53 mg, 0.17 mmol), under N_2, dry *N*-methylpyrrolidinone (2 mL) and *N*-ethyl-*N*,*N*-diisopropylamine (0.12 mL, 1.33 mmol) were added and the mixture was stirred at 45 °C for 7 days. The reaction mixture was diluted with dichloromethane (5 mL) and added dropwise to Et_2O (200 mL) with stirring. The precipitated was filtered and washed with ether and dried under diminished pressure to obtain **29** as a solid (61 mg, 77%). M_w 31,100; M_w/M_n 1.5; T_g 67 °C (ΔH_g 1.2 j g^{-1} deg^{-1}); T_m 204 °C (ΔH_m 65.9 j g^{-1}); IR: ν 3433 (NH), 1650 (amide I), 1555 cm^{-1} (amide II); ^1H NMR ($CDCl_3$, 200 MHz): δ 3.35 (s, 6 H, 2 OMe), 3.42 (s, 6 H, 2 OMe), 3.44 (s, 6 H, 2 OMe), 3.47 (s, 6 H, 2 OMe), 3.39–3.65 (m, 8 H, H-1′–6′), 3.72 (s, 2 H, $J_{2,3}$ (4,5) 0.0 Hz, H-3/4), 4.09 (s, 2 H, H-2/5), 6.93 (t, 2 H, 2 NH); ^{13}C NMR (50 MHz): δ 36.9 (C-1′/6′), 56.5 (OMe), 58.0 (OMe), 60.8 (OMe), 61.3 (OMe), 78.2 (C-3/4), 79.8 (C-3′/4′), 82.3 (C-2′/5′), 82.4 (C-2/5), 170.5 (C-1/6). Anal. Calcd for $C_{20}H_{38}O_{10}N_2 \cdot 0.5\ H_2O$: C, 50.51; H, 8.27; N, 5.89. Found: C, 50.19; H 8.52; N, 5.99.

Acknowledgements

We thank the C.I.C.Y.T. (Comisión Interministerial de Ciencia y Tecnología) of Spain for financial support (Grants MAT99-0578-C02-01 and MAT2002-04600-C02-01).

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