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SYNTHESIS OF THREE OLIGOSACCHARIDES THAT FORM PART OF THE COMPLEX TYPE OF CARBOHYDRATE MOIETY OF GLYCOPROTEINS

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ABSTRACT

Silver trifluoromethanesulfonate-promoted condensation of 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl bromide with benzyl 3,6-di-*O*-benzyl-α-D-mannopyranoside and benzyl 3,4-di-*O*-benzyl-α-D-mannopyranoside gave the protected 2,4- and 2,6-linked trisaccharides in yields of 54 and 32%, respectively. After exchanging the 2-deoxy-2-phthalimido groups for 2-acetamido-2-deoxy groups and de-blocking, the trisaccharides 2,4-di-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-D-mannose and 2,6-di-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-D-mannose were obtained. Similar condensation of 3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranosyl bromide with benzyl 3,4-di-*O*-benzyl-α-D-mannopyranoside gave a pentasaccharide derivative in 52% yield. After transformations analogous to those applied to the trisaccharides, 2,6-di-*O*-[β-D-galactopyranosyl-(1→4)-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)]-D-mannose was obtained.

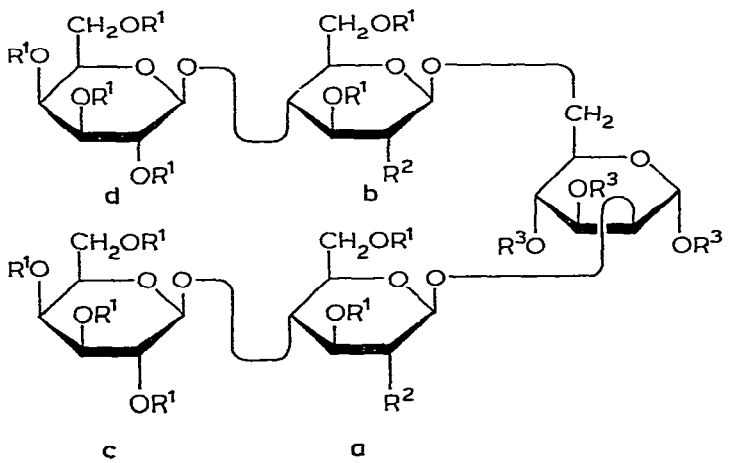
INTRODUCTION

The *N*-glycosylically linked carbohydrate portion of glycoproteins comprising *N*-acetyl-D-lactosaminyl residues (the complex type or *N*-acetyl-D-lactosamine type) may have different degrees of branching[1]. Several syntheses of oligosaccharides derived from these structures have been reported[2–8]. We now report on the synthesis of 2,4-di-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-D-mannose (**1**), 2,6-di-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-D-mannose (**2**), and 2,6-di-*O*-[β-D-galactopyranosyl-(1→4)-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)]-D-mannose (**3**). These oligosaccharides constitute parts of the most highly branched carbohydrate portions of the complex type[1]. Such structural elements have, for instance, been found in orosomucoid (α_1-acid glycoprotein), a glycoprotein present in human blood serum[9].

RESULTS AND DISCUSSION

3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl bromide[10a,b] (**4**) was condensed with benzyl 3,6-di-*O*-benzyl-α-D-mannopyranoside[2,3] (**5**) by using silver trifluoromethanesulfonate as promoter[10b,11]. Benzyl 3,6-di-*O*-benzyl-2,4-di-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-α-D-mannopyranoside (**6**) was obtained in 54% yield after chromatography on silica gel. Compound **6** was treated with hydrazine hydrate[11] and acetylated, to give benzyl 2,4-di-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-3,6-di-*O*-benzyl-α-D-mannopyranoside (**7**). Compound **7** was *O*-deacetylated and then subjected to hydrogenolysis over palladium-on-charcoal. After gel filtration, amorphous 2,4-di-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-D-mannose (**1**), $[\alpha]_D$ −16°, was obtained. Methylation analysis[12] of the alditol of **1** gave 2-deoxy-3,4,6-tri-*O*-methyl-2-*N*-methylacetamido-D-glucose and 1,3,5,6-tetra-*O*-methyl-D-mannitol.

Benzyl 3,4-di-*O*-benzyl-α-D-mannopyranoside (**8**) was prepared in 52% yield by treatment of benzyl 2,3(*R*):4,6(*R*)-di-*O*-benzylidene-α-D-mannopyranoside[13,14] (benzyl *exo*-2,3:4,6-di-*O*-benzylidene-α-D-mannopyranoside) with lithium aluminium hydride–aluminium chloride[14]. Condensation of bromide **4** with mannoside **8** gave, after silica gel chromatography, benzyl 3,4-di-*O*-benzyl-2,6-di-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-D-mannopyranoside (**9**) in 32% yield. Compound **9** was transformed into benzyl 2,6-di-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-3,4-di-*O*-benzyl-α-D-mannopyranoside (**10**), as described for **6**. Compound **10** was *O*-deacetylated and then *O*-debenzylated to give, after



3 $R^1 = H$, $R^2 = NHAc$, $R^3 = H$

12 $R^1 = Ac$, $R^2 = NPhth$, $R^3 = Bzl$

13 $R^1 = Ac$, $R^2 = NHAc$, $R^3 = Bzl$

gel filtration, amorphous 2,6-di-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-D-mannose (**2**), $[\alpha]_D$ −33°. Methylation analysis[12] of the alditol of **2** gave 2-deoxy-3,4,6-tri-*O*-methyl-2-*N*-methylacetamido-D-glucose and 1,3,4,5-tetra-*O*-methyl-D-mannitol.

3,6-Di-*O*-acetyl-2-deoxy-2-phthalimido-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranosyl bromide[2,3] (**11**) and mannoside **8** were condensed by using silver trifluoromethanesulfonate as promoter[10b,11]. After chromatography on silica gel, pentasaccharide **12** was obtained in 52% yield. This compound was transformed into its acetamido derivative **13** and thence into the free pentasaccharide **3**, $[\alpha]_D$ −21°, as described for the corresponding transformations of **6** and **7**. Methylation analysis[12] of the alditol of **3** gave 2,3,4,6-tetra-*O*-methyl-D-galactose, 2-deoxy-3,6-di-*O*-methyl-2-*N*-methylacetamido-D-glucose, and 1,3,4,5-tetra-*O*-methyl-D-mannitol.

The ^{1}H- and ^{13}C-n.m.r. spectra obtained for the oligosaccharides **1**, **2**, and **3** were in good agreement with those obtained from related natural[15–17] and synthetic[3,4] compounds.

Biological experiments performed with these compounds will be reported elsewhere.

EXPERIMENTAL

General methods. — These were as described earlier[3]. In the n.m.r. data given below for compounds **1**, **2**, **6**, **7**, **9**, and **10**, single-primed numerals refer to the 2-linked D-glucosaminyl groups, and double-primed numerals to the 4- or 6-linked D-glucosaminyl groups.

*Benzyl 3,6-di-*O*-benzyl-2,4-di-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-D-mannopyranoside* (**6**). — Silver trifluoromethanesulfonate (643 mg) and 2,4,6-trimethylpyridine (303 mg) were added to a solution of mannoside **5** (450 mg) in dichloromethane (10 mL), and the mixture was cooled to −40° under nitrogen. A solution of bromide **4** (1.25 g) in dichloromethane (10 mL) was added dropwise with stirring. The mixture was allowed to attain room temperature overnight, and was then filtered and washed with dilute hydrochloric acid, water, saturated, aqueous sodium hydrogencarbonate, and water. The product was purified on silica gel with chloroform–acetone (9:1), to yield **6** as a syrup (696 mg, 54%), $[\alpha]_D^{21}$ +26° (*c* 1, chloroform); t.l.c. (solvent as above): R_F 0.54; ^{13}C-n.m.r. (25.05 MHz, $CDCl_3$): 20.3–20.6 (OAc), 54.4, 55.0 (2 C, C-2′,2″), 61.2, 61.8 (2 C, C-6′,6″), 68.3–78.4 (CH_2Ph, ring C, C-6), 96.8, 96.9 (2 C, C-1,1′), 98.1 (C-1″), 123.0–138.3 (aromatic), and 167.2–170.0 (*C*=O).

Anal. Calc. for $C_{67}H_{68}N_2O_{24}$: C, 62.63; H, 5.30; N, 2.18. Found: C, 62.51; H, 5.39; N, 2.07.

*Benzyl 2,4-di-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-3,6-di-*O*-benzyl-α-D-mannopyranoside* (**7**). — Compound **6** (600 mg) was dissolved in ethanol (30 mL), hydrazine hydrate (6 mL) was added, and the solution was boiled under reflux for 6 h. After cooling, the solution was concentrated to dryness. The residue was acetylated with acetic anhydride–pyridine (1:1, 10 mL) at room tempera-

ture overnight. After concentration, the product was purified on silica gel with ethyl acetate–ethanol (19:1), to yield **7** as a syrup (362 mg, 70%), $[\alpha]_D^{21}$ +7° (*c* 1, chloroform); t.l.c. (solvent as above): R_F 0.60; ^{13}C-n.m.r. (25.05 MHz, $CDCl_3$): 20.6–25.0 (OAc, NHAc), 54.5, 54.7 (2 C, C-2′,2″), 61.9 (2 C, C-6′,6″), 68.4–78.5 (CH_2Ph, C-6, ring C), 96.8 (C-1), 98.6 (C-1′), 100.6 (C-1″), 127.9–138.5 (aromatic), and 169.2–171.7 (*C*=O).

*2,4-Di-*O*-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-*D*-mannose* (**1**). — A catalytic amount of sodium was added to a solution of **7** (265 mg) in methanol (20 mL). The mixture was left at room temperature overnight, neutralised with acetic acid, and concentrated to dryness. The product was dissolved in 90% aqueous acetic acid (100 mL) and hydrogenated at 400 kPa over 10% palladium-on-charcoal (300 mg) overnight. After filtration and concentration, the product was de-salted on a column (2.5 × 80 cm) of Sephadex G-15 by elution with water. After freeze-drying, **1** was obtained as an amorphous powder (101 mg, 72%), $[\alpha]_D^{21}$ −16° (*c* 1, water); ^{1}H-n.m.r. (200 MHz, D_2O): δ 2.05, 2.07 (6 H, 2 s, NHAc), 4.52 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1″), 4.56 (d, 0.9 H, $J_{1,2}$ 8.3 Hz, H-1′ when H-1 is in α-form), 4.86 (d, 0.1 H, $J_{1,2}$ ~8.3 Hz, H-1′ when H-1 is in β-form), 4.91 (bs, 0.1 H, H-1β), and 5.18 (d, 0.9 H, $J_{1,2}$ 1.5 Hz, H-1α); ^{13}C-n.m.r. (25.05 MHz, D_2O): δ 23.4, 23.6 (2 C, NHAc), 56.6, 56.8 (2 C, C-2′,2″), 61.8, 61.9, 62.3 (3 C, C-6,6′,6″), 69.2–73.9 (ring C), 92.1 (0.9 C, C-1α), 95.1 (0.1 H, C-1β), 101.0 (0.9 C, C-1′ when C-1 is in α-form), 102.7 (0.1 C, C-1′ when C-1 is in β-form), 102.8 (C-1″), and 175.6, 176.0 (*C*=O).

*Benzyl 3,4-di-*O*-benzyl-α-*D*-mannopyranoside* (**8**). — Lithium aluminium hydride (2.0 g) was added to a solution of benzyl 2,3(*R*):4,6(*R*)-di-*O*-benzylidene-α-D-mannopyranoside[13,14] (2.55 g) in ether–dichloromethane (1:1, 60 mL). Aluminium chloride (6.0 g) in ether (30 mL) was added dropwise to the boiling mixture (under reflux). After 4 h of boiling, the reagents were decomposed by addition of ethyl acetate and water. After work-up, the product was purified on silica gel with ethyl acetate–toluene (3:1), to yield **8** as a syrup (1.33 g, 52%), $[\alpha]_D^{21}$ +55° (*c* 1, chloroform); t.l.c. (solvent as above): R_F 0.45; ^{1}H-n.m.r. (99.60 MHz, $CDCl_3$): δ 3.80–4.83 (m, 12 H, ring H and CH_2Ph), 4.95 (bs, 1 H, H-1), and 7.29–7.31 (m, 15 H, aromatic); ^{13}C-n.m.r. (25.05 MHz, $CDCl_3$): 61.3 (C-6), 68.3, 69.0 (2 C, CH_2Ph), 71.8, 71.9 (2 C, C-2, CH_2Ph), 73.7 (C-5), 75.0 (C-4), 79.7 (C-3), 98.6 (C-1), and 127.3–138.1 (aromatic). Methylation of **8** followed by catalytic hydrogenolysis (palladium-on-charcoal catalyst) gave 2,6-di-*O*-methyl-D-mannose on analysis[12].

*Benzyl 3,4-di-*O*-benzyl-2,6-di-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl)-α-*D*-mannopyranoside* (**9**). — Mannoside **8** (330 mg) and bromide **4** (1.3 g) were condensed by using silver trifluoromethanesulfonate (650 mg)–2,4,6-trimethylpyridine (350 mg) as promoter, as described for the preparation of compound **6**. The product was purified on silica gel with chloroform–acetone (9:1) to yield **9** as a syrup (300 mg, 32%), $[\alpha]_D^{21}$ +9° (*c* 1, chloroform); t.l.c. (solvent as above): R_F 0.48; ^{13}C-n.m.r. (25.05 MHz, $CDCl_3$): δ 20.3–20.5 (OAc), 54.4 (2 C, C-2′,2″), 61.9 (2 C, C-6′,6″), 68.4–78.3 (CH_2Ph, C-6, ring C), 95.5 (C-1′), 96.2 (C-1), 98.4 (C-1″), 123.1–137.8 (aromatic), and 166.8–170.0 (*C*=O).

Anal. Calc. for $C_{67}H_{68}N_2O_{24}$: C, 62.63; H, 5.30; N, 2.18. Found: C, 62.49; H, 5.42; N, 2.35.

Benzyl 2,6-di-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-3,4-di-O-benzyl-α-D-mannopyranoside (**10**). — Compound **9** (285 mg) was treated sequentially with hydrazine hydrate and acetic anhydride–pyridine, as described above for the preparation of compound **7**. After purification on silica gel with ethyl acetate–ethanol (19:1), **10** (154 mg, 63%), m.p. 226–228° (from ethanol), $[\alpha]_D^{21}$ +9° (*c* 1, chloroform), was obtained; ^{13}C-n.m.r. (25.05 MHz, $CDCl_3$): δ 20.6–23.6 (OAc, NHAc), 54.4, 55.8 (2 C, C-2′,2″), 61.9, 62.4 (2 C, C-6′,6″), 67.4–78.2 (CH_2Ph, C-6, ring C), 97.2, 97.4 (2 C, C-1,1′), 101.2 (C-1″), 126.9–138.8 (aromatic), and 169.0–172.7 (*C*=O).

Anal. Calc. for $C_{55}H_{68}N_2O_{22}$: C, 59.56; H, 6.18; N, 2.52. Found: C, 59.41; H, 6.19; N, 2.46.

2,6-Di-O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-D-mannose (**2**). — Compound **10** (111 mg) was treated with sodium methoxide in methanol, followed by catalytic hydrogenation, as described above for the preparation of compound **1**. After purification by gel filtration and freeze-drying, **2** was obtained as an amorphous powder (46 mg, 78%), $[\alpha]_D^{21}$ −33° (*c* 1, water); ^{1}H-n.m.r. (200 MHz, D_2O): δ 2.03 (s, 6 H, NHAc), 4.57 (d, 1.9 H, $J_{1,2}$ 8.0 Hz, H-1″ and H-1′ when H-1 is in α-form), 4.88 (d, 0.1 H, $J_{1,2}$ 8.0 Hz, H-1′ when H-1 is in β-form), 4.90 (bs, 0.1 H, H-1β), and 5.15 (bs, 0.9 H, H-1α); ^{13}C-n.m.r. (25.05 MHz, D_2O): δ 23.6, 23.7 (2 C, NHAc), 56.8 (2 C, C-2′,2″), 62.0 (2 C, C-6′,6″), 68.8–78.6 (C-6, ring C), 92.4 (0.9 C, C-1α), 95.0 (0.1 C, C-1β), 100.9 (0.9 C, C-1′ when C-1 is in α-form), 102.3 (0.1 C, C-1′ when C-1 is in β-form), 102.7 (C-1″), and 175.8 (*C*=O).

Benzyl 3,4-di-O-benzyl-2,6-di-O-[(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-O-(3,6-di-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)]-α-D-mannopyranoside (**12**). — Silver trifluoromethanesulfonate (1.14 g) and 2,4,6-trimethylpyridine (0.54 g) were added to a solution of mannoside **8** (0.65 g) in dichloromethane (10 mL), and the mixture was cooled to −40° under nitrogen. A solution of bromide **11** (3.39 g) in dichloromethane was then added dropwise with stirring. The mixture was allowed to attain room temperature overnight, and was then filtered and washed with dilute hydrochloric acid, water, saturated, aqueous sodium hydrogencarbonate, and water. The product was purified on silica gel with ethyl acetate–toluene (3:2), to yield pentasaccharide **12** as a syrup (1.40 g, 52%). Crystallisation from methanol gave prisms, m.p. 116–119°, $[\alpha]_D^{21}$ −8° (*c* 1, chloroform); ^{13}C-n.m.r. (25.05 MHz, $CDCl_3$): 20.4–20.6 (OAc), 54.7 (2 C, C-2^a, C-2^b), 60.8, 62.0 (4 C, C-6^{a-d}), 66.6–78.4 (CH_2Ph, C-6, ring C), 95.5 (C-1^a), 96.2 (C-1), 98.5 (C-1^b), 100.9 (2 C, C-1^c, C-1^d), 123.0–138.0 (aromatic), and 167.1–170.2 (*C*=O).

Anal. Calc. for $C_{91}H_{100}N_2O_{40}$: C, 58.73; H, 5.38; N, 1.51. Found: C, 58.70; H, 5.54; N, 1.44.

Benzyl 3,4-di-O-benzyl-2,6-di-O-[(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-O-(2-acetamido-3,6-di-O-acetyl-2-deoxy-β-D-glucopyranosyl)]-α-D-mannopyranoside (**13**). — Compound **12** (1.0 g) was treated sequentially with hydrazine hydrate

and acetic anhydride–pyridine, as described above for the preparation of compound **7**. After purification on silica gel with ethyl acetate–toluene (19:1), pentasaccharide **13** was obtained as a syrup (520 mg, 57%). Crystallisation from methanol gave small needles, m.p. 151–155°, $[\alpha]_D^{21}$ ±0° (*c* 1, chloroform); ^{13}C-n.m.r. (25.05 MHz, $CDCl_3$): 20.4–23.5 (NHAc, OAc), 54.1, 56.4 (2 C, C-2^a, C-2^b), 61.0, 62.2, 62.8 (4 C, C-6^{a-d}), 66.9–78.5 (CH_2Ph, C-6, ring C), 97.1, 97.5 (2 C, C-1, C-1^a), 100.8, 101.0, 101.5 (3 C, C-1^b, C-1^c, C-1^d), 127.4–139.2 (aromatic), and 168.9–171.9 (*C*=O).

Anal. Calc. for $C_{79}H_{100}N_2O_{38}$: C, 56.31; H, 5.94; N, 1.66. Found: C, 56.16; H, 5.90; N, 1.64.

2,6-Di-O-[*β*-D-*galactopyranosyl*-(*1→4*)-O-(*2-acetamido-2-deoxy-β*-D-*glucopyranosyl*)]-D-*mannose* (**3**). — Compound **13** (416 mg) was treated with sodium methoxide in methanol, followed by catalytic hydrogenation, as described above for the preparation of compound **1**. After de-salting of the product by gel filtration and freeze-drying, pentasaccharide **3** was obtained as an amorphous powder (202 mg, 90%), $[\alpha]_D^{21}$ −21° (*c* 1, water); ^{1}H-n.m.r. (200 MHz, D_2O): *δ* 2.03 (s, 6 H, NHAc), 4.46 (d, 2 H, $J_{1,2}$ 7.6 Hz, H-1^c, H-1^d), 4.60 (d, 1.9 H, $J_{1,2}$ ~8.0 Hz, H-1^b and H-1^a when H-1 is in α-form), 4.87 (d, 0.1 H, $J_{1,2}$ ~8.0 Hz, H-1^a when H-1 is in *β*-form), 4.90 (bs, 0.1 H, H-1*β*), and 5.16 (bs, 0.9 H, H-1α); ^{13}C-n.m.r. (25.05 MHz, D_2O): 23.5, 23.7 (2 C, NHAc), 56.3 (2 C, C-2^a, C-2^b), 61.3–62.2 (4 C, C-6^{a-d}), 68.6–79.7 (C-6, ring C), 92.3 (0.9 C, C-1α), 95.1 (0.1 C, C-1*β*), 100.7 (C-1^a), 102.7 (C-1^b), 104.1 (2 C, C-1^c, C-1^d), and 175.7 (*C*=O).

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