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SYNTHESIS OF *p*-TRIFLUOROACETAMIDOPHENYL 3,6-DI-*O*-{2-*O*-[α-D-MANNOPYRANOSYL 6-(DISODIUM PHOSPHATE)]-α-D-MANNOPYRANOSYL}-α-D-MANNOPYRANOSIDE

HÅKAN OTTOSSON

Department of Organic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm (Sweden)

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ABSTRACT

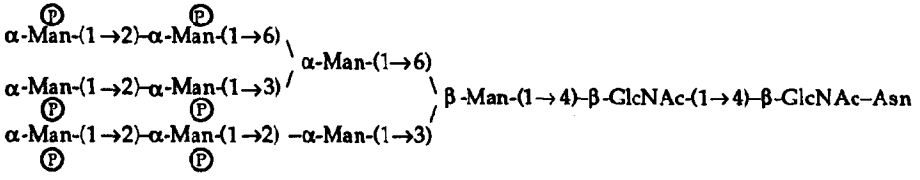
Reaction of *p*-trifluoroacetamidophenyl 2,4-di-*O*-benzyl-α-D-mannopyranoside with 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl chloride gave a trisaccharide derivative which was *O*-deacetylated and then treated with ethyl 2,3,4-tri-*O*-benzyl-6-*O*-dibenzyloxyphosphoryl-1-thio-α-D-mannopyranoside. The resulting pentasaccharide derivative was deprotected to yield the title compound which represents a part of the recognition marker on lysosomal enzymes.

INTRODUCTION

The recognition marker involved in the intracellular transfer of lysosomal enzymes to the lysosomes consists of high-mannose oligosaccharides with D-mannose 6-phosphate as an essential component[1–4]. This marker (*e.g.*, 1[5]) may be 6-phosphorylated at one or several of the mannose residues indicated with Ⓟ.

The synthesis of the carbohydrate sequence of the title compound, as the methyl glycoside without phosphate groups, has been reported[6], as has the 8-(methoxycarbonyl)octyl glycoside with and without phosphate groups[7]. Syntheses of several other phosphorylated manno-oligosaccharides have also been reported[8–10].

The synthesis of *p*-trifluoroacetamidophenyl 3,6-di-*O*{2-*O*-[α-D-mannopyranosyl-6-(disodium phosphate)]-α-D-mannopyranosyl}-α-D-mannopyranoside is now reported. An account of the synthesis of the protected pentasaccharide has been given[11].



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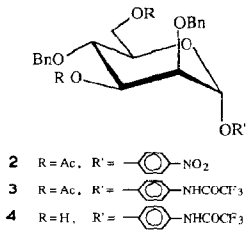
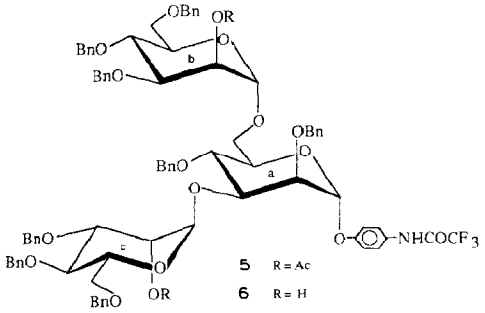
RESULTS AND DISCUSSION

In planning the strategy of the synthesis, account was taken of the difficulty in removing diphenyl groups from phosphates in a compound that contains amino or amido groups.

Hydroxyl groups were protected as benzyl ethers and phosphate groups as benzyl esters since these can be removed by hydrogenolysis. Glycosyl bromides with silver trifluoromethanesulfonate promotion[12–14] and ethyl 1-thioglycosides with dimethyl(thiomethyl)sulfonium trifluoromethanesulfonate promotion[15] were used for the glycosylations. Phosphorylation was effected at the monosaccharide level *via* phosphite esters as used in the synthesis of nucleic acids[16].



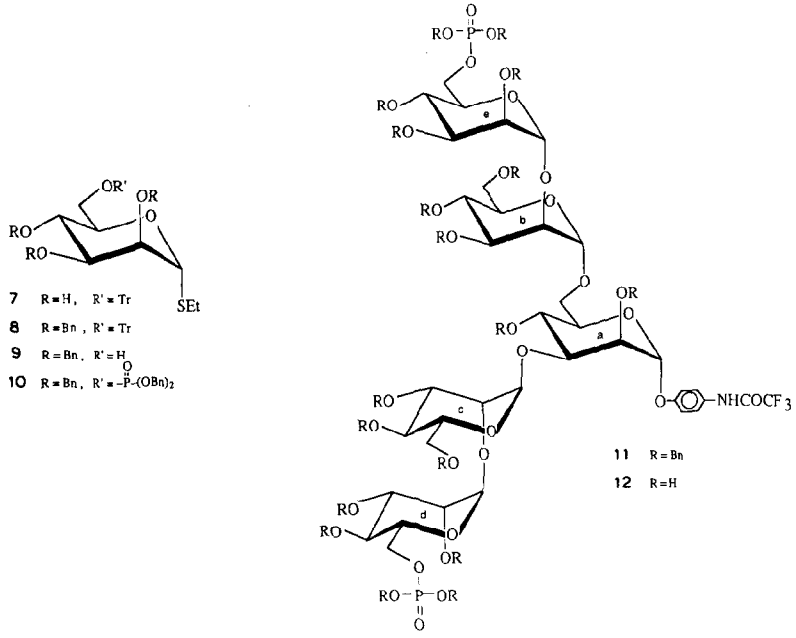


Treatment of 1,3,6-tri-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranose[17] with hydrogen bromide in dichloromethane gave the glycosyl bromide[7] which reacted with *p*-nitrophenol, using silver trifluoromethanesulfonate[12–15] as promoter, to give the *p*-nitrophenyl glycoside **2** (80%). The $J_{C\text{-}1,H\text{-}1}$ value of 173 Hz indicated **2** to be α. Hydrogenation (Pd/C) of **2** and *N*-trifluoroacetylation of the product gave **3** (87%). Treatment of **3** with methanolic sodium methoxide then yielded **4** (94%) after purification.

Crude 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl chloride[6] was condensed with **4** in dichloromethane–toluene, using silver trifluoromethanesulfonate as promoter, to give 89% of **5**. The ^{13}C resonances of **5** for anomeric carbons at 95.7 ($J_{C\text{-}1,H\text{-}1}$ 168 Hz), 97.6 ($J_{C\text{-}1,H\text{-}1}$ 172 Hz), and 100.0 p.p.m. ($J_{C\text{-}1,H\text{-}1}$ 172 Hz) indicated each sugar residue to be α. Treatment of **5** with methanolic sodium methoxide gave the partially substituted trisaccharide derivative **6** (94%).

Ethyl 1-thio-α-D-mannopyranoside[18,19] and chlorotriphenylmethane reacted in pyridine to give **7** (88%), benzylation of which gave **8** (88%); detritylation of **8** then yielded **9** (91%) as a syrup.

Reaction of the alcohol **9** with tri-imidazole phosphoramidite[16] gave the monoester which, with benzyl alcohol, yielded the phosphite triester. Oxidation of the phosphite triester *in situ* with 3-chloroperbenzoic acid[20] yielded the phosphotriester **10** (75%). The ^{13}C-n.m.r. data [66.5 ($^2J_{C,P}$ 5 Hz), 69.0 ($^2J_{C,P}$ 5 Hz), 69.1 p.p.m. ($^2J_{C,P}$ 5 Hz)] and the ^{31}P signal at −1.0 p.p.m. (apparent septet, $^3J_{H,P}$ 7 Hz)



are consistent with a 6-(dibenzyl phosphate). The ratio of the ^1H signals for the methyl group and in the region 3.8–5.3 p.p.m. was 3:17, indicating the presence of two benzyl groups.

Compounds **10** and **6** were condensed using dimethyl(thiomethyl)sulfonium trifluoromethanesulfonate[15] as promoter, to give **11** (53%). The ^{13}C signals for the anomeric carbons at 95.4 ($J_{C\text{-}1,H\text{-}1}$ 170 Hz), 98.5 ($J_{C\text{-}1,H\text{-}1}$ 171 Hz), 98.9 ($J_{C\text{-}1,H\text{-}1}$ 172 Hz), 99.1 ($J_{C\text{-}1,H\text{-}1}$ 171 Hz), and 101.3 p.p.m. ($J_{C\text{-}1,H\text{-}1}$ 172 Hz) confirmed each residue to be α.

Removal of the protecting groups from **11** was accomplished by hydrogenolysis at 400 kPa and gave the title compound **12** (97%) as an amorphous powder.

EXPERIMENTAL

General methods. — Concentrations were performed under reduced pressure at <40° (bath). Unless otherwise stated, reaction mixtures were diluted with dichloromethane, filtered through Celite, washed with water, dried (Na_2SO_4), and concentrated. Optical rotations were recorded at 22–25° with a Perkin–Elmer 241 polarimeter. N.m.r. spectra for solutions in $CDCl_3$ (internal Me_4Si) and D_2O (internal acetone, 31 p.p.m., 30°) were recorded with JEOL FX-100, GX-270, and GX-400 instruments. ^{31}P-N.m.r. spectra were referenced against external aq. 1% phosphoric acid. Assignments were made by comparison with model compounds. T.l.c. was performed on Silica Gel 60 F_{254} (Merck) with detection by u.v. light or by charring with sulphuric acid. Column chromatography was performed on silica

gel (0.035–0.070 mm, Amicon). Dichloromethane was distilled from phosphorus pentaoxide. Toluene was dried over sodium wire and pyridine with molecular sieves (4 Å).

The glycosyl residues in the trisaccharide derivatives **5** and **6** and pentasaccharide derivatives **11** and **12** are labelled as shown in the formulae.

p-*Nitrophenyl 3,6-di-O-acetyl-2,4-di-O-benzyl-α-*D-*mannopyranoside* (**2**). — To a solution of 1,3,6-tri-*O*-acetyl-2,4-di-*O*-benzyl-α-D-mannopyranose[17] (1.20 g, 2.4 mmol) in dichloromethane (10 mL) was added, at room temperature, glacial acetic acid (1 mL) saturated with hydrogen bromide. After 1 h, the solution was concentrated to dryness and the excess of acid was removed by co-distillation twice with toluene. A solution of the residue in dry dichloromethane–toluene (40 mL, 1:1) was stirred with powdered molecular sieves (4 Å, 2 g) and *p*-nitrophenol (1.0 g, 7.3 mmol) for 10 min at room temperature, then cooled to −20°. A solution of silver trifluoromethanesulfonate (940 mg, 3.7 mmol) and 2,4,6-trimethylpyridine (970 μL, 7.3 mmol) in dry dichloromethane–toluene (20 mL, 1:1) was added dropwise, the mixture was stirred for 4 h at −20°, pyridine (1 mL) was added, and the mixture was left overnight at −20° and then worked-up. Column chromatography (toluene–ethyl acetate, 6:1) of the product yielded **2** (1.10 g, 80%), isolated as a syrup, $[\alpha]_D$ +66° (*c* 1, chloroform); R_F 0.52. ^{13}C-N.m.r. data (25 MHz, $CDCl_3$): δ 20.7, 21.9 (OAc), 62.7 (C-6), 71.1–75.2 (CH_2Ph, ring C), 96.2 (C-1, $J_{C\text{-}1,H\text{-}1}$ 173 Hz), 116.5, 125.6, 142.7, 160.7 (*p*-nitro-Ph), 126.6–137.6 (aromatic), 170.1, 170.4 (C=O).

p-*Trifluoroacetamidophenyl 3,6-di-O-acetyl-2,4-di-O-benzyl-α-*D-*mannopyranoside* (**3**). — A solution of **2** (700 mg, 1.2 mmol) in ethanol (40 mL) was hydrogenolysed over 10% Pd/C (130 mg) at 1 atm. for 2 h, then filtered and concentrated to dryness. To a solution of the residue in dry pyridine (6 mL) was added trifluoroacetic anhydride (500 μL, 3.5 mmol) dropwise at −40°. The mixture was stirred for 30 min and then worked-up. Column chromatography (toluene–ethyl acetate, 4:1) of the product yielded **3** (680 mg, 87%). Crystallisation from ethyl acetate–light petroleum gave material with m.p. 130–134°, $[\alpha]_D$ +53° (*c* 1, chloroform); R_F 0.46. ^{13}C-N.m.r. data (25 MHz, $CDCl_3$): δ 20.6, 20.9 (OAc), 62.9 (C-6), 70.4–75.3 (CH_2Ph, ring C), 96.1 (C-1), 117.1, 122.3, 130.3, 153.7 (*p*-trifluoroacetamido Ph), 127.7–137.6 (aromatic), 170.5, 170.8 (C=O).

Anal. Calc. for $C_{32}H_{32}F_3NO_9$ (631.61): C, 60.85; H, 5.1; N, 2.2. Found: C, 60.4; H, 4.9; N, 2.2.

p-*Trifluoroacetamidophenyl 2,4-di-O-benzyl-α-*D-*mannopyranoside* (**4**). — A catalytic amount of sodium methoxide was added to a solution of **3** (470 mg, 0.740 mmol) in methanol (20 mL). The solution was stored for 2 h at room temperature, then neutralized with glacial acetic acid, and concentrated to dryness. Column chromatography (toluene–ethyl acetate, 2:1) of the residue yielded **4** (380 mg, 94%), isolated as an amorphous solid, $[\alpha]_D$ +57° (*c* 1, chloroform); R_F 0.37. ^{13}C-N.m.r. data (25 MHz, $CDCl_3$): δ 61.8 (C-6), 71.5–78.1 (CH_2Ph, ring C), 96.0 (C-1), 117.0, 122.6, 130.2, 154.0 (*p*-trifluoroacetamido Ph), 128.0–138.3 (aromatic), 155.2 (C=O, $^2J_{C,F}$ 38 Hz).

p-*Trifluoroacetamidophenyl 3,6-di*-O-*(2*-O-*acetyl-3,4,6-tri*-O-*benzyl*-α-D-*mannopyranosyl)-2,4-di*-O-*benzyl*-α-D-*mannopyranoside* (**5**). — A solution of crude 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl chloride[6] (~2.3 mmol) in dichloromethane–toluene (20 mL, 1:1) was stirred with a mixture of **4** (320 mg, 0.59 mmol) and molecular sieves (4 Å, 0.5 g) under nitrogen for 10 min at room temperature. The temperature was lowered to −70°, a solution of silver trifluoromethanesulfonate (460 mg, 1.8 mmol) and 2,4,6-trimethylpyridine (160 μL, 1.2 mmol) in dry dichloromethane–toluene (10 mL, 1:1) was added dropwise, the temperature was allowed to rise to −15° during 2 h, and pyridine (1 mL) was added . After work-up, column chromatography (iso-octane–acetone–chloroform, 8:4:1) of the product yielded **5** (780 mg, 89%), isolated as an amorphous solid, $[\alpha]_D$ +52° (*c* 1, chloroform); R_F 0.25 (toluene–ethyl acetate, 6:1). ^{13}C-N.m.r. data (67.5 MHz, $CDCl_3$): δ 20.9, 21.1 (OAc), 68.5–78.6 (CH_2Ph, ring C, C-6a,6b,6c), 95.7 (C-1a, $J_{C\text{-}1,H\text{-}1}$ 168 Hz), 97.6 (C-1b, $J_{C\text{-}1,H\text{-}1}$ 172 Hz), 100.0 (C-1c, $J_{C\text{-}1,H\text{-}1}$ 172 Hz), 117.0, 122.4, 129.6, 154.2 (*p*-trifluoroacetamido Ph), 127.7–138.6 (aromatic), 170.1, 170.3 (C=O).

Anal. Calc. for $C_{86}H_{88}F_3NO_{19}$ (1496.64): C, 69.0; H, 5.9; N, 0.9. Found: C, 68.9; H, 5.3; N, 1.3.

p-*Trifluoroacetamidophenyl 2,4-di*-O-*benzyl-3,6-di*-O-*(3,4,6-tri*-O-*benzyl*-α-D-*mannopyranosyl)*-α-D-*mannopyranoside* (**6**). — A solution of **5** (640 mg, 0.43 mmol) in methanol (20 mL) was treated, as for **3** above, with a catalytic amount of sodium methoxide. Column chromatography (toluene–ethyl acetate, 2:1) of the product yielded **6** (570 mg, 94%), isolated as an amorphous solid, $[\alpha]_D$ +64° (*c* 1, chloroform); R_F 0.16. ^{13}C-N.m.r. data (67.5 MHz, $CDCl_3$): δ 65.7–80.0 (CH_2Ph, ring C, C-6a,6b,6c), 95.7 (C-1a), 99.3 (C-1b), 101.7 (C-1c), 117.0, 122.3, 129.5, 154.3 (*p*-trifluoroacetamido Ph), 127.6–138.5 (aromatic).

Anal. Calc. for $C_{82}H_{84}F_3NO_{17}$ (1412.57): C, 69.7; H, 6.0; N, 1.0. Found: C, 68.9; H, 5.9; N, 0.9.

Ethyl 1-thio-6-O-*triphenylmethyl*-α-D-*mannopyranoside* (**7**). — Ethyl 1-thio-α-D-mannopyranoside[18,19] was synthesized[21] from penta-*O*-acetyl-D-mannose.

A solution of ethyl 1-thio-α-D-mannopyranoside (5.3 g, 22 mmol) and chlorotriphenylmethane (9.8 g, 33 mmol) in pyridine (50 mL) was kept for 1 h at ~100°, then concentrated to dryness. Column chromatography (toluene–ethyl acetate, 1:1, 0.5% pyridine) of the product yielded **7** (9.2 g, 88%), isolated as a syrup, $[\alpha]_D$ +83° (*c* 1, chloroform); R_F 0.32 (toluene–ethyl acetate, 1:1). ^{13}C-N.m.r. data (25 MHz, $CDCl_3$): δ 14.7 (CH_3), 24.7 (CH_2-S), 64.5–72.3 (ring C, C-6), 83.6 (C-1), 87.0 (CPh_3), 125.3–143.8 (aromatic).

Anal. Calc. for $C_{27}H_{30}O_5S$ (466.59): C, 69.5; H, 6.5. Found: C, 67.5; H, 6.7.

Ethyl 2,3,4-tri-O-*benzyl-1-thio-6*-O-*triphenylmethyl*-α-D-*mannopyranoside* (**8**). — A solution of **7** (1.7 g, 3.7 mmol) and benzyl bromide (1.9 mL, 16 mmol) in $HCONMe_2$ (15 mL) was added dropwise to sodium hydride (~0.40 g, 17 mmol) at 0°. The suspension was stirred for 2 h, methanol (0.5 mL) was added, and the mixture was worked-up. Column chromatography (toluene) yielded **8** (2.4 g, 88%). Recrystallisation from toluene–iso-octane gave material with m.p. 74–78°, $[\alpha]_D$ +62° (*c* 1, chloroform); R_F 0.24. ^{13}C-N.m.r. data (25 MHz, $CDCl_3$): δ 14.9 (CH_3),

25.0 (CH_2-S), 62.9 (C-6), 72.1–80.4 (ring C, CH_2Ph), 81.6 (C-1), 86.3 (CPh_3), 125.2–144.1 (aromatic).

Anal. Calc. for $C_{48}H_{48}O_5S$ (736.97): C, 78.2; H, 6.6. Found: C, 78.4; H, 6.5.

*Ethyl 2,3,4-tri-*O*-benzyl-1-thio-α-*D*-mannopyranoside* (**9**). — A solution of **8** (500 mg, 0.68 mmol) and *p*-toluenesulfonic acid (0.1 g) in chloroform–methanol (25 mL, 2:1) was stirred at room temperature for 30 min. Saturated aq. sodium hydrogencarbonate was added, and the organic layer was separated, washed with water, and concentrated to dryness. Column chromatography (toluene–ethyl acetate, 4:1) of the product yielded **9** (300 mg, 91%), isolated as a syrup, $[\alpha]_D$ +88° (*c* 1, chloroform); R_F 0.35. ^{13}C-N.m.r. data (25 MHz, $CDCl_3$): δ 14.9 (CH_3), 25.2 (CH_2-S), 62.0 (C-6), 72.1–80.3 (ring C, CH_2Ph), 82.2 (C-1), 127.6–138.5 (aromatic).

*Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-dibenzyloxyphosphoryl-1-thio-α-*D*-mannopyranoside* (**10**). — To a solution of imidazole (830 mg, 12.2 mmol) in dichloromethane (20 mL) under nitrogen at −30° were added phosphorus trichloride (350 μL, 3.9 mmol) in dichloromethane (5 mL) followed by triethylamine (1.7 mL, 11.9 mmol) in dichloromethane (6 mL). After stirring for 5 min, the mixture was cooled to −40°, a solution of **9** (1.8 g, 3.6 mmol) in dichloromethane (8 mL) was added dropwise, and the temperature was allowed to rise to −10° during 30 min and then lowered to −25°. Benzyl alcohol (1.1 mL, 10.8 mmol) in dichloromethane (5 mL) was added dropwise, and the mixture was stirred for 30 min, then cooled to −40°. 3-Chloroperoxybenzoic acid (880 mg, 80–90%) in dichloromethane (20 mL) was added dropwise, the mixture was stirred for 1 h, and aq. 10% sodium thiosulphate (5 mL) followed by saturated aq. sodium hydrogencarbonate (5 mL) were added. The organic phase was washed consecutively with water, ice-cold M hydrochloric acid, water, saturated aq. sodium hydrogencarbonate, and water, then concentrated. Column chromatography (toluene–ethyl acetate, 4:1) of the product yielded **10** (2.0 g, 75%), isolated as a syrup, $[\alpha]_D$ +52° (*c* 1, chloroform); R_F 0.34. N.m.r. data ($CDCl_3$): ^{13}C (67.5 MHz), δ 14.9 (CH_3), 25.2 (CH_2-S), 66.5 (d, 5 Hz, C-6), 69.1–80.2 (CH_2Ph, ring C), 81.8 (C-1), 127.7–138.2 (aromatic); ^{31}P (109 MHz) δ −1.01.

p-*Trifluoroacetamidophenyl 2,4-di-*O*-benzyl-3,6-di-*O*-[3,4,6-tri-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-dibenzyloxyphosphoryl-α-*D*-mannopyranosyl)-α-*D*-mannopyranosyl]-α-*D*-mannopyranoside* (**11**). — To a mixture of **10** (370 mg, 0.49 mmol), **6** (120 mg, 0.085 mmol), and molecular sieves (1 g) in dichloromethane (3 mL) was added dimethyl(thiomethyl)sulfonium trifluoromethanesulfonate (400 mg, 1.6 mmol) during 1 h at room temperature. The mixture was stirred for 30 min, triethylamine (1 mL) was added, and the mixture was subjected to column chromatography (toluene–ethyl acetate, 4:1). The fractions containing **11** were then subjected to further column chromatography (toluene–acetone, 10:1), to yield **11** (130 mg, 53%), isolated as a syrup, $[\alpha]_D$ +23° (*c* 0.75, chloroform); R_F 0.32 (toluene–ethyl acetate, 4:1). N.m.r. data ($CDCl_3$): ^{13}C (67.5 MHz), δ 65.2–80.0 (CH_2Ph, C-6, ring C), 95.4 (C-1a, $J_{C\text{-}1,H\text{-}1}$ 170 Hz), 98.5, 98.9, 99.1 (C-1b,1d,1e, $J_{C\text{-}1,H\text{-}1}$ 171, 172, 171 Hz), 101.3 (C-1c, $J_{C\text{-}1,H\text{-}1}$ 172 Hz), 117.0–153.7 (aromatic); ^{31}P (109 MHz), δ −0.98, −1.38.

p-Trifluoroacetamidophenyl 3,6-di-O-{2-O-[α-D-mannopyranosyl 6-(disodium phosphate)]-α-D-mannopyranosyl}-α-D-mannopyranoside (**12**). — A solution of **11** (200 mg, 0.071 mmol) in ethyl acetate–ethanol–water (8:3:3, 14 mL) was hydrogenolysed over 10% Pd/C (70 mg) at 400 kPa overnight, then filtered, and concentrated. The product was eluted from a column (2.5 × 80 cm) of BioGel P2 with water. The carbohydrate-containing fractions were combined and freeze-dried, to obtain **12** (H^+ form) as an amorphous powder (81 mg, 97%). After dissolution in water, passing through Dowex 50W-X8 (Na^+), and freeze-drying, the sodium salt was obtained as an amorphous powder, $[\alpha]_D$ +65° (*c* 1.7, water). ^{13}C-N.m.r. data (67.5 MHz, D_2O): δ 61.9–79.4 (C-6, ring C), 98.7, 98.8, 101.3, 102.9, 102.9 (C-1), 118.5, 124.8, 130.5, 154.4 (aromatic).

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