Carbohydrate Research, 120 (1983) 17–24
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SYNTHESIS OF A NONA- AND AN UNDECA-SACCHARIDE THAT FORM PART OF THE COMPLEX TYPE OF CARBOHYDRATE MOIETY OF GLYCOPROTEINS*

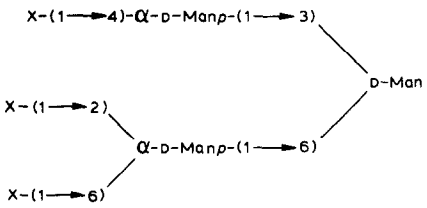
HANS LÖNN AND JÖRGEN LÖNNGREN

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

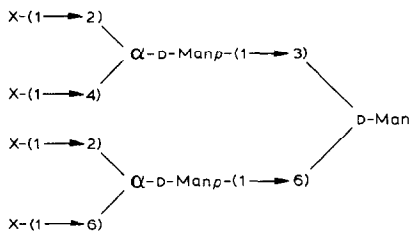
(Received May 10th, 1982; accepted for publication, August 10th, 1982)

ABSTRACT

Silver trifluoromethanesulfonate-promoted 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 2,4-di-*O*-benzyl-6-*O*-(3,4-di-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-(3,6-di-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside gave nonasaccharide and undecasaccharide derivatives. The nonasaccharide **2** and the undecasaccharide **3** were obtained by removal of the protecting groups followed by *N*-acetylation.



2



3

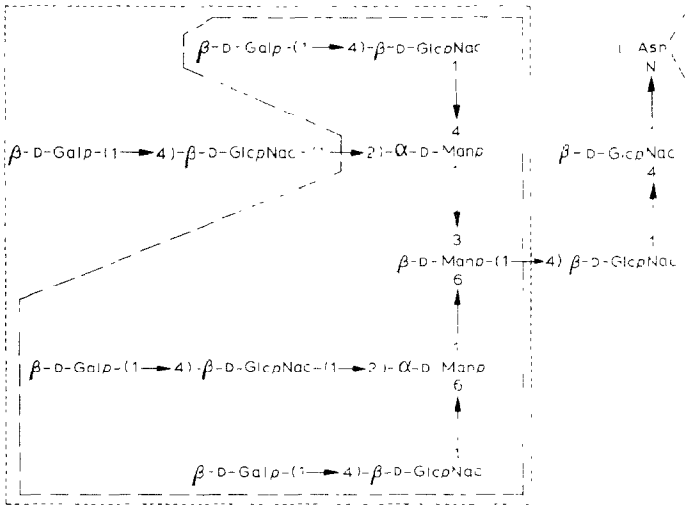
X = β-D-Galp-(1→4)-β-D-GlcpNAc—

INTRODUCTION

The *N*-glycosylically linked carbohydrate portions in glycoproteins are of two major types, namely, high-mannose (oligomannosidic) and complex (*N*-acetyl-D-lactosaminic)[1]. The latter type has been found with two, three, or four *N*-acetyl-D-lactosaminyl residues which usually are substituted with *N*-acetylneuraminic acid (sialic acid) on the D-galactosyl groups. Structure **1** is a representative example of

* Dedicated to Professor Elvin A. Kabat.

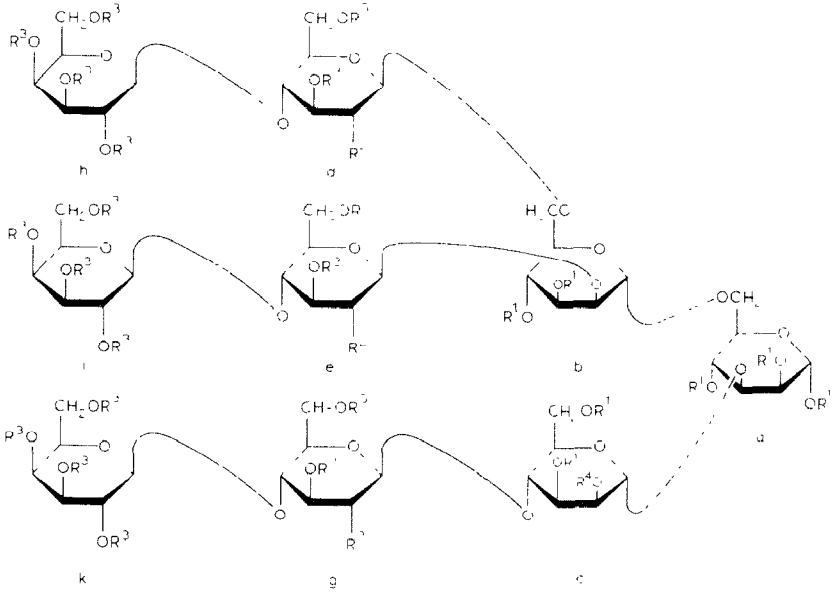
0008-6215/83/$ 03.00



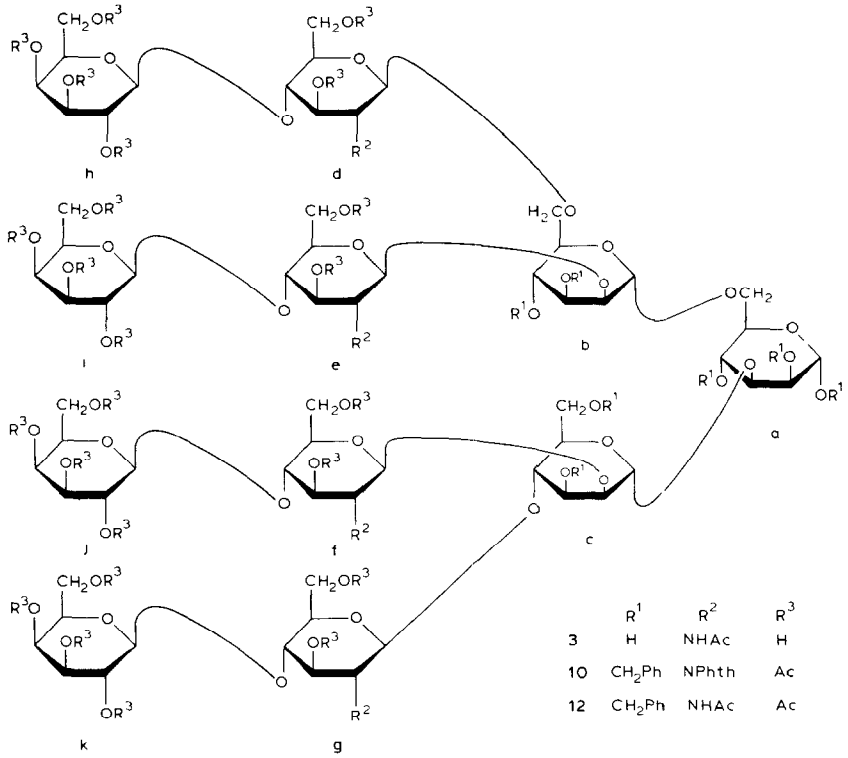
1

2 outlined by -- -- —

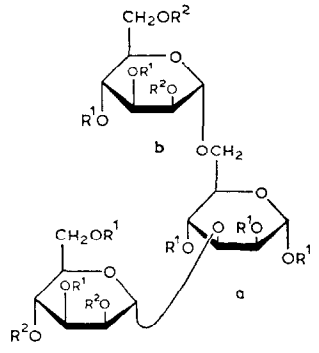
3 outlined by ---- --



	R^1	R^2	R^3	R^4
2	H	NHAc	H	H
9	CH_2Ph	NPhth	Ac	H
11	CH_2Ph	NHAc	Ac	Ac

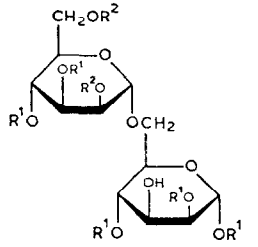


	R^1	R^2	R^3
3	H	NHAc	H
10	CH_2Ph	NPhth	Ac
12	CH_2Ph	NHAc	Ac



4 $R^1 = CH_2Ph, R^2 = H$

8 $R^1 = CH_2Ph, R^2 = Ac$



7 $R^1 = CH_2Ph, R^2 = Ac$

such a carbohydrate portion without sialic acid groups. Several syntheses of oligosaccharides derived from these structures have been reported[2-13].

We now report the synthesis of the nonasaccharide **2** and undecasaccharide **3**. These oligosaccharides constitute parts of the most highly branched carbohydrate

portions of the complex type of glycoprotein (*i.e.*, structure **1**). Such structural elements have been found, for instance, in orosomucoid (α_1-acid glycoprotein), which is present in human blood serum[1,14].

RESULTS AND DISCUSSION

For the preparation of **2** and **3**, a block synthesis was used. The trisaccharide derivative benzyl 2,4-di-*O*-benzyl-6-*O*-(3,4-di-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-(3,6-di-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**4**) was condensed with 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] (**5**).

The preparation of the blocked mannotrisaccharide **4** required two glycosylations. 1,2,6-Tri-*O*-acetyl-3,4-di-*O*-benzyl-α-D-mannopyranose[15] was treated with hydrogen bromide in dichloromethane to give 2,6-di-*O*-acetyl-3,4-di-*O*-benzyl-D-mannopyranosyl bromide (**6**). Bromide **6** was condensed with benzyl 2,4-di-*O*-benzyl-α-D-mannopyranoside[7], using silver trifluoromethanesulfonate(silver triflate)–2,4,6-trimethylpyridine as promoter[16,17]. The disaccharide **7** was obtained in 37% yield after chromatography on silica gel. That a (1→6)-linked disaccharide derivative had been obtained was indicated by its ^{13}C-n.m.r. spectrum, in which only one signal at $\delta \sim 63$ was discernible, *i.e.*, the other primary hydroxyl group was glycosylated.

2,4-Di-*O*-acetyl-3,6-di-*O*-benzyl-D-mannopyranosyl bromide[13] was condensed with **7** by the foregoing procedure, to yield, after chromatography, the trisaccharide derivative **8** (59%). The ^{13}C-n.m.r. spectrum of **8** showed, *inter alia*, three signals in the anomeric region at δ 99.8 ($^1J_{C\text{-}1,H\text{-}1}$ 169 Hz), 98.0 ($^1J_{C\text{-}1,H\text{-}1}$ 172 Hz), and 96.2 ($^1J_{C\text{-}1,H\text{-}1}$ 169 Hz). These coupling constants indicate[18] that both glycosylations gave α-D-mannosidic linkages. Compound **8** was *O*-deacetylated with sodium methoxide in methanol to give **4** (77%).

Bromide **5**[2,3] was condensed with **4**, using silver triflate–2,4,6-trimethylpyridine as promoter[16,17]. Chromatography of the products gave the pure nonasaccharide derivative **9** (29%) and contaminated undecasaccharide derivative **10**. Attempted further purification of **10** was unsuccessful.

The 2-deoxy-2-phthalimido groups in **9** were exchanged for 2-acetamido-2-deoxy groups by treatment with hydrazine hydrate followed by acetic anhydride–pyridine, to give, after chromatography, **11** (61%). Similar treatment of crude **10** gave, after chromatography, pure **12**. The yield of **12** from **4** for the condensation and hydrazinolysis–acetylation reactions was 5.3%.

The protecting groups were removed from **11** and **12** by treatment with methanolic sodium methoxide followed by catalytic hydrogenolysis (Pd/C), to give, after gel filtration and freeze-drying, amorphous **2** and **3** in yields of 77 and 67%, respectively.

The structures of **2** and **3** were evident from their ^{1}H- and ^{13}C-n.m.r. spectra, which appeared as expected from comparisons with related natural and synthetic compounds[2,3,5,7,8,13,19]. Methylation analysis[20] of the alditol of **2** gave 2,3,4,6-tetra-*O*-methyl-D-galactose, 2-deoxy-3,6-di-*O*-methyl-2-*N*-methylacetamido-D-gluco-

se, 2,3,6-tri-*O*-methyl-D-mannose, 3,4-di-*O*-methyl-D-mannose, and 1,2,4,5-tetra-*O*-methyl-D-mannitol. Methylation analysis of the alditol of **3** gave the same methyl ethers except that 2,3,6-tri-*O*-methyl-D-mannose was replaced by 3,6-di-*O*-methyl-D-mannose.

Biological experiments performed with these oligosaccharides will be reported elsewhere.

EXPERIMENTAL

General methods. — These were as described earlier[3]. Elemental analyses were not obtained for syrupy products, but they were shown to be pure by chromatography and n.m.r. spectroscopy.

2,6-Di-O-acetyl-3,4-di-O-benzyl-D-mannopyranosyl bromide (**6**). — 1,2,6-Tri-*O*-acetyl-3,4-di-*O*-benzyl-α-D-mannopyranose[15] (1.97 g) was stirred in dichloromethane (75 mL) saturated with hydrogen bromide, for 25 min at 0°. The solution was concentrated to dryness, yielding crude **6** as a syrup which was used in the next step. T.l.c.: R_F 0.67 (toluene–ethyl acetate, 3:1). The ^{1}H-n.m.r. spectrum (99.60 MHz, $CDCl_3$) contained, *inter alia*, a doublet at δ 6.33 (~0.9 H, $J_{1,2}$ 1.2 Hz), indicating that mainly α-bromide had been obtained.

Benzyl 2,4-di-O-benzyl-6-O-(2,6-di-O-acetyl-3,4-di-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**7**). — Silver triflate (1.54 g), 2,4,6-trimethylpyridine (343 mg), and ground molecular sieves (~5 g, 3Å) were added to a solution of benzyl 2,4-di-*O*-benzyl-α-D-mannopyranoside[7] (1.70 g) in dichloromethane (50 mL), and the mixture, under nitrogen, was cooled to −25°. Bromide **6** [from 1,2,6-tri-*O*-acetyl-3,4-di-*O*-benzyl-α-D-mannopyranose (1.97 g) (see above)] in dichloromethane (10 mL) was added during 20 min with stirring. The mixture was allowed to attain room temperature and pyridine (0.5 mL) was added. The mixture was filtered and the solution was washed with dilute aqueous sodium thiosulfate, dilute hydrochloric acid, water, saturated aqueous sodium hydrogencarbonate, and water, and concentrated. The product was purified on silica gel with light petroleum–ethyl acetate (2:1), to yield **7** as a syrup (1.24 g, 37%), $[\alpha]_{578}^{22}$ +52° (*c* 1.1, chloroform); t.l.c. (solvent as above): R_F 0.41; ^{13}C-n.m.r. (25.05 MHz, $CDCl_3$): δ 20.8, 21.0 (OAc), 63.2 (C-6′), 66.6–78.5 (CH_2Ph, C-6, ring C), 95.7 (C-1), 97.7 (C-1′), 126.9–138.3 (aromatic), 169.9, and 170.6 (C=O).

Benzyl 2,4-di-O-benzyl-3-O-(2,4-di-O-acetyl-3,6-di-O-benzyl-α-D-mannopyranosyl)-6-O-(2,6-di-O-acetyl-3,4-di-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**8**). — Compound **7** (1.10 g) and 2,4-di-*O*-acetyl-3,6-di-*O*-benzyl-D-mannopyranosyl bromide[13] (954 mg) were condensed by using silver triflate (771 mg) and 2,4,6-trimethylpyridine (108 mg) as promoter, as described for the preparation of **7**. The product was purified on silica gel with light petroleum–ethyl acetate (2:1), to yield **8** as a syrup (972 mg, 59%), $[\alpha]_{578}^{22}$ +33° (*c* 0.4, chloroform); t.l.c. (solvent as above): R_F 0.34; ^{13}C-n.m.r. (25.05 MHz, $CDCl_3$): δ 20.6, 20.7, 20.9 (OAc), 63.3 (C-6^b), 65.2–77.5 (CH_2Ph, C-6′s, ring C), 96.2 (C-1^a, $^1J_{C\text{-}1,H\text{-}1}$ 169 Hz), 98.0 (C-1^b,

$^1J_{C\text{-}1,H\text{-}1}$ 172 Hz), 99.8 (C-1^c, $^1J_{C\text{-}1,H\text{-}1}$ 169 Hz), 127.4–138.4 (aromatic), 169.5, and 169.8 (*C*=O).

Benzyl 2,4-di-O-benzyl-6-O-(3,4-di-O-benzyl-α-D-mannopyranosyl)-3-O-(3,6-di-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**4**). — A catalytic amount of sodium was added to a solution of **8** (910 mg) in methanol (50 mL). The mixture was left at room temperature overnight, neutralised with acetic acid, and concentrated to dryness. The product was purified on silica gel with toluene–ethyl acetate (1:2), to give **4** as a syrup (613 mg, 77%), $[\alpha]_{578}^{22}$ +38° (*c* 0.5, chloroform); t.l.c. (solvent as above): R_F 0.53; ^{13}C-n.m.r. (25.05 MHz, $CDCl_3$): δ 61.4 (C-6^b), 67.2–79.5 (CH_2Ph, C-6's, ring C), 96.5 (C-1^a), 100.0 (C-1^b), 102.2 (C-1^c), and 127.6–138.8 (aromatic).

Benzyl 2,4-di-O-benzyl-6-O-{3,4-di-O-benzyl-2,6-di-O-[O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)]-α-D-mannopyranosyl}-3-O-{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)-(1→4)-(3,6-di-O-benzyl-α-D-mannopyranosyl)}-α-D-mannopyranoside (**9**) and *benzyl 2,4-di-O-benzyl-6-O-{3,4-di-O-benzyl-2,6-di-O-[O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)]-α-D-mannopyranosyl}-3-O-{3,6-di-O-benzyl-2,4-di-O-[O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-(3,6-di-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)]-α-D-mannopyranosyl}-α-D-mannopyranoside* (**10**). — A mixture of silver triflate (1.50 g), 2,4,6-trimethylpyridine (0.71 g), compound **4** (483 mg), and ground molecular sieves (3.0 g, 3Å) in dichloromethane (75 mL) was cooled to −25° under nitrogen. Bromide **5**[2,3] (2.68 g) in dichloromethane (32 mL) was added in four portions after 0, 1, 2, and 4 h. After each addition, the mixture was allowed to attain room temperature and was then cooled to −25° before the next addition. After the last addition, the mixture was allowed slowly to attain room temperature overnight. After work-up, the product was purified on silica gel with chloroform–ethyl acetate–methanol (32:63.5), to yield **9** as a syrup (396 mg, 29%) and impure **10** as a syrup (705 mg). Compound **9** had $[\alpha]_{578}^{22}$ +19° (*c* 0.5, chloroform); t.l.c. (solvent as above). R_F 0.50; ^{13}C-n.m.r. (50 MHz, $CDCl_3$): δ 20.6 (OAc), 55.1, 55.9 (3 C, C-2^{d,e,g}), 60.9–78.8 (CH_2Ph, C-6's, ring C), 96.7 (C-1^a), 96.8 (C-1^e), 97.6 (C-1^b), 98.1 (C-1^g), 98.7 (C-1^d), 101.2 (4 C, C-1^{c,h,i,k}), 123.4–138.6 (aromatic), and 167.2–170.2 (*C*=O). The crude **10** showed R_F 0.35 in t.l.c., but several minor components (R_F ~0.20–0.40) were discernible. The ^{13}C-n.m.r. spectrum showed several unidentified peaks which made definite assignments uncertain. The crude material was used in the next reaction.

Benzyl 2,4-di-O-benzyl-6-O-{3,4-di-O-benzyl-2,6-di-O-[O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-(2-acetamido-3,6-di-O-acetyl-2-deoxy-β-D-glucopyranosyl)]-α-D-mannopyranosyl}-3-O-{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)-(1→4)-(2-O-acetyl-3,6-di-O-benzyl-α-D-mannopyranosyl)}-α-D-mannopyranoside (**11**). — Compound **9** (270 mg) was dissolved in ethanol (60 mL), hydrazine hydrate (8 mL) was added, and the solution was boiled under reflux overnight, cooled, and concentrated

to dryness. The residue was acetylated with acetic anhydride–pyridine (45 mL, 2:1) at 100° for 1 h. After concentration, the product was purified on silica gel with chloroform–acetone (3:2), to yield **11** as a syrup (154 mg, 61%), $[\alpha]_{578}^{22}$ +15° (*c* 0.3, chloroform); t.l.c. (solvent as above): R_F 0.53; ^{13}C-n.m.r. (25.05 MHz, $CDCl_3$): δ 20.5–24.8 (NHAc, OAc), 54.4, 54.6 (3 C, C 2^{d,e,g}), 61.0–78.6 (*C*H_2Ph, C-6′s, ring C), 96.8 (C-1^a), 97.9, 98.1 (2 C, C-1^{b,e}), 99.5 (C-1^c), 100.9, 101.4 (5 C, C-1^{d,g,h,i,k}), 126.8–139.2 (aromatic), and 169.0–171.8 (*C*=O).

*Benzyl 2,4-di-*O*-benzyl-6-*O*-{3,4-di-*O*-benzyl-2,6-di-*O*-[*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-(1→4)-(2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)]-α-*D*-mannopyranosyl}-3-*O*-{3,6-di-*O*-benzyl-2,4-di-*O*-[*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl]-(1→4)-(2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)]-α-*D*-mannopyranosyl}-α-*D*-mannopyranoside* (**12**). — Crude **10** (690 mg) was treated sequentially with hydrazine hydrate and acetic anhydride–pyridine, as described above for the preparation of compound **11**. The product was purified on silica gel with chloroform–acetone (3:2), to yield **12** as a syrup (80 mg, 5.3% from **4**), $[\alpha]_{578}^{22}$ +0.4° (*c* 0.5, chloroform); t.l.c. (solvent as above): R_F 0.32; ^{13}C-n.m.r. (25.05 MHz, $CDCl_3$): δ 20.6–23.5 (OAc, NHAc), 53.9–54.6 (4 C, C-2^{d,e,f,g}), 60.9–78.5 (*C*H_2Ph, C-6′s, ring C), 96.7 (C-1^a), 97.5, 97.9 (2 C, C-1^{b,e}), 99.4 (C-1^f), 100.0 (C-1^c), 100.8, 101.1, 101.4 (6 C, C-1^{d,g,h,i,j,k}), 126.2–139.3 (aromatic), and 169.2–170.5 (*C*=O).

*6-*O*-{2,6-di-*O*-[*O*-β-*D*-galactopyranosyl-(1→4)-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)]-α-*D*-mannopyranosyl}-3-*O*-{*O*-β-*D*-galactopyranosyl-(1→4)-*O*-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-(1→4)-α-*D*-mannopyranosyl}-*D*-mannose* (**2**). — A catalytic amount of sodium was added to a solution of **11** (124 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 (50 mL) and hydrogenolysed at 400 kPa over 10% palladium-on-charcoal (220 mg) overnight. After filtration, the product was de-salted on a column (2.5 × 90 cm) of Sephadex G-25 by elution with water. After freeze-drying, **2** was obtained as an amorphous powder (51 mg, 77%), $[\alpha]_{578}^{22}$ +5° (*c* 0.2, water); ^{1}H-n.m.r. (99.60 MHz, D_2O, 85°): δ 2.05, 2.08 (2 s, 3 H, 6 H, NHAc), 4.46 (d, 3 H, $J_{1,2}$ 7.5 Hz, H-1^{h,i,k}), 4.60 (broad d, 3 H, $J_{1,2}$ ~8 Hz, H-1^{d,e,g}), 4.87 (broad s, 1.4 H, H-1^b and H-1^{a}β), and 5.12 (broad s, 1.6 H, H-1^c and H-1^{a}α); ^{13}C-n.m.r. (25.05 MHz, D_2O): δ 23.4, 23.6, 23.7 (3 C, NHAc), 56.4 (3 C, C-2^{d,e,g}), 61.3–79.8 (C-6′s, ring C), 95.0 (0.3 C, C-1^{a}β), 95.4 (0.7 C, C-1^{a}α), 98.1 (C-1^b), 100.8 (C-1^e), 102.6 (2 C, C-1^{d,g}), 103.1 (C-1^c), 104.1 (3 C, C-1^{h,i,k}), 175.5, and 175.7 (3 C, *C*=O).

*6-*O*-{2,6-di-*O*-[*O*-β-*D*-galactopyranosyl-(1→4)-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)]-α-*D*-mannopyranosyl}-3-*O*-{2,4-di-*O*-[*O*-β-*D*-galactopyranosyl-(1→4)-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)]-α-*D*-mannopyranosyl}-*D*-mannose* (**3**). — Compound **12** (74 mg) was treated with sodium methoxide in methanol, followed by catalytic hydrogenolysis, as described above for the preparation of compound **2**. After de-salting and freeze-drying, the undecasaccharide **3** was obtained as an amorphous powder (27 mg, 67%), $[\alpha]_{578}^{22}$ +3° (*c* 0.4, water); ^{1}H-n.m.r. (99.60

MHz, D_2O, 85°): δ 2.02 (s, 12 H, NHAc), 4.51 (d, 4 H, $J_{1,2}$ 7.5 Hz, H-$1^{h,i,j,k}$), 4.60 (broad d, 4 H, $J_{1,2}$ ~8 Hz, H-$1^{d,e,f,g}$), 4.85 (broad s, 1.3 H, H-1^{b} and H-$1^{a}\beta$), and 5.12 (broad s, 1.7 H, H-1^{c} and H-$1^{a}\alpha$); ^{13}C-n.m.r. (25.05 MHz, D_2O). δ 23.7, 24.0 (4 C, NHAc), 56.5, 56.7 (4 C, C-$2^{d,e,f,g}$), 61.7–80.4 (C-6's, ring C), 95.3 (0.3 C, C-$1^{a}\beta$), 95.7 (0.7 C, C-$1^{a}\alpha$), 98.6 (C-1^{b}), 100.5 (C-1^{c}), 101.2 (2 C, C-$1^{e,f}$), 102.9 (2 C, C-$1^{d,g}$), 104.5 (4 C, C-$1^{h,i,j,k}$), and 175.4–176.1 (4 C, *C*=O).

ACKNOWLEDGMENTS

We thank Professors P. J. Garegg and B. Lindberg for their interest, and the Swedish Natural Science Research Council for financial support.

REFERENCES

1 J. MONTREUIL, *Adv. Carbohydr. Chem. Biochem.*, 37 (1980) 157–223.
2 J. ARNARP AND J. LÖNNGREN, *Chem. Commun.*, (1980) 1000–1002.
3 J. ARNARP AND J. LONNGREN, *J. Chem. Soc., Perkin Trans. 1*, (1981) 2070–2074.
4 T. OGAWA AND S. NAKABAYASHI, *Carbohydr. Res.*, 93 (1981) c1–c5.
5 J. ARNARP, M. HARALDSSON, AND J. LONNGREN, *Carbohydr. Res.*, 97 (1981) 307–313.
6 T. OGAWA, K. KATANO, AND M. MATSUI, *Carbohydr. Res.*, 64 (1978) c3–c9.
7 J. ARNARP AND J. LÖNNGREN, *Acta Chem. Scand., Ser. B*, 32 (1978) 696–697.
8 J. ARNARP, J. LÖNNGREN, AND H. OTTOSSON, *Carbohydr. Res.*, 98 (1981) 154–156.
9 J. ALAIS AND A. VEYRIÈRES, *Carbohydr. Res.*, 92 (1981) 310–313.
10 R. KAIFU AND T. OSAWA, *Carbohydr. Res.*, 52 (1976) 179–185.
11 C. D. WARREN, C. AUGÉ, M. L. LAVER, S. SUZUKI, D. POWER, AND R. W. JEANLOZ, *Carbohydr. Res.*, 82 (1980) 71–83.
12 C. AUGÉ, C. D. WARREN, R. W. JEANLOZ, M. KISO, AND L. ANDERSON, *Carbohydr. Res.*, 82 (1980) 85–95.
13 J. ARNARP, M. HARALDSSON, AND J. LÖNNGREN, *J. Chem. Soc., Perkin Trans. 1*, (1982) 1841–1844.
14 B. FOURNET, G. STRECKER, J. MONTREUIL, L. DORLAND, J. HAVERKAMP, J. F. G. VLIEGENTHART, K. SCHMID, AND J. B. BINETTE, *Biochemistry*, 17 (1978) 5206–5214.
15 T. OGAWA AND K. SASAJIMA, *Carbohydr. Res.*, 93 (1981) 67–81; M. M. PONPIPOM, *ibid.*, 59 (1977) 311–317.
16 R. U. LEMIEUX, T. TAKEDA, AND B. Y. CHUNG, *Am. Chem. Soc. Symp. Ser.*, 39 (1976) 90–115.
17 D. R. BUNDLE AND S. JOSEPHSON, *J. Chem. Soc., Perkin Trans. 1*, (1979) 2736–2739.
18 K. BOCK AND C. PEDERSEN, *J. Chem. Soc., Perkin Trans. 2*, (1974) 293–297.
19 J. F. G. VLIEGENTHART, H. v. HALBEEK, AND L. DORLAND, *Pure Appl. Chem.*, 53 (1981) 45–77, and references cited therein.
20 P.-E. JANSSON, L. KENNE, H. LIEDGREN, B. LINDBERG, AND J. LONNGREN, *Chem. Commun., Univ. Stockholm*, 8 (1976) 1–75.