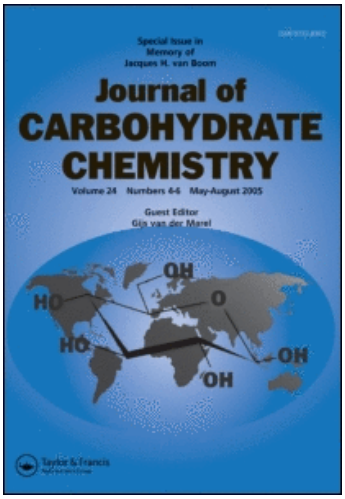


Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Syntheses of 4- and/or 4'-Phosphate Derivatives of Methyl 3-*O*-l-*Glycero*-α-d-*manno*-heptopyranosyl-l-*glycero*α-d-*manno*-heptopyranoside and Their 2-(4-Trifluoro-acetamidophenyl)ethyl Glycoside Analogues.

Kerstin Ekelöf[a]; Stefan Oscarson[a]

[a] Department of Organic ChemistryArrhenius Laboratory, Stockholm University, Stockholm, Sweden

To cite this Article Ekelöf, Kerstin and Oscarson, Stefan(1995) 'Syntheses of 4- and/or 4'-Phosphate Derivatives of Methyl 3-*O*-l-*Glycero*-α-d-*manno*-heptopyranosyl-l-*glycero*α-d-*manno*-heptopyranoside and Their 2-(4-Trifluoro-acetamidophenyl)ethyl Glycoside Analogues.', Journal of Carbohydrate Chemistry, 14: 3, 299 — 315

To link to this Article: DOI: 10.1080/07328309508002073

URL: http://dx.doi.org/10.1080/07328309508002073

J. CARBOHYDRATE CHEMISTRY, 14(3), 299-315 (1995)

SYNTHESES OF 4- AND/OR 4'-PHOSPHATE DERIVATIVES OF METHYL 3-*O*-L-*GLYCERO*-α-D-*MANNO*-HEPTOPYRANOSYL-L-*GLYCERO*-α-D-*MANNO*-HEPTOPYRANOSIDE AND THEIR 2-(4-TRIFLUOROACETAMIDOPHENYL)ETHYL GLYCOSIDE ANALOGUES.

Kerstin Ekelöf and Stefan Oscarson*

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

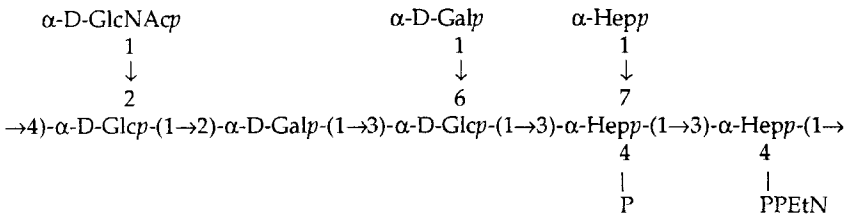
Received June 6, 1994 - Final Form November 23, 1994

ABSTRACT

Syntheses are described of the three disaccharides: methyl 3-*O*-L-*glycero*-α-D-*manno*-heptopyranosyl-L-*glycero*-α-D-*manno*-heptopyranoside 4-phosphate, methyl 3-*O*-(L-*glycero*-α-D-*manno*-heptopyranosyl 4-phosphate)-L-*glycero*-α-D-*manno*-heptopyranoside, and methyl 3-*O*-(L-*glycero*-α-D-*manno*-heptopyranosyl 4-phosphate)-L-*glycero*-α-D-*manno*-heptopyranoside 4-phosphate together with their 2-(4-trifluoroacetamidophenyl)ethyl glycoside analogues. These correspond to phosphorylated structures found in the inner core region of lipopolysaccharides from *Salmonella*. The known derivative methyl 6,7-di-*O*-acetyl-2,3,4-tri-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranoside was used as a common heptose precursor. Phosphorylation on suitably protected disaccharide derivatives was performed by treatment with phosphorus triimidazolate in dichloromethane followed by the addition of benzyl alcohol and *in situ* oxidation with *m*-chloroperbenzoic acid to give the dibenzyltriester phosphate derivatives, which after deprotection gave the target compounds.

INTRODUCTION

Structural analyses of phosphorylated bacterial polysaccharides are most often performed on dephosphorylated material since this improves the chromatographic properties and also removes the problem of heterogeneity, both native and induced, due to variance in the phosphate group substitution.



Hepp= L-*glycero*-D-*manno*-heptopyranosyl

Figure 1

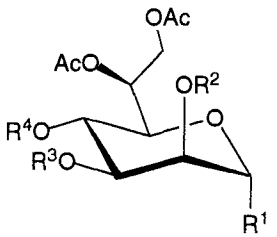
In spite of this a structural suggestion for the phosphorylated Ra core of *Salmonella* bacteria was early proposed.[1] Corrections of the proposed structure have been made for the Kdo-region,[2] but the hexose and heptose region still stands as in the original suggestion with a phosphate group probably in the 4-position of the branched heptose moiety and an aminoethanol pyrophosphate group in the 4-position of the other heptose moiety in the main chain (Fig. 1).

We have synthesized a number of structures from the *Salmonella* Ra core,[3-7] *i. e.* containing the heptose part,[3,4] to be tested as inhibitors for monoclonal antibodies directed towards core structures in native bacteria. None of these synthetic heptose-containing oligosaccharides have been good inhibitors for the interaction between the antibodies and lipopolysaccharides from different mutants of the bacteria.[8,9] One obvious reason for this is the absence of phosphates in the synthetic oligosaccharides, other reasons could be the size of the antigen or some heterogeneity in the native material not expressed in the synthetic analogues.

To further investigate the specificity of the antibodies, larger epitopes have been synthesized,[10] and we now describe the synthesis of phosphorylated derivatives corresponding to structures in the heptose part of the Ra core. These derivatives, which are synthesized both as their methyl glycosides and as spacer [2-(4-trifluoroacetamidophenyl)ethyl] glycosides, will also be of value as model substances in the analyses of phosphorylated heptose structures, as inhibitors in the investigation of the binding of phages to the core region, as antigens and in affinity chromatography.

RESULTS AND DISCUSSION

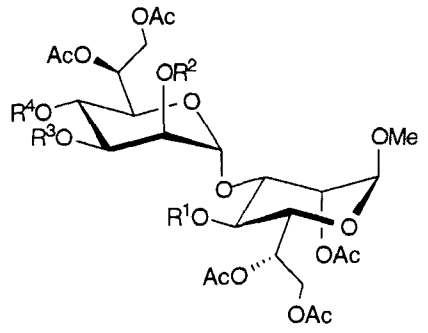
Methyl 6,7-di-*O*-acetyl-2,3,4-tri-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranoside (**1**)[4] is used as precursor for all heptose moieties in the target products. Catalytic hydrogenolysis to remove the benzyl groups gives the 2,3,4-triol **2**.[4] Treatment of **2** with trimethyl orthoacetate in the presence of 4-toluenesulfonic acid gave the 2,3-orthoacetate, which *in situ* was monochloroacetylated and then opened under acidic conditions to give **3** (81%), with a free 3-OH[11] ready for coupling and a selectively removable monochloroacetate in the 4-position to allow later phosphorylation. The synthesis of the 2-(4-trifluoroacetamidophenyl)ethyl glycoside analogue **4** of **3** has already been reported.[3]

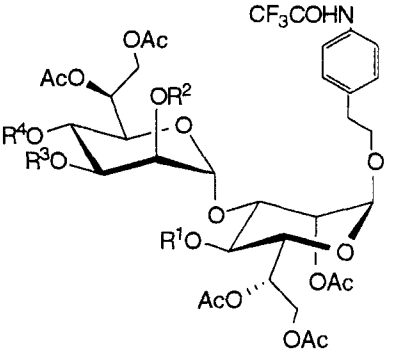


1 R^1= OMe, R^2= R^3= R^4= Bn
2 R^1= OMe, R^2= R^3= R^4= H
3 R^1= OMe, R^2= Ac, R^3= H, R^4= ClAc
4 R^1= $O(CH_2)_2PhNHCOCF_3$, R^2= Ac, R^3= H, R^4= ClAc
5 R^1= SEt, R^2= R^3= R^4= Bn

Acetolysis of **1** followed by treatment with ethyl mercaptan and zinc chloride gave the suitable heptosyl donor **5**.[3] Coupling between **5** and **3** or **4** using dimethyl(thiomethyl)sulfonium triflate (DMTST)[12] as promoter and diethyl ether as solvent then gave the α-disaccharides **6** and **7** in excellent yields (94% and 95%, respectively). Selective removal of the monochloroacetate using hydrazine dithiocarbonate[13] yielded the 4-OH derivatives **8** (83%) and **9** (88%), whereas catalytic hydrogenolysis (→**14**, 70% and →**15**, 81%) followed by isopropylidenation at OH-2′,3′ gave the 4′-OH derivatives **16** (78%) and **17** (92%). Finally, the 4,4′-diols were obtained by debenzylation of **8** (→**22**, 81%) and **9** (→**23**, 85%) followed by isopropylidenation to yield **24** (90%) and **25** (92%).

All phosphorylations on the suitably protected derivatives **8**, **9**, **16**, **17**, **24** and **25** were performed using phosphorus trichloride and imidazole followed by treatment with benzyl alcohol and oxidation with *m*-chloroperbenzoic acid[14] to give the fully protected dibenzyl phosphate compounds **10** (80%), **11** (68%), **18**(81%), **19** (78%), **26** (66%), and **27** (55%).

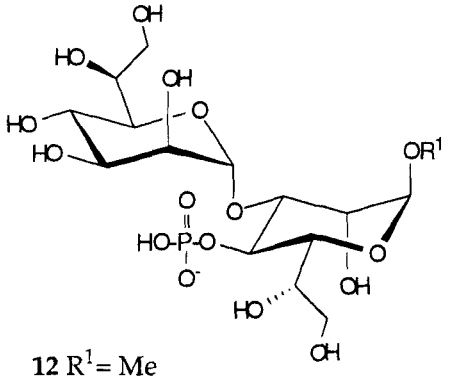




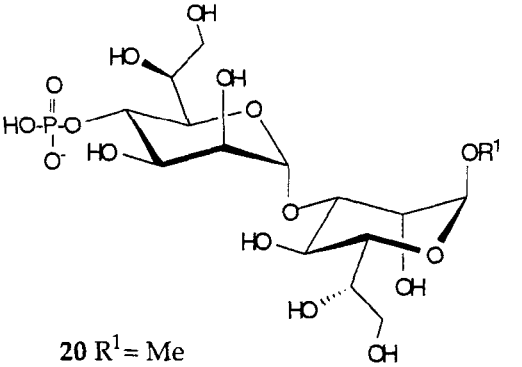
6 R^1= ClAc, R^2= R^3= R^4= Bn
7 R^1= ClAc, R^2= R^3= R^4= Bn
8 R^1= H, R^2= R^3= R^4= Bn
9 R^1= H, R^2= R^3= R^4= Bn
10 R^1= $PO(OBn)_2$, R^2= R^3= R^4= Bn
11 R^1= $PO(OBn)_2$, R^2= R^3= R^4= Bn
14 R^1= ClAc, R^2= R^3= R^4= H
15 R^1= ClAc, R^2= R^3= R^4= H
16 R^1= ClAc, R^2, R^3= $(CH_3)_2CH$, R^4= H
17 R^1= ClAc, R^2, R^3= $(CH_3)_2CH$, R^4= H
18 R^1= ClAc, R^2, R^3= $(CH_3)_2CH$, R^4= $PO(OBn)_2$
19 R^1= ClAc, R^2, R^3= $(CH_3)_2CH$, R^4= $PO(OBn)_2$
22 R^1= R^2= R^3= R^4= H
23 R^1= R^2= R^3= R^4= H
24 R^1= H, R^2, R^3= $(CH_3)_2CH$, R^4= H
25 R^1= H, R^2, R^3= $(CH_3)_2CH$, R^4= H
26 R^1= R^4= $PO(OBn)_2$, R^2, R^3= $(CH_3)_2CH$
27 R^1= R^4= $PO(OBn)_2$, R^2, R^3=$(CH_3)_2CH$

Deprotection in two steps (deacetylation followed by catalytic hydrogenolysis) for **10** and **11** then gave the first two target compounds, the 4-phosphates **12** (60%) and **13** (66%). Deprotection of **18**, **19**, **26** and **27** could also be performed in the same two steps (deacetylation followed by catalytic hydrogenolysis), since the isopropylidene acetals were cleaved in the acidic conditions developed during the hydrogenolysis, generating the other four target compounds, the 4′-phosphates **20** (54%) and **21** (55%) and the 4,4′-diphosphates **28** (51%) and **29** (43%). As discussed in the introduction, the chromatographic properties of phosphorylated oligosaccharides are sometimes a problem. We used an FPLC-column eluted with a pyridinium acetate buffer for the last purification step. Passing of the samples through two consecutive

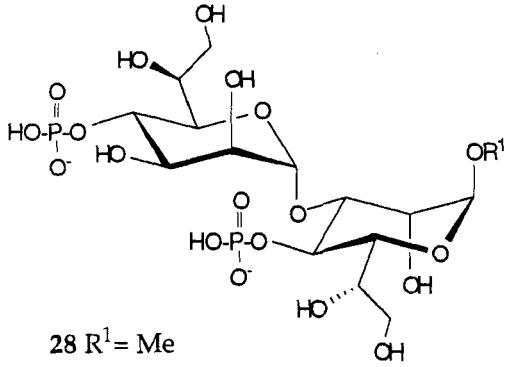
ion exchange columns (Dowex-50 H^+ and Na^+) then gave the end products as their monosodium salts.



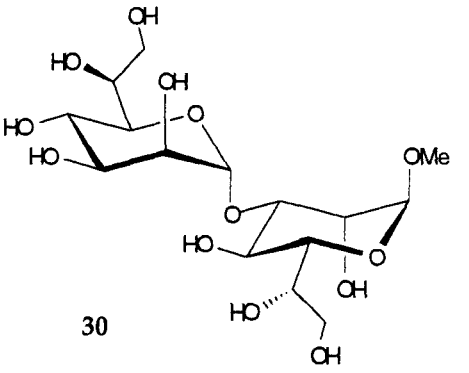
12 R^1= Me
13 R^1= $(CH_2)_2PhNHCOCF_3$



20 R^1= Me
21 R^1= $(CH_2)_2PhNHCOCF_3$



28 R^1= Me
29 R^1= $(CH_2)_2PhNHCOCF_3$



30

The target molecules were characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy. The ^1H and ^{13}C NMR spectra of the methyl glycosides **12**, **20** and **28** have been fully assigned using 2D NMR experiments and compared to the spectra of the non-phosphorylated methyl diheptoside **30** (Table 1 and 2). The chemical shift differences in the α-position due to phosphorylation were found to be 4.1-5.0 ppm in ^{13}C NMR and 0.45-0.49 ppm in the ^1H NMR spectra, respectively. NMR spectra were also run on compound **20** as the disodium salt (pH 8-9), the α-shift was then changed and found to be 2.5 ppm (^{13}C) and 0.41 ppm (^1H), values in agreement with those found for similar model compounds.[15]

Table 1. ^{1}H and ^{31}P NMR shifts from compounds **12, 20, 28** and **30** recorded at 25 °C relative to internal TSP (δ_H 0.00) or external phosphoric acid (δ_P 0.00), $^{3}J_{H,P}$ in square brackets.

Substance (pH 5)		H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-1'	H-2'	H-3'	H-4'	H-5'	H-6'	H-7'	P
12 (4-P)	δ	4.72	4.01	3.97	4.40	3.69	4.14	3.70-3.84	5.19	4.20	3.92	3.87	3.66	4.03	3.70-3.84	0.78 [9.8 Hz]
20 (4'-P)	δ	4.74	4.02	3.83	3.96	3.59	4.03	3.67-3.76	5.16	4.08	4.05	4.36	3.78	4.07	3.67-3.76	0.84 [8.7 Hz]
28 (4 & 4'-P)	δ	4.72	4.05	3.99	4.41	3.74	4.10	3.66-3.81	5.15	4.18	4.05	4.34	3.74	4.10	3.66-3.81	1.00 [8.5 Hz] 0.60 [10.9Hz]
30 (no P)	δ	4.73	4.06	3.83	3.95	3.58	4.03	3.63-3.79	5.13	4.01	3.89	3.87	3.70	4.03	3.63-3.79	—
(pH 8)																
20 (4'-P)	δ	4.74	4.06	3.83	3.96	3.59	4.05	3.66-3.78	5.15	4.05	4.04	4.28	3.74	4.15	3.66-3.78	4.52 [8.6 Hz]

Table 2. ^{13}C NMR shifts from compounds **12, 20, 28** and **30** recorded at 25 °C relative to internal acetone (δ_C 31.0).

Substance (pH 5)		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'	C-7'
12 (4-P)	δ	101.7	71.2	76.5	70.4	72.2	69.1	62.9	102.8	70.4	71.2	66.9	72.5	69.7	63.7
20 (4'-P)	δ	101.6	70.4	79.0	66.4	71.9	69.4	63.1 or 63.6	102.8	70.6	70.9	71.6	71.6 (d)	69.1	63.1 or 63.6
28 (4 & 4'-P)	δ	101.6	70.8 or 70.9	76.8	70.9	71.6 or 71.7	69.1 or 69.2	62.9 or 63.2	102.6	70.4	70.8 or 70.9	71.8	71.6 or 71.7	69.1 or 69.2	62.9 or 63.2
30 (no P)	δ	101.7	70.8	79.0	66.3	71.9	69.4	63.6	103.2	70.5	71.3	66.8	72.5	69.6	63.6
(pH 8)															
20 (4´-P)	δ	101.6	70.4	78.9	66.4	71.9	69.4	63.1 or 63.6	102.8	70.4	71.5	69.8 (d)	72.1 (d)	69.1	63.1 or 63.6

EXPERIMENTAL

General methods. Concentrations were performed under reduced pressure at <40 °C (bath) except for concentrations of solutions in *N,N*-dimethylformamide for which 50 °C were used. NMR spectra were recorded at 25 °C unless otherwise stated, using a JEOL GX-270 instrument. The following reference signals were used: ^{13}C, Me_4Si (δ=0.00) in $CDCl_3$ and acetone (δ=31.0) in D_2O; ^{1}H, Me_4Si (δ=0.00) in $CDCl_3$ and sodium [$^{2}H_4$]-3-(trimethylsilyl)propanoate (TSP) (δ=0.00) in D_2O; ^{31}P, external phosphoric acid (δ=0.00). Mass spectra were run on the free acids and recorded on a JEOL SX102 instrument in the negative ionization FAB mode using a xenon gun (acceleration voltage 6 kV), triethanolamine as matrix and a mixture of polyethylene glycol 400/polyethylene glycol 600 1:1 as standard. Optical rotations were recorded at room temperature with a Perkin-Elmer 241 polarimeter. TLC was performed on Silica Gel F_{254} (Merck) with detection by UV light and/or by charring with 8% sulfuric acid. Silica gel (0.040-0.063 mm, Amicon) was used for column chromatography. FPLC were run on a column of research gel filtration medium of the same type as Superdex 30 prep grade (Pharmacia Bioprocess Technology AB) but with a lower exclusion limit and eluted with 0.1 M pyridinium acetate (aqueous, pH 5.4).

Methyl 2,6,7-Tri-*O*-acetyl-4-*O*-chloroacetyl-L-*glycero*-α-D-*manno*-heptopyranoside (**3**). Trimethyl orthoacetate (0.78 mL, 6.2 mmol) was added to a solution of methyl 6,7-di-*O*-acetyl-L-*glycero*-α-D-*manno*-heptopyranoside (**2**)[4] (1.6 g, 5.2 mmol) and 4-toluenesulfonic acid (0.6 mL, 5% in acetonitrile) in dry acetonitrile (80 mL) and the mixture was stirred at room temperature for 30 min. Pyridine (4.8 mL) was added and the solution was diluted with toluene, concentrated and toluene was coevaporated twice from the residue. Dichloromethane:pyridine (15:1, 140 mL), chloroacetyl chloride (0.48 mL, 6.0 mmol) and 4-dimethylaminopyridine (a few crystals) were added to the residue and stirring was continued for 2 h. The solution was diluted with dichloromethane and washed with water. The organic phase was dried ($MgSO_4$) filtered and concentrated. Aqueous trifluoroacetic acid (90%, 1.0 mL) was added to a solution of the residue in acetonitrile (80 mL). After 30 min the solution was concentrated and the residue subjected to silica gel column chromatography (toluene-ethyl acetate 3:1) to give **3** (1.8 g, 81%), $[\alpha]_D$ -11° (*c* 1.0, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.7, 21.0 (acetyl CH_3), 40.7 (CH_2Cl),

55.5 (OCH_3), 62.1, 67.2, 68.0, 68.3, 69.7, 72.3 (C-2-7), 98.9 (C-1), 167.4, 170.4, 170.6 (acetyl C=O); ^1H, δ 4.81 (1 H, H-1), 5.07 (1 H, H-2), 5.09 (1 H, H-4), 5.35 (1 H, H-6).

Anal. Calcd for $C_{16}H_{23}O_{11}Cl$: C, 45.0; H, 5.4. Found: C, 45.0; H, 5.4.

Methyl 3-*O*-(6,7-Di-*O*-acetyl-2,3,4-tri-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranosyl)-2, 6, 7-tri-*O*-acetyl-4-*O*-chloroacetyl-L-*glycero*-α-D-*manno*-heptopyranoside (6). DMTST (816 mg, 3.16 mmol) was added at 0 °C to a solution of **3** (340 mg, 0.80 mmol) and ethyl 6,7-di-*O*-acetyl-2,3,4-tri-*O*-benzyl-1-thio-L-*glycero*-α-D-*manno*-heptopyranoside (**5**)[3] (580 mg, 0.95 mmol) in dry diethyl ether (50 mL) containing molecular sieves (4 Å). The mixture was stirred for 5 h at room temperature, triethylamine was added and stirring was continued for 30 min. The mixture was concentrated and the residue purified on a silica gel column (toluene-ethyl acetate 4:1) to give **6** (730 mg, 94%), $[\alpha]_D$ +23° (*c* 1.0, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.6, 20.8, 21.4 (acetyl CH_3), 40.4 (CH_2Cl) 55.5 (OCH_3), 61.8, 62.3, 66.8, 68.3, 68.6, 68.7, 71.2, 71.6, 71.9, 72.8, 73.5, 74.5, 74.7, 79.3 (C-2-7, 2′-7′, CH_2Phx3), 98.8 (C-1), 100.4 (C-1′), 125.3-138.2 (aromatic C), 166.1, 170.0, 170.2, 170.3, 170.4 (acetyl C=O).

Anal. Calcd for $C_{48}H_{57}O_{19}Cl$: C, 59.2; H, 5.9. Found: C, 59.2; H, 5.8.

2-(4-Trifluoroacetamidophenyl)ethyl 3-*O*-(6,7-Di-*O*-acetyl-2,3,4-tri-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranosyl)-2, 6, 7-tri-*O*-acetyl-4-*O*-chloroacetyl-L-*glycero*-α-D-*manno*-heptopyranoside (7). 2-(4-Trifluoroacetamidophenyl)ethyl 2,6,7-tri-*O*-acetyl-4-*O*-chloroacetyl-L-*glycero*-α-D-*manno*-heptopyranoside (**4**)[3] (920 mg, 0.147 mmol) was coupled to **5** as described for **3** above, to give **7** (1.6 g, 95%), $[\alpha]_D$ -4° (*c* 1.0, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.7, 20.9, 21.4 (acetyl CH_3), 35.1 (CH_2Ar), 40.4 (CH_2Cl), 62.7, 62.8, 66.8, 68.4, 68.6, 68.8, 71.5, 71.6, 71.9, 72.9, 73.5, 74.1, 74.3, 74.8, 79.4 (C-2-7, 2′-7′, CH_2Phx3, OCH_2CH_2), 96.9 (C-1), 100.9 (C-1′), 121.6-138.1 (aromatic C), 166.1, 170.0, 170.3, 170.4, 170.7, 170.8 (acetyl C=O).

Methyl 3-*O*-(6,7-Di-*O*-acetyl-2,3,4-tri-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranosyl)-2, 6, 7-tri-*O*-acetyl-L-*glycero*-α-D-*manno*-heptopyranoside (8). To a stirred solution of **6** (900 mg, 0.92 mmol) in *N,N*-dimethylformamide: dichloromethane (1:1, 20 mL) was added hydrazine dithiocarbonate[13] (150 mg, 2.0 mmol) and the mixture was stirred at room temperature for 18 h, then diluted with dichloromethane and washed with 1M H_2SO_4, water, and sodium hydrogencarbonate (aq, sat.). The organic layer was separated, dried ($MgSO_4$), filtered and concentrated. Silica gel chromatography (toluene-ethyl acetate 2:1)

of the residue gave **8** (690 mg, 83%), $[\alpha]_D$ +0.2° (*c* 1.0, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.7, 20.9 21.0 (acetyl CH_3), 55.3 (OCH_3), 61.8, 62.4, 67.3, 68.4, 69.4, 70.3, 71.2, 71.7, 71.8, 72.1, 72.7, 73.6, 75.2, 79.7 (C-2-7, 2′-7′, CH_2Phx3), 98.8 (C-1), 99.5 (C-1′), 127.5-138.2 (aromatic C), 169.8, 170.2, 170.4, 170.5, 172.6 (acetyl C=O).

Anal. Calcd for $C_{46}H_{56}O_{18}$: C, 61.6; H, 6.3. Found: C, 61.2; H, 6.2.

2-(4-Trifluoroacetamidophenyl)ethyl 3-*O*-(6,7-di-*O*-acetyl-2,3,4-tri-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranosyl)-2,6,7-tri-*O*-acetyl-L-*glycero*-α-D-*manno*-heptopyranoside (**9**). Compound **7** (880 mg, 0.75 mmol) was dechloroacetylated as described for **6** to yield, after silica gel chromatography (toluene-ethyl acetate 2:1), **9** (730 mg, 88%), $[\alpha]_D$ +15° (*c* 1.0, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.6, 20.7, 20.8, 20.9, 21.4 (acetyl CH_3), 35.2 (CH_2Ar), 62.4, 62.9, 67.1, 68.4, 68.7, 69.5, 70.5, 71.6, 71.7, 72.1, 73.6, 73.7, 75.1, 79.6 (C-2-7, 2′-7′, CH_2Phx3, OCH_2CH_2), 97.2 (C-1), 99.9 (C-1′), 113.8, 118.0 (CF_3) 121.4-138.2 (aromatic), 154.7, 155.2 (CF_3CO), 169.9, 170.4, 170.6, 170.8, 172.4 (acetyl C=O).

Methyl 3-*O*-(6,7-Di-*O*-acetyl-2,3,4-tri-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranosyl)-2,6,7-tri-*O*-acetyl-4-*O*-dibenzyloxyphosphoryl-L-*glycero*-α-D-*manno*-heptopyranoside (**10**). To a solution of imidazole (103 mg, 1.5 mmol) in dry dichloromethane (3 mL) was added phosphorus trichloride (44 mL, 0.50 mmol) in dichloromethane (0.5 mL) and triethylamine (230 mL, 1.7 mmol) in dichloromethane (0.5 mL). The solution was stirred at 0 °C under an atmosphere of nitrogen for 10 min, after which **8** (113 mg, 0.13 mmol) in dichloromethane (1.5 mL) was added dropwise during 15 min. After stirring for 30 min, benzyl alcohol (158 mL, 1.6 mmol) in dichloromethane (0.5 mL) was added dropwise. After an additional 40 min, 3-chloroperbenzoic acid (130 mg, 0.76 mmol) in dichloromethane (1.0 mL) was added dropwise during 5 min. The stirring was continued for 1.5 h at 0 °C. To the solution was added sodium thiosulfate (aq 10%, 1.0 mL) and sodium hydrogencarbonate (aq sat., 1.0 mL). The organic layer was separated and washed with water, 1M HCl, water and sodium hydrogencarbonate (aq), dried ($MgSO_4$), filtered and concentrated. Silica gel chromatography (light petroleum bp 60-70 °C-ethyl acetate 1:1) of the residue gave **10** (117 mg, 80%), $[\alpha]_D$ -6° (*c* 0.95, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.7, 20.9 (acetyl CH_3), 55.4 (OCH_3), 60.9, 62.2, 67.9, 68.5, 68.8(d), 69.7 (d), 70.0 (d), 71.1, 71.4, 72.1, 73.1 (d), 73.3, 73.4, 74.3, 75.0, 77.5, 79.8 (C-2-7, 2′-7′, CH_2Phx5), 98.3 (C-1), 100.3 (C-1′), 127.2-139.0 (aromatic C), 170.0, 170.2, 170.5 (acetyl C=O); ^{31}P, δ -1.76.

Anal. Calcd for $C_{60}H_{69}O_{21}P$: C, 62.3; H, 6.0; P, 2.7. Found: C, 62.1; H, 6.1; P, 2.8.

2-(4-Trifluoroacetamidophenyl)ethyl 3-*O*-(6,7-Di-*O*-acetyl-2,3,4-tri-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranosyl)- 2, 6, 7 -tri-*O*-acetyl-4-*O*-(dibenzyl)phosphoryl-L-*glycero*-α-D-*manno*-heptopyranoside (11). Compound **9** (125 mg, 0.11 mmol) was phosphorylated as described for **8** to yield, after silica gel chromatography (light petroleum bp 60-70 °C-ethyl acetate 2:1), **11** (105 mg, 68%), $[\alpha]_D$ -0.6° (*c* 1.0, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.7, 20.8, 20.9 (acetyl CH_3), 35.1 (CH_2Ar), 62.1, 62.9, 67.8, 68.7, 68.9, 69.3 (d), 69.7 (d), 71.3, 71.6, 72.0, 72.2, 73.0 (d), 73.3, 74.2, 74.6, 75.0, 79.8 (C-2-7, 2′-7′, CH_2Phx5, OCH_2CH_2), 96.6 (C-1), 101.0 (C-1′), 121.5-139.0 (aromatic C), 169.9, 170.0, 170.3, 170.6, 170.8 (acetyl C=O); ^{31}P, δ -2.16.

Methyl 3-*O*-L-*Glycero*-α-D-*manno*-heptopyranosyl-L-*glycero*-α-D-*manno*-heptopyranoside 4-sodium phosphate (12). A solution of **10** (80 mg, 0.07 mmol) in methanol (2 mL) was treated with a catalytic amount of 1M sodium methoxide. After 15 min the solution was neutralized with Dowex-50 (H^+) resin, filtered and hydrogenolyzed over 10% Pd/C (50 mg) at 400 kPa for 20 h. The solution was filtered and concentrated. Purification of the residue on a FPLC superdex column gave, after lyophilization, **12** (24 mg, 60%) as the pyridinium salt. To obtain the sodium salt, the compound was passed through a Dowex-50 (H^+) column, followed by a Dowex-50 (Na^+) column. The pH value of the obtained compound was 5. $[\alpha]_D$ +85° (*c* 0.8, water). For NMR data see Tables 1 and 2.

HRMS: Calcd for $C_{15}H_{28}O_{16}P$ $[M-H]^+$: 495.1115; found: 495.1138.

2-(4-Trifluoroacetamidophenyl)ethyl 3-*O*-L-*Glycero*-α-D-*manno*-heptopyranosyl-L-*glycero*-α-D-*manno*-heptopyranoside 4-sodium phosphate(13). Compound **11** (80 mg, 0.06 mmol) was deprotected as described for **10** to yield, after FPLC, **13** (30 mg, 66%) as the pyridinium salt. The sodium salt was obtained as described for **12**. $[\alpha]_D$ +70° (*c* 0.5, water). NMR data (D_2O): ^{13}C, δ 35.5 (CH_2Ar), 63.2, 64.1, 66.8, 68.3, 69.1, 69.7, 70.4, 70.9(d, J 5.5 Hz), 71.2 (2 C), 72.2, 72.6, 76.1 (C-2-7, 2′-7′, OCH_2CH_2), 99.7 (C-1), 102.8 (C-1′), 123.2, 130.8, 133.8, 139.3 (aromatic); ^1H, δ 4.31(q, 1H, H-4) 4.74 (s, 1H, H-1), 5.12 (s, 1H, H-1'); ^{31}P, δ 0.74 (d, *J* 11.0 Hz).

HRMS: Calcd for $C_{24}H_{34}O_{17}PNF_3$ $[M-H]^+$: 696.1516; found: 696.1506.

Methyl 3-*O*-(6,7-di-*O*-acetyl-L-*glycero*-α-D-*manno*-heptopyranosyl)-2, 6, 7-tri-*O*-acetyl-4-*O*-chloroacetyl-L-*glycero*-α-D-*manno*-heptopyranoside (14). A

solution of **6** (225 mg, 0.23 mmol) in ethyl acetate: ethanol (1:1, 10 mL) was hydrogenolyzed over 10% Pd/C (100 mg) at 400 kPa for 40 h. The mixture was filtered, concentrated and purified on a silica gel column (toluene-ethyl acetate 1:3) to give **14** (113 mg, 70%), $[\alpha]_D$ +28° (*c* 1.1, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.7, 20.9 21.0 (acetyl CH_3), 40.4 (CH_2Cl), 55.5 (OCH_3), 61.8, 62.6, 66.5, 66.9, 68.3, 68.9, 69.3 70.0, 70.7, 71.3, 71.4, 72.8, (C-2-7, 2′-7′), 99.1 (C-1), 101.9 (C-1′), 166.4, 170.4, 170.6, 170.7, 172.0 (acetyl C=O).

Anal. Calcd for $C_{27}H_{38}O_{19}Cl$: C, 46.1; H, 5.6. Found: C, 44.5; H, 5.4.

2-(4-Trifluoroacetamidophenyl)ethyl 3-*O*-(6,7-Di-*O*-acetyl-L-*glycero*-α-D-*manno*-heptopyranosyl)-2,6,7-tri-*O*-acetyl-4-*O*-chloroacetyl-L-*glycero*-α-D-*manno*-heptopyranoside (15). Compound **7** (285 mg, 0.24 mmol) was debenzylated as described for **6** to yield, after silica gel column chromatography (ethyl acetate), **15** (178 mg, 81%), $[\alpha]_D$ +14° (*c* 0.8, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.7, 20.9, (acetyl CH_3), 35.2 (CH_2Ar), 40.3 (CH_2Cl) 62.7, 62.8, 66.5, 66.8, 68.5, 68.7, 69.5, 69.9, 70.4, 71.2, 71.6, 73.3 (C-2-7, 2′-7′, OCH_2CH_2), 97.2 (C-1), 102.0 (C-1′), 121.4-137.1 (aromatic C), 166.3, 170.4, 170.8, 172.4 (acetyl C=O).

Methyl 3-*O*-(6,7-Di-*O*-acetyl-2,3-*O*-isopropylidene-L-*glycero*-α-D-*manno*-heptopyranosyl)- 2, 6, 7 -tri-*O*-acetyl-4-*O*-chloroacetyl-L-*glycero*-α-D-*manno*-heptopyranoside (16). To a solution of **14** (148 mg, 0.21 mmol) in *N,N*-dimethylformamide was added dimethoxypropane (104 mL, 0.84 mmol) and a catalytic amount of 4-toluenesulfonic acid. The mixture was stirred at room temperature for 18 h, neutralized with sodium hydrogencarbonate, filtered and concentrated. The residue was purified on a silica gel column (toluene-ethyl acetate 2:1) to give **16** (122 mg, 78%), $[\alpha]_D$ +10° (*c* 1.0, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.7, 20.9 (acetyl CH_3), 25.9, 28.0 ($C(CH_3)_2$), 40.3 (CH_2Cl), 55.6 (OCH_3), 61.8, 62.7, 66.8, 68.3, 68.9, 69.5, 69.6, 71.2, 73.6, 75.2, 77.1 (C-2-7, 2′-7′), 99.2 (C-1), 99.8 (C-1′), 109.6 ($C(CH_3)_2$), 166.4, 170.0, 170.4, 171.8 (acetyl C=O).

Anal. Calcd for $C_{30}H_{43}O_{19}Cl$: C, 48.5; H, 5.8. Found: C, 48.0; H, 5.8.

2-(4-Trifluoroacetamidophenyl)ethyl 3-*O*-(6,7-Di-*O*-acetyl-2,3-*O*-isopropylidene-L-*glycero*-α-D-*manno*-heptopyranosyl)-2, 6, 7-tri-*O*-acetyl-4-*O*-chloroacetyl-L-*glycero*-α-D-*manno*-heptopyranoside (17). Compound **15** (178 mg, 0.20 mmol) was protected as described for **16** to yield, after silica gel column chromatography (toluene-ethyl acetate 1:1), **17** (164 mg, 92%), $[\alpha]_D$ +2° (*c* 0.7, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.7, 20.9, (acetyl CH_3), 26.0, 28.0 ($C(CH_3)_2$), 35.2 (CH_2Ar), 40.2 (CH_2Cl), 62.6, 62.7, 66.7, 68.2, 68.7, 68.8, 69.4, 71.3,

73.8, 75.1, 77.2 (C-2-7, 2′-7′, OCH_2CH_2), 97.3 (C-1), 100.0 (C-1′), 109.6 ($C(CH_3)_2$), 121.4-136.9 (aromatic C), 166.4, 170.1, 170.4, 170.7 170.8, 171.9 (acetyl C=O).

Methyl 3-*O*-(6,7-Di-*O*-acetyl-4-*O*-dibenzyloxyphosphoryl-2,3-*O*-isopropylidene-L-*glycero*-α-D-*manno*-heptopyranosyl)-2, 6, 7-tri-*O*-acetyl-4-*O*-chloroacetyl-L-*glycero*-α-D-*manno*-heptopyranoside (18). **16** (196 mg, 0.26 mmol) was phosphorylated as described for compound **8** above to give **18** (215 mg, 81%), $[\alpha]_D$ +6° (*c* 1.0, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.7, 20.9, 21.0 (acetyl CH_3), 26.3, 27.8 ($C(CH_3)_2$), 40.3 (CH_2Cl), 55.6 (OCH_3), 61.7, 61.8, 66.8, 67.6, 68.3, 69.0, 69.3, 69.4, 71.2, 73.3, 73.7 (d), 75.4, 76.2 (C-2-7, 2′-7′, CH_2Phx2), 99.1, 99.2 (C-1,1′), 110.2 ($C(CH_3)_2$), 125.3-129.0 (aromatic C), 166.5, 170.0, 170.3, 170.4 (acetyl C=O); ^{31}P, δ -1.46.

Anal. Calcd for $C_{44}H_{56}O_{22}ClP$: C, 52.7; H, 5.6; P, 3.1. Found: C, 52.4; H, 5.6;P, 3.1.

2-(4-Trifluoroacetamidophenyl)ethyl 3-*O*-(6,7-Di-*O*-acetyl-4-*O*-dibenzyloxyphosphoryl- 2, 3- *O*-isopropylidene-L-*glycero*-α-D-*manno*-heptopyranosyl)- 2, 6, 7 -tri-*O*-acetyl-4-*O*-chloroacetyl-L-*glycero*-α-D-*manno*-heptopyranoside (19). Compound **17** (164 mg, 0.18 mmol) was phosphorylated as described for compound **8** above, to give **19** (161 mg, 78%), $[\alpha]_D$ -0.6° (*c* 1.0, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.7, 20.9, (acetyl CH_3), 26.2, 27.8 ($C(CH_3)_2$), 35.2 (CH_2Ar), 40.2 (CH_2Cl), 61.7, 62.6, 66.7, 67.4, 67.6, 68.7 (d), 68.9, 69.4, 71.2, 73.6, 73.8 (d), 75.4, 76.1, 77.3 (C-2-7, 2′-7′, CH_2Phx2), 97.2 (C-1), 99.5 (C-1′), 110.2 ($C(CH_3)_2$), 121.6-137.0 (aromatic C), 166.5, 170.0, 170.3, 170.4 170.6, 170.8 (acetyl C=O); ^{31}P, δ -1.58.

Methyl 3-*O*-(L-*Glycero*-α-D-*manno*-heptopyranosyl 4-sodium phosphate)-L-*glycero*-α-D-*manno*-heptopyranoside (20). Compound **18** (116 mg, 0.11 mmol) was deprotected as described for compound **10** above to give, after FPLC, 35 mg (54%) of **20** as the pyridinium salt. The sodium salt was obtained as described for compound **12** above. $[\alpha]_D$ +90° (*c* 0.7, water). For NMR data see Tables 1 and 2

HRMS: Calcd for $C_{15}H_{28}O_{16}P$ $[M-H]^+$: 495.1115; found: 495.1113.

2-(4-Trifluoroacetamidophenyl)ethyl 3-*O*-(D-*Glycero*-α-D-*manno*-heptopyranosyl 4-sodium phosphate)-L-*glycero*-α-D-*manno*-hepto-pyranoside (21). Compound **19** (112 mg, 0.10 mmol) was deprotected as described for **10** to yield, after FPLC, **21** (42 mg, 55%) as the pyridinium salt. The sodium salt was obtained as described for **12.** $[\alpha]_D$ +73° (*c* 1.2, water). NMR data (D_2O): ^{13}C, 35.5 (CH_2Ar), 63.5, 64.0, 66.3, 68.6, 69.3 (2 C), 70.6 (2 C), 71.0, 71.4 (d), 71.8 (d), 72.4,

78.4, (C-2-7, 2′-7′,OCH_2CH_2), 100.0 (C-1), 102.7 (C-1′), 123.1, 130.7, 133.8, 139.3(aromatic C); ^1H, δ 4.41 (q, 1H, H-4'), 4.79 (s, 1H, H-1), 5.16 (s, 1H, H-1'); ^{31}P, δ 1.27 (d, *J* 9.7 Hz).

HRMS: Calcd for $C_{24}H_{34}O_{17}PNF_3$ $[M-H]^+$: 696.1516; found: 696.1552.

Methyl 3-*O*-(6,7-Di-*O*-acetyl-L-*glycero*-α-D-*manno*-heptopyranosyl)-2,6,7-tri-*O*-acetyl-L-*glycero*-α-D-*manno*-heptopyranoside (22). A solution of **8** (320 mg, 0.36 mmol) in ethyl acetate: ethanol (1:1, 10 mL) was hydrogenolyzed over Pd/C (10%, 100 mg) at 400 kPa for 44 h. The mixture was filtered, concentrated and purified on a silica gel column (ethyl acetate) to give **22** (180 mg, 81%), $[\alpha]_D$ +39° (*c* 1.05, chloroform). NMR data ($CDCl_3$): ^{13}C δ 20.7, 20.9 21.0 (acetyl CH_3), 55.2 (OCH_3), 62.5, 62.6, 66.8, 67.0, 68.9, 69.5, 70.0, 71.1, 71.3, 73.8 (C-2-7, 2′-7′), 99.1 (C-1), 101.9 (C-1′), 170.5, 170.6, 170.8, 171.8, 172.2 (acetyl C=O).

Anal. Calcd for $C_{25}H_{38}O_{18}$: C, 47.9; H, 6.1. Found: C, 47.2; H, 6.0.

2-(4-Trifluoroacetamidophenyl)ethyl 3-*O*-(6,7-Di-*O*-acetyl-L-*glycero*-α-D-*manno*-heptopyranosyl)- 2, 6, 7- tri-*O*-acetyl-L-*glycero*-α-D-*manno*-heptopyranoside (23). Compound **9** (300 mg, 0.26 mmol) was debenzylated as described for **8** above to yield **23** (192 mg, 85%), $[\alpha]_D$ +33° (*c* 0.7, chloroform). NMR data ($CDCl_3$): ^{13}C δ 20.7, 20.9, (acetyl CH_3), 35.2 (CH_2Ar), 62.9, 63.1, 66.7, 66.9, 68.5, 69.1, 69.6, 69.9, 70.7, 71.2, 71.4, 74.4 (C-2-7, 2′-7′, OCH_2CH_2), 97.4 (C-1), 102.1 (C-1′), 121.2-137.1 (aromatic C), 170.5, 170.8, 171.0, 172.1, 172.5 (acetyl C=O).

Methyl 3-*O*-(6,7-Di-*O*-acetyl-2,3-*O*-isopropylidene-L-*glycero*-α-D-*manno*-heptopyranosyl)- 2, 6, 7 -tri-*O*-acetyl-L-*glycero*-α-D-*manno*-heptopyranoside (24). To a solution of **22** (180 mg, 0.29 mmol) in *N,N*-dimethylformamide (5 mL) was added dimethoxypropane (140 mL, 1.14 mmol) and a catalytic amount of 4-toluenesulfonic acid. The mixture was stirred at room temperature for 18 h, neutralized with sodium hydrogencarbonate, filtered and concentrated. The residue was purified on a silica gel column (toluene-ethyl acetate 1:2) to give **24** (173 mg, 90%), $[\alpha]_D$ +13° (*c* 1.0, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.7, 20.9, 21.4 (acetyl CH_3), 26.3, 28.2 ($C(CH_3)_2$), 55.3 (OCH_3), 62.5, 67.6, 68.5, 68.9, 69.4, 69.5, 71.2, 71.3, 72.4, 75.3, 77.6 (C-2-7, 2′-7′), 98.9, 99.1 (C-1, 1′), 109.5 ($C(CH_3)_2$), 170.0, 170.4, 171.9, 172.5 (acetyl C=O).

Anal. Calcd for $C_{28}H_{42}O_{18}$: C, 50.4; H, 6.4. Found: C, 51.2; H, 6.5.

2-(4-Trifluoroacetamidophenyl)ethyl 3-*O*-(6,7-Di-*O*-acetyl-2,3-*O*-isopropylidene-L-*glycero*-α-D-*manno*-heptopyranosyl)-2, 6, 7-tri-*O*-acetyl-L-*glycero*-α-D-*manno*-heptopyranoside (**25**). Compound **23** (246 mg, 0.30 mmol) was protected as described for **22** to yield, after column chromatography (toluene-ethyl acetate 1:1), **25** (237 mg, 92%), $[\alpha]_D$ +19° (c 1.0, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.7, 20.9, (acetyl CH_3), 26.2, 28.2 ($C(CH_3)_2$), 35.2 (CH_2Ar), 62.5, 63.0, 67.3, 68.4, 68.8, 68.9, 69.4, 69.5, 71.3, 71.6, 73.0, 75.2 (C-2-7, 2′-7′, OCH_2CH_2), 97.5 (C-1), 99.2 (C-1′), 109.5 ($C(CH_3)_2$), 121.3-136.1 (aromatic C), 170.0, 170.6, 172.0 172.4 (acetyl C=O).

Methyl 3-*O* -(6,7-Di-*O*-acetyl-4-*O*-dibenzyloxyphosphoryl-2,3-*O*-isopropylidene-L-*glycero*-α-D-*manno*-heptopyranosyl)-2, 6, 7-tri-*O*-acetyl-4-*O*-dibenzyloxyphosphoryl-L-*glycero*-α-D-*manno*-heptopyranoside (26). To a solution of imidazole (430 mg, 6.32 mmol) in dry dichloromethane (5 mL) was added phosphorus trichloride (180 mL, 2.06 mmol) in dichloromethane (0.8 mL) and triethylamine (930 mL, 6.67 mmol) in dichloromethane (1.5 mL). The solution was stirred at 0 °C under an atmosphere of nitrogen for 10 min. A solution of **24** (170 mg, 0.26 mmol) in dichloromethane (2 mL) was added dropwise during 15 min. After stirring for 30 min, benzyl alcohol (670 mL, 6.47 mmol) in dichloromethane (0.6 mL) was added dropwise. After an additional 40 min the solution was washed with water and 1M HCl, dried ($MgSO_4$), filtered and concentrated. The residue was dissolved in dichloromethane (10 mL) and a solution of 3-chloroperbenzoic acid (540 mg, 3.15 mmol) in dichloromethane (1.5 mL) was added dropwise during 5 min. The stirring was continued for 1.5 h at 0 °C. To the solution was added aqueous sodium thiosulfate (10%, 1.5 mL) and aqueous sodium hydrogencarbonate (sat., 1.5 mL). The organic layer was separated and washed with water, 1M HCl, water and aqueous sodium hydrogencarbonate, dried ($MgSO_4$), filtered and concentrated. Silica gel chromatography (light petroleum bp 60-70 °C-ethyl acetate 1:1) of the residue gave **26** (205 mg, 66%), $[\alpha]_D$ -4° (*c* 0.8, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.8, 21.0, 21.1, 21.6 (acetyl CH_3),26.5, 28.1 ($C(CH_3)_2$), 55.5 (OCH_3), 61.1, 61.6, 67.4+67.5 (d), 67.8, 69.0 (d), 69.4, 69.5, 69.7, 69.8, 71.6, 72.7, 73.5 (d), 74.1 (d), 75.6, 76.3 (C-2-7, 2′-7′, CH_2Phx4), 98.8, 98.9 (C-1, 1′), 110.1 ($C(CH_3)_2$), 125.4-129.2 (aromatic C), 170.2, 170.4 (acetyl C=O); ^{31}P, δ - 1.18, -1.42.

Anal. Calcd for $C_{56}H_{66}O_{24}P_2$: C 56.8; H, 5.6. Found: C, 56.6; H, 5.7.

2-(4-Trifluoroacetamidophenyl)ethyl 3-*O*-(6,7-Di-*O*-acetyl-4-*O*-dibenzyloxyphosphoryl- 2, 3 -*O*-isopropylidene-L-*glycero*-α-D-*manno*-

heptopyranosyl)-2,6,7-tri-*O*-acetyl-4-*O*-dibenzyloxyphosphoryl-L-*glycero*-α-D-*manno*-heptopyranoside (27). Compound **25** (150 mg, 0.17 mmol) was phosphorylated as described for compound **24** above to yield, after column chromatography (light petroleum bp 60-70 °C-ethyl acetate 1:2), **27** (134 mg, 55%), $[\alpha]_D$ +28° (*c* 1.2, chloroform). NMR data ($CDCl_3$): ^{13}C, δ 20.7,20.8, 20.9 (acetyl CH_3), 26.4, 27.9 ($C(CH_3)_2$), 35.2 (CH_2Ar), 61.6, 62.1, 67.3, 67.4, 67.6, 67.7, 68.9, 69.4, 69.7, 71.4, 73.1, 73.2 (d), 73.9 (d), 75.4, 76.1 (C-2-7, 2′ -7′, OCH_2CH_2, CH_2Phx4), 96.9 (C-1), 99.1 (C-1′), 109.9 ($C(CH_3)_2$), 121.5-136.7(aromatic C), 170.1, 170.3, 170.5 170.7 (acetyl C=O); ^{31}P, δ -1.38, -1.49.

Methyl 3-*O*-(L-*Glycero*-α-D-*manno*-heptopyranosyl 4-sodium phosphate)-L-*glycero*-α-D-*manno*-heptopyranoside 4-sodium phosphate (28). Compund **26** (89 mg, 0.075 mmol) was deprotected as described for compound **10** above to give, after FPLC, 22 mg (51%) of **28** as the pyridinium salt. The sodium salt was obtained as described for **12**. $[\alpha]_D$ +84° (*c* 0.9, water). For NMR data see Tables 1 and 2.

HRMS: Calcd for $C_{15}H_{31}O_{19}P_2$ $[M-H]^+$: 575.0778; found: 575.0813.

2-(4-Trifluoroacetamidophenyl)ethyl 3-*O*-(L-*Glycero*-α-D-*manno*-heptopyranosyl 4-sodium phosphate)-L-*glycero*-α-D-*manno*-hepto-pyranoside 4-sodium phosphate (29). Compound **27** (134 mg, 0.097 mmol) was deprotected as described for **10** to yield, after FPLC, **29** (39 mg, 43%) as the pyridinium salt. The sodium salt was obtained as described for **12**. $[\alpha]_D$ +75° (*c* 1.5, water). NMR data (D_2O): ^{13}C, δ 35.5 (CH_2Ar), 63.2, 63.6, 68.3, 69.1, 69.4, 70.3, 70.8, 70.9 (d), 71.1, 71.7, 71.8, 72.1 (d), 76.0 (C-2-7, 2'-7', OCH_2CH_2), 99.7 (C-1), 102.4 (C-1'), 114.6, 118.8 (CF_3), 123.2, 130.7, 133.8, 139.3 (aromatic C), 157.5, 158.1 (CF_3CO); ^1H, δ 4.26-4.38 (m, 2H, H-4, 4'), 4.74 (s, 1H, H-1), 5.14 (s, 1H, H-1'); ^{31}P, δ 0.66 (d, *J* 11.0 Hz), 0.90 (d, *J* 9.8 Hz).

HRMS: Calcd for $C_{24}H_{35}O_{20}NF_3P_2$ $[M-H]^+$: 776.1180; found: 776.1188.

ACKNOWLEDGEMENTS

We thank Professor Per J. Garegg for his interest in this work and the Swedish Research Council for Engineering Studies for financial support.

REFERENCES

1. C. Galanos, O. Lüderitz, E. T. Rietschel, and O. Westphal, *Int. Rev. Biochem.*, **14**, 239 (1977).
2. C. R. H. Raetz, *Annu. Rev. Biochem.*, **59**, 129 (1990).

3. P. J. Garegg, S. Oscarson, H. Ritzén, and M. Szönyi, *Carbohydr. Res.*, **228**, 121 (1992).
4. P. J. Garegg, S. Oscarson, and M. Szönyi, *Carbohydr. Res.*, **205**, 125 (1990).
5. T. Norberg, M. Walding, and E. Westman, *J. Carbohydr. Chem.*, **7**, 283 (1988).
6. T. Norberg and H. Ritzén, *Glycoconjugate J.*, **3**. 135 (1986).
7. A.-C. Helland, *Chem. Commun.*, Univ. Stockholm, No 5 (1991).
8. J. M. C. Luk, Doctoral dissertation thesis, Karolinska Institute, 1991.
9. S. Lind, Doctoral dissertation thesis, Karolinska Institute, 1992.
10. S. Oscarson and H. Ritzén, *Carbohydr. Res.*, **254**, 81 (1994).
11. R. U. Lemieux, K. B. Hendriks, R. V. Stick, and K. James, *J. Am. Chem. Soc.*, **97**, 4056 (1975).
12. P. Fügedi and P. J. Garegg, *Carbohydr. Res.*, **149**, c9 (1986).
13. C. A. A. van Boeckel and T. Beetz, *Tetrahedron Lett.*, **35**, 3775 (1983).
14. H. Ottosson, *Carbohydr. Res.*, **197**, 101 (1990).
15. C. Bernlind, S. Oscarson, and G. Widmalm, *Carbohydr. Res.*, **263**, 173 (1994).