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Synthesis of linear oligosaccharides: L-*glycero*-α-D-*manno*-heptopyranosyl derivatives of allyl α-glycosides of D-glucose, kojibiose, and 3-*O*-α-kojibiosyl-D-glucose, substrates for synthetic antigens

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ABSTRACT

Synthesis of the title oligosaccharides was performed with the use of peracetylated L-*glycero*-β-D-*manno*-heptosyl trichloroacetimidate as the heptosyl donor and (oligo)glucosyl acceptors bearing acyl and acetal protecting groups.

INTRODUCTION

Synthesis of protein-free neoglycoconjugates with pendant, immunologically significant carbohydrates can be based on copolymerization of acrylamide with sugar derivatives carrying an *N*-substituted acrylamide fragment[1–3]. One of the approaches[3,4] makes use of allyl glucosides, the aglycon moiety of which is further modified by reaction with 2-aminoethanethiol (cysteamine) followed by *N*-acryloylation. In another approach, the product of the cysteamine addition is treated with glutaraldehyde; the resulting Schiff's base is next condensed with a selected protein (e.g., bovine serum albumin, BSA).

$$\mathrm{SugOCH_2CH{=}CH_2} \longrightarrow \mathrm{SugO(CH_2)_3S(CH_2)_2NH_2} \longrightarrow$$
$$\longrightarrow \mathrm{SugO(CH_2)_3S(CH_2)_2NHCOCH{=}CH_2}$$
$$\longrightarrow \mathrm{SugO(CH_2)_3S(CH_2)_2N{=}CH(CH_2)_3CHO}$$

It is this approach that was chosen for preparation of neo-glycoconjugates bearing fragments of the outer-core region of the lipopolysaccharide from *Es-*

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cherichia coli K-12[5]. In this communication, the synthesis of allyl glycosides of three related oligosaccharides (**1–3**) is described:

L-α-D-Hep*p*-(1 → 6)-α-D-Glc*p*-OAll (**1**)
L-α-D-Hep*p*-(1 → 6)-α-D-Glc*p*-(1 → 2)-α-D-Glc*p*-OAll (**2**)
L-α-D-Hep*p*-(1 → 6)-α-D-Glc*p*-(1 → 2)-α-D-Glc*p*-(1 → 3)-α-D-Glc*p*-OAll (**3**)

RESULTS AND DISCUSSION

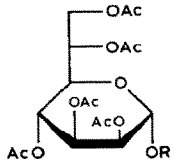
Syntheses of all the three target oligosaccharide derivatives involved as a common feature the use of glycosyl acceptors with acyl and acetal protecting groups, whose removal did not require hydrogenolysis, incompatible with the presence of the allyl group, and a single heptosyl donor **4**.

The successful glycosylation with this imidate is documented[4]. The precursor of **4**, the HO-1 derivative **5**, could be prepared in one step by selective 1-*O*-deacetylation of the peracetate **6** with hydrazinium acetate without recourse to a two-stage procedure[4].

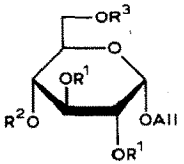
As glycosyl acceptors for heptosylation we tested two allyl α-D-glucopyranoside derivatives, **7** and **8**. Allyl α-D-glucopyranoside could not be prepared by alcoholysis of D-glucose in the presence of hydrogen chloride[6]. The syrupy reaction product was acetylated and appeared to contain anomeric allyl glucosides in a ratio close to unity as shown by ^{13}C NMR data (δ 94.56 and 99.25 for C-1α and C-1β, respectively). Treatment of this mixture with titanium tetrachloride in dichloromethane (cf. ref 7) enriched it in the α anomer **9** which was isolated by chromatography followed by crystallization. Sequential Zemplén *O*-deacetylation of **9**, selective tritylation, benzoylation, and detritylation afforded **7** in 34% overall yield.

Alternatively, allyl α-D-glucopyranoside was formed as the main product by the alcoholysis of D-glucose in the presence of a strong cation-exchange resin. It was isolated as a crystalline isopropylidene acetal-dibenzoate **10**. Deacetonation of **10** with pyridinium perchlorate[8] yielded the diol **8**.

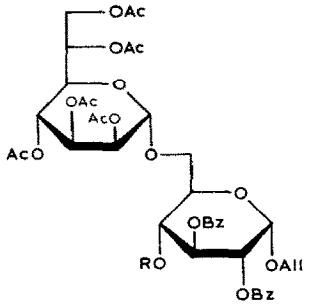
Coupling of the imidate **4** with the alcohol **7** in the presence of trimethylsilyl trifluoromethanesulfonate (triflate) in dichloromethane gave 61% of a disaccharide product **11**. Its structure was confirmed by the ^{13}C NMR spectrum which contained, *inter alia*, signals for two α-anomeric carbon atoms (δ 97.61, Hep*p*; and 94.91, Glc*p*) and C-6 of 6-*O*-substituted glucopyranose (δ 66.65). In an analogous coupling of the imidate **4** with the diol **8**, the yield of the target disaccharide derivative **12** was lower (37%). In both cases, the mixtures contained several byproducts which were not investigated. The ^{13}C NMR spectrum of **12** contained, *inter alia*, signals for C-6 of glucose (δ 66.14) and two α-anomeric carbon atoms (δ 97.85, Hep*p*; and 95.05, Glc*p*). *O*-Deacylation of both **11** and **12** afforded **1**; in its ^{13}C NMR spectrum were present characteristic signals for C-1 (δ 98.8) and C-1′ (δ 100.6).



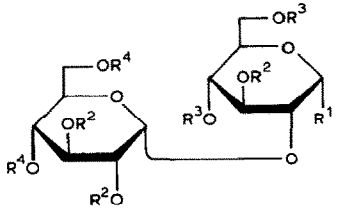
4 R = C(=NH)CCl$_3$
5 R = H
6 R = Ac



7 R^1 = R^2 = Bz, R^3 = H
8 R^1 = Bz, R^2 = R^3 = H
9 R^1 = R^2 = R^3 = Ac
10 R^1 = Bz, R^2, R^3 = Me$_2$C



11 R = Bz
12 R = H



13 R^1 = OAc, R^2 = R^3 = R^4 = Ac
15 R^1 = Br, R^2 = R^3 = R^4 = Ac
17 R^1 = OAll, R^2 = R^3 = R^4 = Ac
18 R^1 = OAll, R^2 = R^3 = R^4 = H
19 R^1 = OAll, R^2 = H, R^3 = R^4 = PhCH
20 R^1 = OAll, R^2 = Bz, R^3 = R^4 = PhCH
21 R^1 = OAll, R^2 = Bz, R^3 = H, R^4 = PhCH
22 R^1 = OAll, R^2 = Bz, R^3 = PhCH, R^4 = H
23 R^1 = OAll, R^2 = Bz, R^3 = R^4 = H
24 R^1 = OAll, R^2 = R^3 = Bz, R^4 = H

In the synthesis of the trisaccharide glycoside **2**, the preparation of kojibiose preceded its allyl glycosidation and heptosylation. A mixture of kojibiose and sophorose peracetates **13** and **14** in a ratio of 10:11 [^{13}C NMR data, δ (C-1') 95.45 and (C-1) 101, respectively], prepared according to Helferich and Zinner[9], was not separated but treated with hydrogen bromide in acetic acid[10] to give a mixture of the respective glycosyl bromides **15** and **16**. Peracetylated sophorosyl bromide **16** crystallized readily and the target, peracetylated kojibiosyl bromide **15** was additionally purified from the mother liquor by flash chromatography.

Interaction of the biosyl bromide **15** with allyl alcohol in benzene in the presence of tetrabutylammonium bromide at 60°C afforded, in virtually quantitative yield, peracetylated allyl α-kojibioside **17**, which was then *O*-deacetylated to give allyl α-kojibioside **18**. In order to have an access to the trioside **2** from the allyl bioside **18**, we had to possess a specifically protected derivative of the latter with HO-6' free, and this was a challenge. For instance, tritylation of **18** did not show any selectivity and a mixture of products was obtained. Benzylidenation of **18**

afforded the bis-acetal **19** which was benzoylated (→ **20**) and subjected to mild, acid-catalyzed methanolysis in the presence of pyridinium perchlorate[8]. A mixture of two isomeric diols **21** and **22** and the tetraol **23** was obtained, the yield and ratio of the products being dependent on the duration of methanolysis. The structure of the isomeric monoacetals **21** and **22** was ascertained on the basis of ^{1}H NMR spectra, signals for H-3 and H-3′ being characteristic. Their position for bis-acetal **20** was at δ 5.96 and at δ 5.5–5.6 for tetraol **23**. Thus, the signal for H-3 adjacent to a 1,3-dioxolane ring was shifted downfield relative to its position in a monocyclic derivative. Hence, a monoacetal with chemical shifts of 5.62 and 5.92 ppm for H-3 and H-3′, respectively, is the 4′,6′-*O*-benzylidene derivative **21**, while signals at δ 5.93 and 5.58 for H-3 and H-3′ should correspond to the 4,6-*O*-benzylidene derivative **22**. It is also worthy of note that proton H-6a in **20** and **22** (not in **21** or **23**, nor H-6b protons) resonates as an isolated doublet of doublets at δ 4.30.

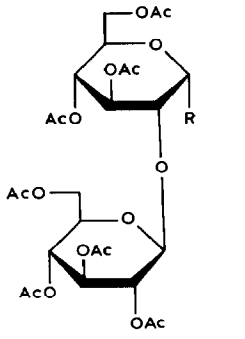
The monoacetal **21** was benzoylated and debenzylidenated to give the target heptosyl acceptor **24**. Signals for H-4, 6a, and 6b in its ^{1}H NMR spectrum are shifted strongly downfield as compared to those for H-4′, 6′a, and 6′b, which unambiguously proved its structure.

This diol was glycosylated with the heptosyl donor **4** in dichloromethane in the presence of trimethylsilyl trifluoromethanesulfonate to give the protected trisaccharide glycoside **25** in 52.5% yield. The anomeric region of its ^{13}C NMR spectrum contained three signals with δ 94.9, 95.2, and 97.8, which correspond to C-1, C-1′, and C-1″, respectively. In the spectrum of the target trioside **2**, obtained from **25** by deacylation, the respective signals were at δ 95.9, 97.7, and 100.9.

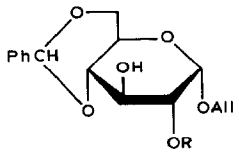
Assembly of an allyl glucotrioside fragment of the tetrasaccharide **3** with three 1,2-*cis*-glycosidic bonds could not be based entirely on the use of benzyl protecting groups, and kojibiose derivatives with the nonparticipating glucosyl group at O-2 were tested as α-glycosylating agents. The successful use of 2-*O*-(glycosyl)-glycosyl bromides for selective 1,2-*cis*-glycosylation of alcohols is documented[11–13], although in one case a glycosyl donor of this kind was found to be unreactive[14].

As the "reducing" terminus in an attempted synthesis of a glucotrioside precursor of the tetrasaccharide **3**, the 2-benzoate **26** was chosen and prepared from the known[15] diol **27** by monobenzoylation via its 2,3-*O*-stannylidene derivative according to ref 16.

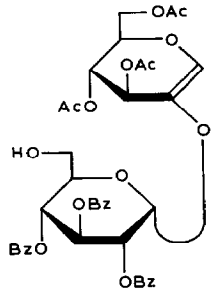
The known[12] kojibiose derivative **28** was prepared in 77% yield, together with a small amount of the corresponding sophorose derivative, by condensation of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl bromide with 1,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose in the presence of mercuric cyanide. It was debenzylated by hydrogenolysis, and the product was 6′-*O*-tritylated and then benzoylated to give derivative **29**. This was conventionally detritylated (→ **30**) and chloroacetylated to **31**. Under standard conditions, it was converted into the specifically acylated biosyl bromide **32** which was found to be unsuitable as a glycosyl donor; it was unreactive in Helferich glycosylation, whereas in the presence of silver trifluoromethanesulfonate it underwent decomposition without formation of condensation products



14 R = OAc
16 R = Br



26 R = Bz
27 R = H



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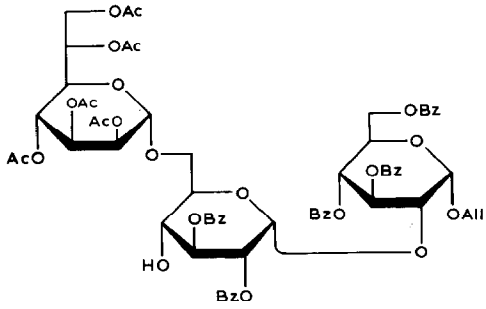

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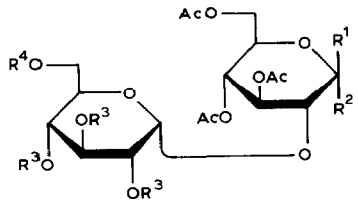
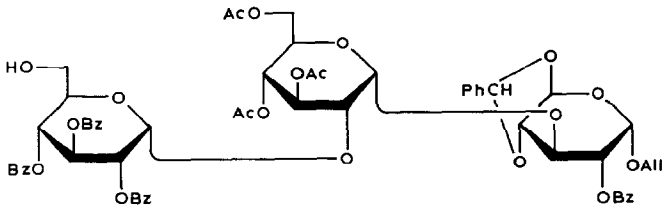


28 R^1 = H, R^2 = OAc, R^3 = R^4 = Bzl
29 R^1 = H, R^2 = OAc, R^3 = Bz, R^4 = Tr
30 R^1 = R^4 = H, R^2 = OAc, R^3 = Bz
31 R^1 = H, R^2 = OAc, R^3 = Bz, R^4 = $COCH_2Cl$
32 R^1 = H, R^2 = Br, R^3 = Bz, R^4 = $COCH_2Cl$
33 R^1 = $OC(=NH)CCl_3$, R^2 = H, R^3 = Bz
R^4 = $COCH_2Cl$
34 R^1 = R^2 = H, OH, R^3 = Bz, R^4 = $COCH_2Cl$
35 R^1 = H, R^2 = $OC(=NH)CCl_3$, R^3 = Bz
R^4 = $COCH_2Cl$

with the acceptor **26**. It was equally ineffective in an attempted allyl glycosylation under the conditions employed for the preparation of **17**.

Successful biosylation of **26** was effected with trichloroacetimidate **33**, prepared by hydrolysis of **32** in the presence of silver carbonate (→ **34**) followed by reaction with trichloroacetonitrile in the presence of potassium carbonate[17]. The anomeric trichloroacetimidate **35** was separated from **33** by flash chromatography, and the anomeric configurations of **33** and **35** were unambiguously established on the basis of ^{1}H NMR spectra which contained, *inter alia*, signals at δ 5.97 (d, J 7 Hz, H-1) and 4.20 (bt, H-2) for **33**, and at δ 6.61 (d, J 3.7 Hz, H-1) and 4.07 (dd, J 3.7 and 10 Hz, H-2) for **35**.



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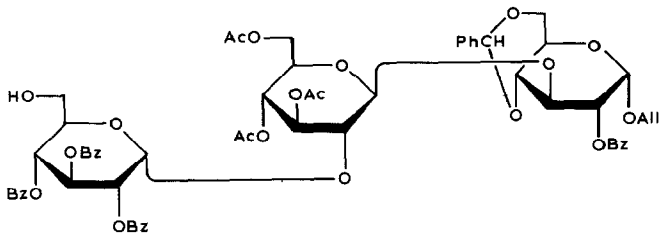

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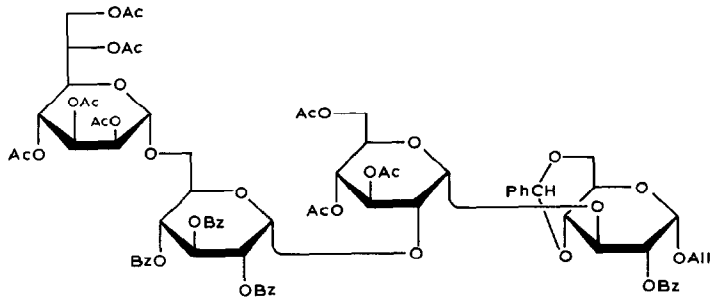

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Trimethylsilyl trifluoromethanesulfonate-promoted condensation of the β-trichloroacetimidate **33** with the glycosyl acceptor **26** resulted in a mixture of products which could be separated by means of HPLC following *O*-de(chloroacetylation) with thiourea. The anomeric trisaccharides **36** and **37** were isolated together with an unsaturated derivative **38**. ^{1}H NMR data indicated the α configuration of C-1′ for **36** and the β configuration for **37**; the signals for H-1′ and H-2′ in these trisaccharide derivatives were found at δ 4.91 (d, *J* 3.8 Hz) and 3.77 (dd, *J* 3.6 and 10 Hz), and, respectively, at 4.80 (d, *J* 7.6 Hz) and 3.66 (dd, *J* 7.7 and 9.0 Hz).

The trisaccharide glycosyl acceptor **36** was heptosylated with the trichloroacetimidate **4** as mentioned above, to give the protected tetrasaccharide **39** in 52% yield. It was deprotected by successive deacetalation and *O*-deacylation; the yield of the target allyl tetraoside **3** was 96%. Its ^{13}C NMR spectrum (δ 97.45, 97.7, 98.9, and 100.8 for the anomeric carbon atoms) corroborated its structure.

Samples of oligosaccharides **1–3** will be converted into artificial antigens. The results will be reported elsewhere.

EXPERIMENTAL

General methods.—TLC was performed on Kieselgel 60 or Kieselgel 60F (Merck), and column chromatography on Silasorb (CSFR). Optical rotations were determined for solutions in $CHCl_3$ with a Jasco DIP-360 automatic polarimeter (Japan) at $20 \pm 2°C$. Mp's were determined on a Kofler apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded with Bruker WM-250 and AM-300 spectrometers in $CDCl_3$ solutions with Me_4Si as internal standard. Mass spectra (LSIMS, positive mode) were recorded on an AMD-604 mass spectrometer.

*Allyl 2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranoside* (**9**).—D-Glucose (10 g, 55 mmol) was vigorously stirred in allyl alcohol (15 mL) containing HCl [prepared by addition of acetyl chloride (1.2 mL, 16 mmol) to allyl alcohol] for 6 h at 70°C. The solution was neutralized by anion-exchange resin (HCO_3^-) and concentrated to dryness. The syrupy residue was conventionally acetylated to give a mixture of two products having R_f 0.43 and 0.38. This mixture was dissolved in CH_2Cl_2 (60 mL), treated with titanium tetrachloride (3.9 mL) in CH_2Cl_2 (40 mL) at 0°C, and kept for 17 h at room temperature. It was then poured into ice and extracted with ether (3 × 75 mL), and the extract was washed with aq $NaHCO_3$ (3 × 100 mL) and water (100 mL), and concentrated. The faster-moving α anomer **9** was isolated by column chromatography (1:1 ether–hexane) and crystallization from the same solvent mixture; yield, 8.2 g (38%); mp 50–52°C; $[\alpha]_D$ +129° (*c* 1.1); lit.[18]: mp 51–53°C; $[\alpha]_D$ +131° (*c* 1.1, MeOH). ^1H NMR data: δ 5.87 (m, 1 H, =CH–), 5.51 (dd, 1 H, $J_{2,3}$ 10.5, $J_{3,4}$ 9.5 Hz, H-3), 5.32, 5.23 (2 m, 2 H, $=CH_2$), 5.11 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 5.07 (dd, 1 H, $J_{4,5}$ 10.5 Hz, H-4), 4.90 (dd, 1 H, H-2), 4.27 (dd, 1 H, $J_{5,6a}$ 4.7, $J_{6a,6b}$ 12.7 Hz, H-6a), 4.20 (m, 1 H, OCH_2), 4.09 (dd, 1 H, $J_{5,6b}$ 2.5 Hz, H-6b), 4.08–3.98 (m, 2 H, H-5, OCH_2), 2.11, 2.08, 2.05, 2.05, 2.03 (4 s, 12 H, 4 OAc). ^{13}C NMR data: δ 170.1–169.1 (PhCO), 133.0 ($CH_2CH=CH_2$), 117.7 ($CH_2CH=CH_2$), 94.6 (C-1), 70.4 (C-2), 69.8 (C-3), 68.4, 68.3 (C-4, $CH_2CH=CH_2$), 67.1 (C-5), 61.6 (C-6), 20.2 (CH_3CO).

*Allyl 2,3,4-tri-*O*-benzoyl-α-*D*-glucopyranoside* (**7**).—A solution of tetraacetate **9** (3.88 g, 10 mmol) in methanolic NaOMe (0.1 M, 30 mL) was kept at room temperature for 3 h, the mixture was neutralized with cation-exchange resin (H^+), concentrated, and dried in vacuo. The residue was dissolved in dry pyridine (10 mL), chlorotriphenylmethane (3.6 g, 13 mmol) was added, and after 17 h at room temperature the solution was treated with benzoyl chloride (2.55 mL, 22 mmol). The product was detritylated with aq 90% CF_3CO_2H. Conventional work-up and subsequent column chromatography (5:1 benzene–EtOAc) yielded the alcohol **8** (3.73 g, 70%); $[\alpha]_D$ +5° (*c* 1.17). ^1H NMR data: δ 6.26 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 9.9$ Hz, H-3), 5.87 (m, 1 H, =CH–), 5.50 (pt, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 5.19 (d, 1 H, $J_{1,2}$ 4.0

Hz, H-1), 5.32 (m, 1 H, $=CH_2$), 5.315 (dd, 1 H, H-2), 5.12 (m, 1 H, $=CH_2$), 4.27 (m, 1 H, OCH_2), 4.09 (m, 2 H, H-5, OCH_2), 3.81 (m, 1 H, H-6a), 3.72 (m, 1H, H-6b), 2.64 (dd, 1 H, $J_{OH,6b}$ 5.7, $J_{OH,6a}$ 8.5 Hz, OH). Anal. Calcd for $C_{30}H_{28}O_9$: C, 67.66; H, 5.30. Found: C, 67.60; H, 5.36.

*Allyl 2,3-di-*O*-benzoyl-4,6-*O*-isopropylidene-α-*D*-glucopyranoside* (**10**).—A mixture of D-glucose (10 g, 55 mmol) and strong cation-exchange resin QU-2 (H^+) (2.5 g) was stirred in allyl alcohol (15 mL) at 70°C for 72 h. The resin was filtered off and the solution was evaporated to dryness in vacuo. The residue was acetonated in 5 : 1 acetone–2,2-dimethoxypropane (60 mL) in the presence of toluene-*p*-sulfonic acid (0.5 g) at room temperature for 2 h. An undissolved product was filtered off, and the solution was neutralized with pyridine and concentrated. Column chromatography (10 : 1 benzene–MeOH) of the residue gave a crude syrupy product which was conventionally benzoylated followed by crystallization from ether–pentane to give the dibenzoate **10** (7.5 g, 29%); mp 119–121°C; $[\alpha]_D$ +131° (*c* 2.3). ^1H NMR data: δ 5.94 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 9.5$ Hz, H-3), 5.84 (m, 1 H, =CH–), 5.30 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 5.30 (m, 1 H, $=CH_2$), 5.23 (dd, 1 H, H-2), 5.15 (m, 1 H, $=CH_2$), 4.14, 4.03 (2 m, 2 H, OCH_2), 4.00–3.80 (m, 4 H, H-4,5,6a,6b), 1.51, 1.40 (2 s, 6 H, Me_2C). EIMS: Calcd for $C_{25}H_{25}O_8$ $[M - CH_3]^+$: *m/z* 453.1550. Found: *m/z* 453.1549.

*Allyl 2,3-di-*O*-benzoyl-α-*D*-glucopyranoside* (**8**).—A solution of the acetonide **10** (2.3 g, 4.9 mmol) and pyridinium perchlorate (1 g) in a mixture of nitromethane (40 mL) and MeOH (6 mL) was kept at 50°C for 3 h, cooled to room temperature, treated with pyridine (0.5 mL), and diluted with $CHCl_3$ (50 mL). The solution was washed with water (3 × 20 mL) and concentrated, and the residue was chromatographed to give **8** (1.84 g, 88%); mp 116–118°C; $[\alpha]_D$ +169° (*c* 1.1). ^1H NMR data: δ 5.85 (m, 1 H, =CH–), 5.75 (m, 1 H, H-3), 5.30, 5.16 (2 m, 2 H, $=CH_2$), 5.26 (m, 2 H, H-1,2), 4.25, 4.05 (2 m, 2 H, OCH_2), 3.93 (m, 4 H, H-4,5,6a,6b), 3.15 (d, 1 H, $J_{OH,4}$ 4.5 Hz, OH-4), 2.08 (pt, 1 H, OH-6). ^{13}C NMR data: δ 166.9, 168.0 (2 C, PhCO), 133.35–133.14 (3 C, $CH_2CH{=}CH_2$, Ph), 129.7–128.3 (Ph), 117.5 ($=CH_2$), 95.2 (C-1), 73.7, 71.7 (×2) (C-4,5, OCH_2), 69.2, 68.4 (C-2,3), 61.6 (C-6). LSIMS (+): Calcd for $C_{23}H_{25}O_8$ $[M + H]^+$: *m/z* 429.155. Found: *m/z* 429.155.

*2,3,4,6,7-Penta-*O*-acetyl-*L*-glycero-α-*D*-manno-heptopyranosyl trichloroacetimidate* (**4**).—Benzyl 2,3,4-tri-*O*-benzyl-L-*glycero*-α-D-*manno*-heptopyranoside[19] (0.6 g) was hydrogenated (H_2, Pd–C) and subsequently acetylated to yield peracetylated heptose **6**. To a solution of **6** (382 mg, 0.83 mmol) in DMF (12 mL) was added hydrazinium acetate (92 mg, 1.0 mmol), and the mixture was stirred for 1 h at room temperature, diluted with EtOAc (120 mL), and washed with aq $NaHCO_3$ and water. The organic layer was dried ($MgSO_4$) and concentrated, and the residue was dried in vacuo to give the pentaacetate **5** (350 mg, 100%); R_f 0.23 (3 : 2 benzene–EtOAc). The product was dissolved in CH_2Cl_2 (6 mL), K_2CO_3 (1.2 g) and trichloroacetonitrile (1.75 mL, 17.5 mmol) were added, and the mixture was stirred for 6 h. Then it was diluted with toluene (50 mL), filtered through Celite, and concentrated. Column chromatography of the residue (5 : 1 → 3 : 1 heptane–

EtOAc) yielded **4** (310 mg, 67%); R_f 0.45 (3:2 benzene–EtOAc). The optical rotation and ^{1}H NMR data of **4** were in agreement with the published data[4].

*Allyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4,6,7-penta-O-acetyl-*L*-glycero-α-*D*-manno-heptopyranosyl)-α-*D*-glucopyranoside* (**11**).—A solution of **7** (213 mg, 0.40 mmol) in CH_2Cl_2 (5 mL) was stirred with 4A molecular sieves at room temperature for 1 h, and the imidate **4** (220 mg, 40 mmol) and trimethylsilyl triflate (10 μL, 0.05 mmol) were added under Ar. The mixture was stirred for 1 h, one drop of pyridine was added to destroy the catalyst, and the mixture was diluted with CH_2Cl_2 (50 mL), filtered, washed with aq $NaHCO_3$ and water, and concentrated. Column chromatography of the residue (1:1 heptane–EtOAc) afforded **11** (228 mg, 61%); R_f 0.18 (1:1 heptane–EtOAc). ^{1}H NMR data: δ 6.19 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 9.8$ Hz, H-3), 5.89 (m, 1 H, =CH–), 5.55–5.20 (m, 9 H, H-1,2,4, H-2′,3′,4′,6′, $=CH_2$), 4.40–4.05 (m, 5 H, H-5,7a′,7b′, OCH_2), 3.82 (dd, 1 H, $J_{5,6a}$ 6.6, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.64 (dd, 1 H, $J_{5,6b}$ 2.0 Hz, H-6b), 2.17, 2.13, 2.04, 2.03, 1.99 (5 s, 15 H, 5 Ac). ^{13}C NMR data: δ 170.4–169.6 (5 C, CH_3CO), 165.7–165.4 (3 C, Ph*C*O), 118.2 ($=CH_2$), 97.6 (C-1′), 94.9 (C-1), 71.85, 70.39, 69.5, 69.4, 69.1, 69.0, 68.9, 68.6 (C-2,3,4,5, C-2′,3′,5′, OCH_2), 67.1 (C-6′), 66.65 (C-6), 64.8 (C-4′), 62.4 (C-7′), 20.7–20.6 (CH_3CO). LSIMS (+): Calcd for $C_{47}H_{50}O_{20}$ + Na: *m/z* 957. Found: *m/z* 957.

*Allyl 2,3-di-O-benzoyl-6-O-(2,3,4,6,7-penta-O-acetyl-*L*-glycero-α-*D*-manno-heptopyranosyl)-α-*D*-glucopyranoside* (**12**).—A mixture of the diol **8** (38 mg, 0.089 mmol) and 4A molecular sieves (200 mg) was stirred at room temperature for 0.5 h, then imidate **4** (50 mg, 0.09 mmol) and trimethylsilyl triflate (0.5 mL of 0.04 M solution in CH_2Cl_2) were added under Ar, and stirring was continued for 3 h. The mixture was worked-up as in the previous experiment and the product was purified by column chromatography to give **12** (27 mg, 37%); R_f 0.66 (3:2 benzene–EtOAc); $[\alpha]_D$ +101° (*c* 1.11). ^{1}H NMR data: δ 5.98–5.64 (m, 2 H, =CH–, H-3), 5.40–5.19 (m, 7 H, H-1,2, H-2′,3′,4′,6′, $=CH_2$), 4.98 (bs, 1 H, H-1′), 4.42 (dd, 1 H, $J_{6,7a}$ 4.9, $J_{7a,7b}$ 11.5 Hz, H-7′a), 4.30–3.80 (m, 8 H, H-4,5,6a,6b, H-5′,7′b, OCH_2), 2.20, 2.14, 2.06, 2.01, 1.99 (5 s, 15 H, 5 Ac). ^{13}C NMR data: δ 170.6–169.6 (5 C, CH_3CO), 167.8, 165.7 (Ph*C*O), 133.5, 133.2 (3 C, Ph, $CH_2CH{=}CH_2$), 129.9–128.3 (Ph), 117.85 ($CH_2CH{=}CH_2$), 97.85 (C-1′), 95.05 (C-1), 74.9 (C-4), 71.0, 70.6, 69.4 (2 C), 69.2, 68.65 (2 C) (C-2,3,5, C-2′,3′,5′, $CH_2CH{=}CH_2$), 67.2 (C-6′), 66.1 (C-6), 64.9 (C-4′), 62.4 (C-7′), 20.9, 20.7 (2 C), 20.6 (5 C, CH_3CO). LSIMS (+): Calcd for $C_{40}H_{46}O_{19}$ + Na: *m/z* 853. Found: *m/z* 853.

*Allyl 6-O-(*L*-glycero-α-*D*-manno-heptopyranosyl)-α-*D*-glucopyranoside* (**1**).—To a solution of **11** (196 mg, 0.21 mmol) in 10:1 MeOH–CH_2Cl_2 (3 mL) was added 1 M methanolic NaOMe (0.3 mL) and, after 4 h at room temperature, the mixture was neutralized with cation-exchange resin (H^+), filtered, and concentrated. The residue was diluted with water (2 mL) and filtered through a Sep-Pak C_{18} cartridge; the disaccharide was eluted with water (5–10 mL) and the nonpolar products with MeOH. The aqueous solution was concentrated to 2 mL, and subjected to gel filtration to give a disaccharide fraction (V_{max} 96 mL). After

evaporation and drying, the disaccharide **1** was obtained (64 mg, 74%); $[\alpha]_D$ +69.5° (*c* 1, H_2O). ^{13}C NMR data: δ 135.1 ($CH_2CH{=}CH_2$), 100.6 (C-1′), 98.8 (C-1), 74.8 (C-3), 72.8, 72.6, 72.3, 71.4 (2 C), 70.9, 70.2, 70.1, (C-2,4,5, C-2′,3′,5′,6′, OCH_2), 67.5, 66.55 (C-6,4′), 64.5 (C-7′). LSIMS (+): Calcd for $C_{16}H_{28}O_{12}$ + Na: *m/z* 435.1479. Found: *m/z* 435.1480.

*3,4,6-Tri-*O*-acetyl-2-*O*-(2,3,4,6-tetra-*O*-acetyl-α- and -β-*D*-glucopyranosyl)-α-*D*-glucopyranosyl bromides* (**15** *and* **16**).—To a stirred solution of 1,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose (5.3 g, 15.2 mmol) in MeCN (17 mL) were successively added mercuric cyanide (3.8 g, 15.2 mmol), mercuric bromide (2.7 g, 7.6 mmol), and a solution of tetra-*O*-acetyl-α-D-glucopyranosyl bromide (12.5 g, 30 mmol) in MeCN (20 mL). The mixture was stirred at room temperature for 2 h, diluted with $CHCl_3$ (150 mL), washed with aq 10% KI (2 × 50 mL) and water (50 mL), and concentrated. Column chromatography (4:1 benzene–EtOAc) gave a mixture of **13** and **14** (9.0 g, 87%) in the ratio 10:11. ^{13}C NMR data: δ 101.0 (C-1′ sophorose), 95.45 (C-1′ kojibiose), 90.2 (C-1 sophorose), 88.4 (C-1 kojibiose). A solution of this mixture (9.0 g) in 1:2 $CHCl_3$–acetic acid (45 mL) was treated with acetyl bromide 4.7 mL) and water (1.0 mL) with cooling. After 4 h at room temperature, the mixture was poured into ice (250 g) and extracted with $CHCl_3$ (3 × 100 mL). The extract was washed with water (2 × 100 mL), aq $NaHCO_3$ (2 × 100 mL), and water (100 mL), dried, and concentrated to the volume of 10–15 mL. After addition of ether (50 mL), the bromide **16** crystallized immediately and was separated by filtration (3.2 g, 34.5%); mp 180–181°C; $[\alpha]_D$ +97° (*c* 1.0); lit[20]: mp 190–191°C; $[\alpha]_D$ +97.4° (*c* 0.41). ^1H NMR data: δ 6.45 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.48 (pt, 1 H, $J_{2,3} \approx J_{3,4}$ = 10.0 Hz, H-3), 5.20–5.06 (m, 3 H, H-4,3′,4′), 4.99 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.0 Hz, H-2′), 4.70 (d, 1 H, H-1′), 4.35 (dd, 1 H, $J_{5,6a}$ 4.2, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.30 (m, 1 H, H-5), 4.26 (dd, 1 H, $J_{5,6a}$ 2.7, $J_{6a,6b}$ 12.8 Hz, H-6′a), 4.17 (dd, 1 H, $J_{5,6b}$ 4.4 Hz, H-6′b), 4.08 (dd, 1 H, $J_{5,6b}$ 2.3 Hz, H-6b), 3.60 (dd, 1 H, H-2′), 3.68 (m, 1 H, H-5), 2.11–2.01 (7 s, 21 H, 7 Ac).

The filtrate was concentrated to dryness and the residue was chromatographed (4:1 benzene–EtOAc) to give **15** (2.8 g, 30%); $[\alpha]_D$ +207° (*c* 1.1); lit.[10]: $[\alpha]_D$ +218.5° (*c* 1.2). ^1H NMR data: δ 6.4 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.52 (pt, 1 H, $J_{2,3} \approx J_{3,4}$ = 10.0 Hz, H-3), 5.38 (dd, 1 H, $J_{2,3}$ 10.5, $J_{3,4}$ 9.5 Hz, H-3′), 5.23 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.08 (pt, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 5.05 (pt, 1 H, $J_{4,5}$ 10.5 Hz, H-4′), 4.79 (dd, 1 H, H-2), 4.50 (dd, 1 H, $J_{5,6a}$ 3.9, $J_{6a,6b}$ 10.5 Hz, H-6a), 4.30 (m, 1 H, H-5), 4.19 (d, 2 H, $J_{5,6}$ 3.0 Hz, H-6′a,6′b), 4.14–4.02 (m, 2 H, H-5′,6b), 3.85 (dd, 1 H, H-2), 2.11–2.01 (7 s, 21 H, 7 Ac).

*Allyl 3,4,6-tri-*O*-acetyl-2-*O*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)-α-*D*-glucopyranoside* (**17**).—A mixture of the glycosyl bromide **15** (2.06 g, 2.94 mmol), tetrabutylammonium bromide (1.9 g, 5.9 mmol), allyl alcohol (2.04 mL, 30 mmol), and 3A molecular sieves (5 g) was stirred at 65°C for 20 h. The course of the reaction was monitored by TLC of an aliquot pretreated on a plate with bromine vapours. The reaction product had R_f 0.57, whereas the starting bromide **15** had R_f 0.50 (3:2 benzene–ether). After dilution with $CHCl_3$ (100 mL) and filtration

through Celite, the solution was washed with water (3 × 50 mL), concentrated, and chromatographed with 5:1 benzene–ether. Eluted first was **17** (1.73 g, 87%); R_f 0.50 (3:2 benzene–ether); mp 106–108°C; $[\alpha]_D$ +175° (*c* 1.1). ^{1}H NMR data: δ 5.90 (m, 1 H, =CH–), 5.46 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 9.5$ Hz, H-3), 5.37 (dd, 1 H, $J_{2,3}$ 10.7, $J_{3,4}$ 9.2 Hz, H-3′), 5.34, 5.24 (2 m, 2 H, $=CH_2$), 5.19 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1′), 5.03 (dd, 1 H, $J_{4,5}$ 10.2 Hz, H-4′), 5.00 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.96 (dd, 1 H, $J_{4,5}$ 10.4 Hz, H-4), 4.55 (dd, 1 H, H-2′), 4.26 (dd, 1 H, $J_{5,6a}$ 4.7, $J_{6a,6b}$ 12.6 Hz, H-6a), 4.21 (dd, 1 H, $J_{5,6a}$ 5.0, $J_{6a,6b}$ 12.8 Hz, H-6′a), 4.19 (m, 1 H, OCH_2), 4.13 (dd, 1 H, $J_{5,6b}$ 2.5 Hz, H-6′b), 4.07–3.97 (m, 4 H, H-5,6b,5′, OCH_2), 2.09, 2.07, 2.04, 2.02, 2.00, 1.99 (7 s, 21 H, 7 Ac). ^{13}C NMR data: δ 170.5–169.5 (CH_3CO), 133.05 ($CH_2CH=CH_2$), 118.3 ($=CH_2$), 94.4 (2 C, C-1,1′), 74.6 (C-2), 71.2 (C-3), 70.9 (C-2′), 69.7 (C-3′), 68.7, 68.4 (C-4,4′), 68.0 (2 C), 67.3 (C-5,5′, OCH_2), 61.7, 61.3 (C-6,6′), 20.6 (CH_3CO). Anal. Calcd for $C_{29}H_{40}O_{18}$: C, 51.48; H, 5.96. Found: C, 51.38; H, 6.11.

Eluted next was a mixture of **17** and its β anomer (287 mg). After repeated chromatography, the latter was obtained in a pure state; R_f 0.46 (3:2 benzene–ether). ^{1}H NMR data: δ 5.90 (m, 1 H, =CH–), 5.55 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1′), 5.35 (dd, 1 H, $J_{2,3}$ 10.4, $J_{3,4}$ 9.5 Hz, H-3′), 5.33–5.18 (m, 2 H, $=CH_2$), 5.23 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 9.4$ Hz, H-3), 5.06 (dd, 1 H, $J_{4,5}$ 10.4 Hz, H-4′), 4.98 (dd, 1 H, $J_{4,5}$ 9.3 Hz, H-4), 4.52 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.27 (dd, 1 H, $J_{5,6a}$ 5.0, $J_{6a,6b}$ 7.4 Hz, H-6a), 4.34–3.98 (m, 6 H, H-6b,5′,6′a,6′b, OCH_2), 3.71 (dd, 1 H, H-2), 3.69 (m, 1 H, H-5), 2.11–2.00 (7 s, 21 H, 7 Ac).

*Allyl 3-O-benzoyl-4,6-O-benzylidene-2-O-(2,3-di-O-benzoyl-4,6-O-benzylidene-α-*D*-glucopyranosyl)-α-*D*-glucopyranoside* (**20**).—Deacetylation of **17** (2.08 g, 3.07 mmol) was carried out by treatment of its solution in abs MeOH (40 mL) with M methanolic NaOMe for 4 h at room temperature. After neutralization of the mixture with cation-exchange resin (H^+), the solution was concentrated to give allyl α-kojibioside (**18**; 1.15 g, 98.3%) as a yellow syrup. ^{13}C NMR data: δ 134.5 ($CH_2CH=CH_2$), 120.3 ($CH_2CH=CH_2$), 97.3 (C-1′), 95.6 (C-1), 76.3 (C-2), 73.9 (C-3′), 73.03, 72.98, 72.68, 72.59 (C-3,5,2′,5′), 70.8, 70.7 (C-4,4′), 68.7 (OCH_2), 61.75, 61.6 (C-6,6′).

Compound **18** was mixed with MeCN (40 mL), $PhCH(OEt)_2$ (3 mL), and a catalytic amount of toluene-*p*-sulfonic acid monohydrate and stirred at 30°C until complete dissolution of **18** occurred. The solution was treated with pyridine (2 mL) and concentrated. The residue was dried in vacuo and crystallized from EtOAc–hexane to give **19** (1.3 g, 76%); mp 230°C; $[\alpha]_D$ +119° (*c* 1.04). Conventional benzoylation of **19** followed by column chromatography afforded **20** (1.44 g, 71%); R_f 0.84 (19:1 benzene–EtOAc); mp 200–203°C (ether–hexane); $[\alpha]_D$ +154.5° (*c* 1.04). ^{1}H NMR data: δ 5.96 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 10.0$ Hz, H-3′), 5.95 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 10.0$ Hz, H-3), 5.73 (m, 1 H, =CH–), 5.50 (s, 1 H, PhC*H*), 5.49 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1′), 5.40 (s, 1 H, PhC*H*′), 5.23, 5.12 (2 m, 2 H, $=CH_2$), 5.12 (dd, 1 H, H-2′), 4.93 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 4.28 (dd, 1 H, $J_{5,6a}$ 5.0, $J_{6a,6b}$ 10.5 Hz, H-6a), 4.12–3.97 (m, 5 H, H-2,5,5′,6′a, OCH_2), 3.63 (m, 1 H, OCH_2), 3.76 (pt, 1 H, $J_{4,5}$

10.0 Hz, H-4'), 3.74 (pt 2 H, $J_{3,4}$ 10.0, $J_{5,6b} \approx J_{6a,6b}$ = 10.0 Hz, H-4,6b), 3.51 (m, 1 H, H-6'b). Anal. Calcd for $C_{50}H_{46}O_{14}$: C, 68.95; H, 5.32. Found: C, 68.69; H, 5.35.

Debenzylidenation of **20** (270 mg, 0.30 mmol) was performed by heating at 55°C in the presence of pyridinium perchlorate (60 mg, 0.33 mmol) in 1:2 MeCN–MeOH for 1.5 h. The solution was treated with pyridine (0.1 mL), diluted with $CHCl_3$ (100 mL), and washed with aq $NaHCO_3$ and water. The residue was chromatographed using successive elution with benzene (nonpolar products), 9:1 benzene–ether (unreacted **20**), 3:2 benzene–ether (monoacetals **21** and **22**), and EtOAc (tetraol **23**).

Compound **21** (79 mg, 28%): R_f 0.46 (3:2 benzene–ether); mp 177–179°C (from ether–hexane, after softening at 150°C); $[\alpha]_D$ +201.5° (*c* 0.8). ^{1}H NMR data: δ 5.92 (pt, 1 H, $J_{2,3} \approx J_{3,4}$ = 9.9 Hz, H-3'), 5.62 (m, 2 H, H-3, =CH–), 5.47 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1'), 5.41 (s, 1 H, PhC*H*), 5.17, 5.06 (2 m, 2 H, $=CH_2$), 5.10 (dd, 1 H, H-2'), 4.93 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.12–3.97 (m, 3 H, H-5,6a,6'a), 3.92 (dd, 1 H, H-2), 3.88–3.50 (m, 7 H, H-4,6b, H-4',5',6'b, OCH_2). Anal. Calcd for $C_{43}H_{42}O_{14}$: C, 65.98; H, 5.41. Found: C, 65.80; H, 5.25.

Compound **22** (43 mg, 14%): R_f 0.50 (3:2 benzene–ether). ^{1}H NMR data: δ 5.93 (pt, 1 H, $J_{2,3} \approx J_{3,4}$ = 9.2 Hz, H-3), 5.72–5.54 (m, 2 H, H-3', =CH–), 5.50 (s, 1 H, PhC*H*), 5.41 (d, 1 H, $J_{1,2}$ 4.9 Hz, H-1'), 5.26, 5.06 (2 m, 1 H, $=CH_2$), 5.08 (dd, 1 H, $J_{2,3}$ 9.2 Hz, H-2'), 4.98 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.28 (dd, 1 H, $J_{5,6a}$ 4.8, $J_{6a,6b}$ 10.3 Hz, H-6a), 4.07–3.90 (m, 3 H, H-2,5, OCH_2), 3.90–3.42 (m, 7 H, H-4,6, H-4',5',6'a,6'b, OCH_2).

Compound **23** (44 mg, 18%): R_f 0.30 (EtOAc); mp 160–162°C (EtOAc–hexane); $[\alpha]_D$ +231.5° (*c* 1). ^{1}H NMR data: δ 5.69–5.52 (m, 3 H, H-3,3', =CH–), 5.40 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1'), 5.23, 4.99 (2 m, 2 H, $=CH_2$), 5.03 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 10.2 Hz, H-2'), 4.92 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.02–3.50 (m, 10 H, H-4,5,6a,6b, H-4',5'-6'a,6'b, OCH_2). Anal. Calcd for $C_{36}H_{38}O_{14}$: C, 62.24; H, 5.51. Found: C, 62.00; H, 5.44.

*Allyl 3,4,6-tri-*O*-benzoyl-2-*O*-(2,3-di-*O*-benzoyl-α-*D*-glucopyranosyl)-α-*D*-glucopyranoside* (**24**).—Diol **21** (79 mg, 0.1 mmol) was benzoylated as usual, to give a completely protected product which was dissolved in $CHCl_3$ and treated with 90% CF_3CO_2H. After 1 h at room temperature, the solution was washed with aq $NaHCO_3$ and concentrated, and the residue was subjected to column chromatography (4:1 benzene–ether) to give diol **24** (74 mg, 82%); mp 199–202°C (from EtOAc–hexane); $[\alpha]_D$ +169° (*c* 1.5). ^{1}H NMR data: δ 6.06 (pt, 1 H, $J_{2,3} \approx J_{3,4}$ = 9.4 Hz, H-3), 5.64 (m, 1 H, =CH–), 5.56 (pt, 1 H, $J_{2,3}$ 9.8, $J_{3,4}$ 8.8 Hz, H-3'), 5.54 (pt, 1 H, $J_{4,5}$ 9.4 Hz, H-4), 5.42 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1'), 5.14, 5.04 (2 m, 2 H, $=CH_2$), 5.07 (dd, 1 H, H-2'), 5.02 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.52 (dd, 1 H, $J_{5,6a}$ 2.5, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.40 (dd, 1 H, $J_{5,6b}$ 4.8 Hz, H-6b), 4.34 (m, 1 H, H-5), 4.07 (dd, 1 H, H-2), 4.04, 3.61 (2 m, 2 H, OCH_2), 3.78–3.65 (m, 2 H, H-4',5'), 3.60–3.48 (m, 2 H, H-6'a,6'b). ^{13}C NMR data: δ 170.7–165.4 (Ph*C*O), 133.5–128.4 (Ph, $CH_2CH{=}CH_2$), 118.2 ($=CH_2$), Anal. Calcd for $C_{50}H_{46}O_{16}$: C, 66.51; H, 5.14. Found: C, 66.27; H, 4.95.

Allyl 2-O-[6-O-(L-glycero-α-D-manno-heptopyranosyl)-α-D-glucopyranosyl]-α-D-glucopyranoside (**2**).—A mixture of the imidate **4** (80 mg, 142 μmol), diol **24** (128 mg, 142 μmol), and 4A molecular sieves (200 mg) in CH_2Cl_2 (3 mL) was stirred for 1 h, trimethylsilyl triflate (5 μL, 26 μmol) was added under Ar, and stirring was continued for 1 h at room temperature. Work-up as described for **11** and column chromatography with 1:1 hexane–EtOAc afforded trisaccharide derivative **25** in a yield of 97 mg (52.5%). ^{1}H NMR data: δ 6.03 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 10.0$ Hz, H-3), 5.58 (m, 1 H, =CH–), 5.56 (pt, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 5.48 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 10.0$ Hz, H-3′), 5.45 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1′), 5.30–5.20 (m, 3 H, H-2″,4″,6″), 5.15 (dd, 1 H, H-2′), 5.08, 4.98 (2 m, 2 H, $=CH_2$), 5.01 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.63 (bs, 1 H, H-1″), 4.50 (dd, 1 H, $J_{5,6a}$ 3.0, $J_{6a,6b}$ 12.1 Hz, H-6a), 4.42 (dd, 1 H, $J_{5,6b}$ 5.6 Hz, H-6b), 4.37–4.26 (m, 1 H, H-5), 4.25–4.12 (m, 2 H, H-3″,7″a), 4.07 (dd, 1 H, H-2), 4.07–3.95 (m, 3 H, H-5″,7″b, OCH_2), 3.85–3.65 (m, 3 H, H-4′,5′, OCH_2), 3.53 (dd, 1 H, $J_{5,6a}$ 2.5, $J_{6a,6c}$ 11.0 Hz, H-6′a), 3.20 (dd, 1 H, $J_{5,6b}$ 1.3 Hz, H-6′b), 2.19, 2.12, 2.10, 2.08, 2.07 (5 s, 15 H, 5 Ac). ^{13}C NMR data: δ 170.7–165.4 (10 C, R*C*O), 133.5–128.4 (Ph, $CH_2CH{=}CH_2$), 118.2 ($=CH_2$), 97.8 (C-1″), 95.2, 94.9 (C-1,1′), 75.8, 74.4 (C-2,4′), 71.5, 71.3, 70.9, 69.8, 69.5, 69.2, 68.9, 68.7, 68.5, 67.8 (C-3,4,5, C-2′,3′,5′, C-2″,3″,5″, OCH_2), 67.3 (C-6″), 65.2 (C-6′), 64.9 (C-4″), 63.25 (C-6), 62.6 (C-7″), 20.75 (CH_3CO).

Deacetylation of **25** was carried out as described for **11**, and the product was purified on Sep-Pak followed by gel filtration (V_{max} at 88 mL) to give the trisaccharide **2** in 87% yield; $[\alpha]_D$ +125° (*c* 1.04, H_2O). ^{13}C NMR data (D_2O): δ 134.8 ($CH_2CH{=}CH_2$), 120.4 ($=CH_2$), 100.9 (C1″), 97.7 (C-1′), 95.9 (C-1), 76.8 (C-2), 74.5 (C-3′), 73.2, 72.8 (3 C), 72.3, 71.6, 71.4, 71.1, 70.8, 70.3, 69.9 (11 C, C-3,4,5, C-2′,4′,5′, C-2″,3″,5″,6″, OCH_2), 67.5 (C-6′), 66.45 (C-4″), 64.6 (C-7″), 62.0 (C-6). LSIMS (+): Calcd for $C_{22}H_{38}O_{17}$ + Na: *m/z* 597.2007. Found: *m/z* 597.2007.

Allyl 2-O-benzoyl-4,6-O-benzylidene-α-D-glucopyranoside (**26**).—4,6-*O*-Benzylidene derivative **27**[15] (3.08 g, 10.0 mmol) was boiled in benzene (50 mL) until 10 mL of the solvent was distilled off, then dibutyltin oxide (2.5 g, 10 mmol) was added, and the solution was boiled in a Dean–Stark apparatus for 2 h. The mixture was cooled, benzoyl chloride (1.1 mL, 10 mmol) in benzene (5 mL) was added dropwise, and the solution was kept for 3 h, diluted with ether (100 mL), washed with aq 10% KF (2 × 50 mL) and water (2 × 50 mL), and concentrated. Column chromatography of the residue (9:1 benzene–ether) yielded **26** (syrup, 3.54 g, 86%); $[\alpha]_D$ +98° (*c* 1.0). ^{1}H NMR data: δ 5.84 (m, 1 H, =CH–), 5.29, 5.16 (2 m, 2 H, $=CH_2$), 5.23 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.08 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 4.38 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 9.5$ Hz, H-3), 4.32 (dd, 1 H, $J_{5,6a}$ 5.0, $J_{6a,6b}$ 10.0 Hz, H-6a), 4.21 (m, 1 H, OCH_2), 4.05–3.93 (m, 2 H, H-5, OCH_2), 3.77 (pt, 1 H, $J_{5,6b}$ 10.0 Hz, H-6b), 3.61 (pt, 1 H, $J_{4,5}$ 9.5 Hz, H-4).

1,3,4,6-Tetra-O-acetyl-2-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-α-D-glucopyranose (**28**).—A solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide, obtained from the corresponding 1-*p*-nitrobenzoate (11.7 g, 17.36 mmol) by

reaction with HBr in CH_2Cl_2, in nitromethane (50 mL) was added dropwise to a mixture of 1,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose (6.0 g, 17.2 mmol), mercuric cyanide (4.3 g, 17 mmol), and 3A molecular sieves (5 g), which was previously stirred for 1 h in benzene (50 mL). The mixture was stirred overnight and subjected to the conventional work-up. Column chromatography of the products gave **28** (11.2 g, 77%), a small amount of its β isomer (340 mg), and 2.1 g of their mixture. Compound **28**: $[\alpha]_D$ +90.5° (*c* 1.2); lit.[12] +94° (*c* 1.0). ^{1}H NMR data: δ 6.52 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.54 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 10.2$ Hz, H-3), 5.14 (pt, 1 H, $J_{4,5}$ 10.2 Hz, H-4), 5.15 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1′), 4.34 (dd, 1 H, $J_{5,6a}$ 4.1, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.20–4.08 (m, 2 H, H-5,6b), 4.03 (dd, 1 H, H-2), 3.94–3.85 (m, 2 H, H-3′,5′), 3.78–3.76 (m, 3 H, H-4′,6′a,6′b), 3.56 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-2′), 2.12, 2.07, 2.02, 1.99 (4 s, 12 H, 4 Ac).

Sophorose derivative: $[\alpha]_D$ +79° (*c* 1.48). ^{1}H NMR data: δ 6.50 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 5.56 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 10.0$ Hz, H-3), 5.10 (pt, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.52 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1′), 4.35 (m, 1 H, H-6a), 4.14–3.96 (m, 2 H, H-5,6b), 4.00 (dd, 1 H, H-2), 3.70 (d, 1 H, $J_{5,6a}$ 3.2 Hz, H-6′a), 3.68–3.58 (m, 3 H, H-3′,4′,6′b), 3.50–3.40 (m, 2 H, H-2′,5′), 2.18, 2.10, 2.04, 1.80 (4 s, 12 H, 4 Ac).

*1,3,4,6-Tetra-*O*-acetyl-2-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-trityl-α-*D*-glucopyranosyl)-α-*D*-glucopyranose* (**29**).—A mixture of the disaccharide derivative **28** (4.03 g, 4.63 mmol) and 10% Pd–C (4 g) in 1:1 EtOAc–EtOH (40 mL) was stirred for 6 h at 38°C under H_2, cooled, and filtered through Celite. The filtrate was evaporated and twice coevaporated with pyridine, the residue was dissolved in abs pyridine (20 mL), chlorotriphenylmethane (2.58 g, 9.2 mmol) was added, and the mixture was kept overnight at room temperature. After the usual work-up, the product was purified by column chromatography (benzene → 2:1 benzene–ether) and treated with benzoyl chloride (3.2 mL, 27.6 mmol) in pyridine (20 mL) for 2 h. The mixture was treated with water (0.1 mL), kept for 0.5 h, diluted with $CHCl_3$ (150 mL), and washed with aq $NaHCO_3$ and water. The solution was concentrated and the residue was chromatographed on a silica gel column (9:1 benzene–ether) to give **29** (4.4 g, 90%); $[\alpha]_D$ +109° (*c* 1.2). ^{1}H NMR data: δ 6.43 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.98 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 10$ Hz, H-3′), 5.59 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 10$ Hz, H-3), 5.67 (pt, 1 H, $J_{4,5}$ 10 Hz, H-4′), 5.55 (d, 1 H, H-1′), 5.33 (dd, 1 H, $J_{1,2}$ 4.0 Hz, H-2′), 5.20 (pt, 1 H, $J_{4,5}$ 10 Hz, H-4), 4.42 (ddd, 1 H, H-5′), 4.31 (dd, 1 H, $J_{5,6a}$ 4.5, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.05–4.14 (m, 2 H, H-5,6b), 3.33 (dd, 1 H, $J_{5,6a}$ 5.5, $J_{6a,6b}$ 10.5 Hz, H-6′a), 3.27 (dd, 1 H, $J_{5,6b}$ 3.0 Hz, H-6′b), 2.11, 2.09, 2.08, 1.50 (4 s, 12 H, 4 Ac). Anal. Calcd for $C_{60}H_{56}O_{18}$: C, 67.66; H, 5.30. Found: C, 67.72; H, 5.23.

*1,3,4,6-Tetra-*O*-acetyl-2-*O*-(2,3,4-tri-*O*-benzoyl-α-*D*-glucopyranosyl)-α-*D*-glucopyranose* (**30**).—Hydrolysis of the trityl ether **29** (5.8 g, 5.4 mmol) was performed in $CHCl_3$ (50 mL) containing 90% CF_3CO_2H (5 mL) for 20 min at room temperature. The solution was poured into water (50 mL) and extracted with $CHCl_3$, and the extract was washed with aq $NaHCO_3$ and water, and concentrated. Column chromatography of the residue yielded the alcohol **30** (2.42 g, 54%); $[\alpha]_D$ +136° (*c* 1.1). ^{1}H NMR data: δ 6.40 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 6.09 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 10.5$

Hz, H-3'), 5.55 (pt, 1 H, $J_{2,3} \approx J_{3,4}$ = 10.0 Hz, H-3), 5.53 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1'), 5.53 (pt, 1 H, $J_{4,5}$ 10.5 Hz, H-4'), 5.30 (dd, 1 H, H-2'), 5.10 (pt, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.27 (dd, 1 H, $J_{5,6a}$ 4.7, $J_{6a,6b}$ 13.0 Hz, H-6a), 4.12 (m, 1 H, H-5'), 4.10–4.0 (m, 3 H, H-2,5,6b), 3.87 (dd, 1 H, $J_{5,6a}$ 2.2, $J_{6a,6b}$ 13.3 Hz, H-6'a), 3.71 (dd, 1 H, $J_{5,6b}$ 3.7 Hz, H-6'b), 2.15 (s, 3 H, Ac), 2.05 (3 s, 9 H, 3 Ac). Anal. Calcd for $C_{41}H_{42}O_{18}$: C, 59.85; H, 5.15. Found: C, 59.66; H, 5.17.

*1,3,4,6-Tetra-*O*-acetyl-2-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-chloroacetyl-α-*D*-glucopyranosyl)-α-*D*-glucopyranose* (**31**).—To a cooled (0°C) solution of the alcohol **30** (2.42 g, 2.94 mmol) in CH_2Cl_2 containing pyridine (0.32 mL) was added chloroacetyl chloride (3.7 mL, 3.7 mmol) in CH_2Cl_2 dropwise, and the mixture was stirred for 0.5 h, diluted with $CHCl_3$ (100 mL), and washed with M HCl (20 mL), aq $NaHCO_3$ (20 mL), and water (20 mL). Evaporation of the solvent and chromatography of the residue afforded **31** (2.70 g, 100%); $[\alpha]_D$ +141° (*c* 1.7). ^{1}H NMR data: δ 6.36 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 6.01 (pt, 1 H, $J_{2,3} \approx J_{3,4}$ = 10.3 Hz, H-3), 5.54 (pt, 1 H, $J_{2,3} \approx J_{3,4}$ = 10.0 Hz, H-3'), 5.49 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1'), 5.30 (dd, 1 H, H-2), 5.10 (pt, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.515 (bd, 1 H, $J_{6a,6b}$ 11.0 Hz, H-6'a), 4.39 (m, 1 H, H-5'), 4.33 (dd, 1 H, $J_{5,6b}$ 6.5 Hz, H-6'b), 4.28 (dd, 1 H, $J_{5,6a}$ 4.3, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.21, 4.20 (AB, 2 H, $COCH_2Cl$), 4.11 (dd, 1 H, H-2), 4.12–4.05 (m, 1 H, H-5), 4.03 (dd, 1 H, $J_{5,6b}$ 2.0 Hz, H-6b), 2.17, 2.07, 2.05, 1.60 (4 s, 12 H, 4 Ac). Anal. Calcd for $C_{43}H_{43}O_{19} \cdot H_2O$: C, 56.30; H, 4.94. Found: C, 56.41; H, 4.60.

*3,4,6-Tri-*O*-acetyl-2-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-chloroacetyl-α-*D*-glucopyranosyl)-α-*D*-glucopyranosyl bromide* (**32**).—A solution of **31** in a mixture of CH_2Cl_2 (3 mL) and acetic acid (10 mL) containing acetyl bromide (1.58 mL, 20 mmol) was treated with water (0.32 mL, 18 mmol) in acetic acid (5 mL) at 0°C. After 4 h at room temperature, the solution was poured into ice–water and extracted with $CHCl_3$ (200 mL). The extract was washed with aq $NaHCO_3$ (2 × 50 mL) and water, then evaporated to dryness, and the residue was chromatographed (3:1 heptane–EtOAc) to give the bromide **32** (2.10 g, 76%); $[\alpha]_D$ +146° (*c* 1.2). ^{1}H NMR data: δ 6.41 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 6.08 (pt, $J_{2,3} \approx J_{3,4}$ = 10.3 Hz, H-3'), 5.59 (pt, 1 H, $J_{2,3} \approx J_{3,4}$ = 9.5 Hz, H-3), 5.58 (pt, 1 H, $J_{4,5}$ 10.4 Hz, H-4'), 5.50 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1'), 5.25 (dd, 1 H, H-2'), 5.1 (pt, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.50–4.25 (m, 5 H, H-5,6a, H-5',6'a,6'b), 4.07 (m, 1 H, H-6b), 3.93 (dd, 1 H, H-2), 2.16, 2.06 (2 s, 6 H, 2 Ac). Anal. Calcd for $C_{41}H_{40}BrClO_{17}$: C, 53.52; H, 4.38. Found: C, 53.57; H, 4.20.

*3,4,6-Tri-*O*-acetyl-2-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-chloroacetyl-α-*D*-glucopyranosyl)-α-*D*-glucopyranose* (**34**).—A mixture of the biosyl bromide **32** (1.79 g), silver carbonate (600 mg), and water (1.5 mL) in acetone (15 mL) was stirred overnight at room temperature, then filtered through Celite, and the filtrate was diluted with $CHCl_3$ (100 mL), washed with aq $NaHCO_3$ (2 × 50 mL) and water (50 mL), and concentrated. Column chromatography (3:1 heptane–EtOAc) of the residue gave **34** (1.42 g, 85%); $[\alpha]_D$ +122° (*c* 1.02).

*3,4,6-Tri-*O*-acetyl-2-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-chloroacetyl-α-*D*-glucopyranosyl)-β- and -α-*D*-glucopyranosyl trichloroacetimidates* (**33** *and* **35**).—To a vigorously stirred solution of **34** (1 g, 1.63 mmol) in CH_2Cl_2 (23 mL) was added K_2CO_3 (0.6

g) and, after 0.5 h, the mixture was treated with trichloroacetonitrile (1.6 mL, 16 mmol) and stirred for 4 h at room temperature. The mixture was diluted with toluene (50 mL), filtered through Celite, concentrated, and chromatographed on silica gel (4:1 benzene–EtOAc). Eluted first was a small amount of **35**, then **33** (yield 48%), and, finally, unreacted **34**.

Compound **33**: $[\alpha]_D$ +69° (*c* 1). ^{1}H NMR data: δ 6.03 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 10.0$ Hz, H-3'), 5.97 (d, 1 H, $J_{1,2}$ 7.0 Hz, H-1), 5.71 (m, 1 H, H-4'), 5.44 (dd, 1 H, H-2'), 4.43 (pt, 1 H, $J_{2,3}$ 7.6, $J_{3,4}$ 9.0 Hz, H-3), 5.24 (dd, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 4.41 (m, 3 H, H-5',6'a,6'b), 4.29 (dd, 1 H, $J_{5,6a}$ 3.5, $J_{6a,6b}$ 12.3 Hz, H-6a), 4.20 (pt, 1 H, H-2), 4.18 (AB, 2 H, $ClCH_2CO$), 4.01 (dd, 1 H, $J_{5,6b}$ 2.5 Hz, H-6b), 3.94 (ddd, 1 H, H-5'), 2.10, 2.09, 2.05 (3 s, 9 H, 3 Ac). Anal. Calcd for $C_{43}H_{41}Cl_4NO_{18} \cdot H_2O$: C, 50.65; H, 4.25; N, 1.37. Found: C, 50.04; H, 4.30; N, 1.64.

Compound **35**: $[\alpha]_D$ +95° (*c* 1.67). ^{1}H NMR data: δ 6.62 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 6.0 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 10.0$ Hz, H-3'), 5.62 (pt, 1 H, $J_{4,5}$ 10.0 Hz, H-4'), 5.56 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 10.0$ Hz, H-3), 5.50 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1'), 5.25 (dd, 1 H, H-2), 5.11 (pt, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.46 (dd, 1 H, $J_{5,6a}$ 2.3, $J_{6a,6b}$ 12.3 Hz, H-6'a), 4.36 (m, 1 H, H-5'), 4.31–4.21 (m, 3 H, H-6a,6b,6'b), 4.20 (AB, 2 H, $ClCH_2CO$), 4.10 (m, 1 H, H-5), 4.07 (dd, 1 H, H-2), 2.13, 2.04 (2 s, 9 H, 3 Ac). Anal. Calcd for $C_{43}H_{41}Cl_4NO_{18} \cdot H_2O$: C, 50.65; H, 4.25; N, 1.37. Found: C, 50.29; H, 4.03; N, 1.63.

Allyl O-*(2,3,4-tri-*O*-benzoyl-α-*D*-glucopyranosyl)-(1 → 2)-*O*-(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1 → 3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-*D*-glucopyranoside* (**36**). —A mixture of the imidate **33** (1.18 g, 1.18 mmol), alcohol **26** (565 mg, 1.37 mmol), and 3A molecular sieves was stirred for 1 h in abs ether (50 mL), trimethylsilyl triflate (0.05 mL, 0.25 mmol) was added, and stirring was continued for 1 h at room temperature under Ar. The mixture was filtered, diluted with $CHCl_3$ (100 mL), washed with aq $NaHCO_3$ (2 × 50 mL) and water (50 mL), and concentrated. Column chromatography of the residue (3:1 heptane–EtOAc) afforded a main fraction (1.145 g; R_f 0.60, 3:2 benzene–EtOAc), unreacted **26** (140 mg), and a product with high chromatographic mobility (138 mg; R_f 0.84, 3:2 benzene–EtOAc). The main fraction was dissolved in MeCN (14 mL) containing water (2 mL), thiourea (500 mg) was added, and the solution was kept for 63 h at room temperature. The solution was diluted with $CHCl_3$ (150 mL), washed with aq $NaHCO_3$ (2 × 50 mL) and water, and evaporated. By means of HPLC (1:1 heptane–EtOAc), three products were isolated. Eluted first was the α anomer **36** (450 mg, 32.5%), followed by the β anomer **37** (91 mg, 6.6%), and glycal **38** (153 mg, 17%).

Compound **36**: $[\alpha]_D$ +195.5° (*c* 1.2). ^{1}H NMR data: δ 6.06 (pt, 1 H, $J_{2,3} \approx J_{3,4} =$ 9.9 Hz, H-3''), 5.77 (m, 1 H, =CH–), 5.63 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1''), 5.60 (s, 1 H, PhC*H*), 5.46 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 9.9$ Hz, H-3'), 5.35 (dd, 1 H, H-2''), 5.30 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1'), 5.31 (pt, 1 H, $J_{4,5}$ 9.9 Hz, H-4''), 5.24, 5.12 (2 m, 2 H, $=CH_2$), 4.91 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.85 (pt, 1 H, $J_{4,5}$ 9.9 Hz, H-4'), 4.54 (dd, 1 H, $J_{2,3}$ 3.8 Hz, H-2), 4.41 (pt, 1 H, $J_{3,4}$ 9.6 Hz, H-3), 4.14 (m, 2 H, H-6'a, OCH_2),

4.01–3.90 (m, 5 H, H-4,5',6'b,5", OCH_2), 3.87 (m, 1 H, H-5), 3.77 (dd, 1 H, H-2'), 3.73 (m, 1 H, H-6"a), 3.57 (m, 1 H, H-6"b), 3.45 (pt, 1 H, $J_{5,6a} \approx J_{6a,6b} = 10.4$ Hz, H-6a), 3.25 (pt, 1 H, $J_{5,6b}$ 10.0 Hz, H-6b), 2.25 (m, 1 H, OH), 2.13, 2.06, 1.63 (3 s, 9 H, 3 Ac). Anal. Calcd for $C_{62}H_{62}O_{23} \cdot H_2O$: C, 62.41; H, 5.41. Found: C, 62.57; H, 5.33.

Compound **37**: $[\alpha]_D$ +108° (*c* 1.11). ^{1}H NMR data: δ 5.93 (pt, 1 H, $J_{2,3} \approx J_{3,4} =$ 9.9 Hz, H-3"), 5.77 (m, 1 H, =CH–), 5.64 (d, 1 H, $J_{1,2}$ 4.1 Hz, H-1"), 5.59 (s, 1 H, PhC*H*), 5.25, 5.12 (2 m, 2 H, $=CH_2$), 5.19 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 9.9$ Hz, H-3'), 5.10 (m, 3 H, H-1,2,4"), 5.07 (dd, 1 H, H-2), 4.95 (pt, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.80 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1'), 4.29 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 9.1$ Hz, H-3), 4.16 (m, 1 H), 4.10–4.04 (m, 2 H, H-6'a, OCH_2), 3.97 (dd, 1 H, $J_{5,6b}$ 2.5, $J_{6a,6b}$ 12.3 Hz, H-6'b), 3.94 (m, 1 H, OCH_2), 3.66 (dd, 1 H, H-2'), 3.64 (m, 1 H), 3.50 (m, 2 H), 3.40 (ddd, 1 H, H-5), 3.34 (dd, 1 H, $J_{5,6b}$ 2.5, $J_{6a,6b}$ 12.8 Hz, H-6), 3.20 (m, 1 H), 2.03, 2.01, 1.96 (3 s, 9 H, 3 Ac). Anal. Calcd for $C_{62}H_{62}O_{23} \cdot H_2O$: C, 62.41; H, 5.41. Found: C, 62.44; H, 5.37.

*3,4,6-Tri-*O*-acetyl-1,5-anhydro-2-*O*-(2,3,4-tri-*O*-benzoyl-α-*D*-glucopyranosyl)-*D*-arabino-hex-1-enitol* (**38**): $[\alpha]_D$ +51° (*c* 1.17). ^{1}H NMR data: δ 6.66 (s, 1 H, H-1), 6.22 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 10.0$ Hz, H-3'), 5.58 (d, 1 H, $J_{3,4}$ 4.7 Hz, H-3), 5.53 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1'), 5.51 (d, 1 H, $J_{4,5}$ 10.0 Hz, H-4'), 5.35 (dd, 1 H, H-2'), 5.18 (d, 1 H, $J_{4,5}$ 6.2 Hz, H-4), 4.40 (dd, 1 H, $J_{5,6a}$ 6.2, $J_{6a,6b}$ 11.6 Hz, H-6a), 4.26–4.08 (m, 3 H, H-5,6b,5'), 3.85–3.70 (m, 2 H, H-6'a,6'b), 2.07, 2.06, 2.00 (3 s, 9 H, 3 Ac). Anal. Calcd for $C_{39}H_{38}O_{16}$: C, 61.41; H, 5.02. Found: C, 61.09; H, 4.83.

Allyl O-*(2,3,4,6,7-penta-*O*-acetyl-*L*-glycero-α-*D*-manno-heptopyranosyl)-(1 → 6)-*O*-(2,3,4-tri-*O*-benzoyl-α-*D*-glucopyranosyl)-(1 → 2)-*O*-(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1 → 3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-*D*-glucopyranoside* (**39**).—A mixture of the trisaccharide **36** (240 mg, 0.20 mmol), imidate **4** (120 mg, 0.22 mmol), and 4A molecular sieves (1 g) in CH_2Cl_2 (4 mL) was stirred for 0.5 h and treated with trimethylsilyl triflate (0.05 mL) under Ar. The mixture was stirred overnight at room temperature, filtered through Celite, and worked-up as usual. Column chromatography (1:1 → 1:2 heptane–EtOAc) gave **39** (170 mg, 52%); $[\alpha]_D$ +157° (*c* 1.07); R_f 0.41 (3:2 benzene–EtOAc). ^{1}H NMR data: δ 6.03 (pt, 1 H, $J_{2,3} \approx J_{3,4} \approx 10$ Hz, H-3"), 5.63 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1"), 5.61 (s, 1 H, PhC*H*), 5.58 (pt, 1 H, $J_{2,3} \approx J_{3,4} = 9.9$ Hz, H-3'), 5.42 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 10.2 Hz, H-2"), 5.39 (dd, 1 H, $J_{1,2}$ 3.4, $J_{2,3}$ 10.2, H-2), 4.90 (d, 1 H, $J_{1,2}$ 3.7, H-1), 4.57 (dd, 1 H, $J_{1,2}$ 3.8, $J_{2,3}$ 9.8, H-2'). LSIMS (+): *m/z* 1599 (1.4%, M + Na), 1575 (0.4%, M – H), 1519 (0.5%, M – OAll), 1165 (0.6%, Hep-Glc-Glc), 877 (2.8%, Hep-Glc), 403 (19%, Hep).

*Allyl 3-*O*-{2-*O*-[6-*O*-(*L*-glycero-α-*D*-manno-heptopyranosyl)-α-*D*-glucopyranosyl]-α-*D*-glucopyranosyl}-α-*D*-glucopyranoside* (**3**).—A solution of the protected tetrasaccharide **39** (170 mg, 0.11 mmol) in $CHCl_3$ (10 mL) was treated with 1 mL of aq 90% CF_3CO_2H for 2 h at room temperature, then diluted with $CHCl_3$ (40 mL), and washed with aq $NaHCO_3$ and water. The debenzylidenated product [112 mg; R_f 0.24, 3:2 benzene–EtOAc; $[\alpha]_D$ +140° (*c* 1.0)] was deacylated and purified as

described for **11**, to give **3** (78 mg, 96%) eluted with V_{max} 83 mL. $[\alpha]_D$ + 124° (*c* 1.1, H_2O). ^{13}C NMR data: δ 100.8 (C-1‴), 99.9 (C-1), 97.7 and 97.4 (C-1′,1″), 81.2 (C-3), 77.0 (C-2′), 74.5 (C-3″), 67.4 (C-6″), 66.2 (C-4‴), 64.5 (C-7‴), 61.7 (2 C, C-6,6′). LSIMS (+): Calcd for $C_{28}H_{48}O_{22}$ + Na: *m/z* 759.2535. Found: *m/z* 759.2525.

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REFERENCES

1 N.V. Bovin, I.A. Ivanova, and A.Ya. Khorlin, *Bioorg. Khim.*, 11 (1985) 662–670.
2 A.Ya. Chernyak, G.V.M. Sharma, L.O. Kononov, P. Radha Krishna, A.B. Levinsky, N.K. Kochetkov, and A.V. Rama Rao, *Carbohydr. Res.*, 223 (1992) 303–309.
3 R. Roy and F. Tropper, *Glycoconjugate J.*, 5 (1988) 203–206.
4 H. Paulsen, A. Wulf, and M. Brenken, *Liebigs Ann. Chem.*, (1991) 1127–1145.
5 O. Holst, U. Zähringer, H. Brade, and A. Zamojski, *Carbohydr. Res.*, 215 (1991) 323–335.
6 E.A. Talley, M.D. Vale, and E. Janovsky, *J. Am. Chem. Soc.*, 67 (1945) 2037–2039.
7 E. Pacsu, *Ber.*, 61 (1928) 1508–1513.
8 N.K. Kochetkov, B.A. Dmitriev, N.E. Byramova, and A.V. Nikolaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1978) 652–656.
9 B. Helferich and J. Zinner, *Chem. Ber.*, 95 (1962) 2604–2611.
10 V. Pozsgay and P. Nanasi, *Carbohydr. Res.*, 68 (1979) 157–160.
11 V. Pozsgay, P. Nanasi, and A. Neszmelyi, *Carbohydr. Res.*, 75 (1979) 310–313.
12 G.O. Aspinall and M.K. Gurjar, *Carbohydr. Res.*, 143 (1985) 266–270.
13 O. Kanie, T. Takeda, N. Hada, and Y. Ogihara, *J. Carbohydr. Chem.*, 10 (1991) 561–581.
14 Z. Doboszewski and A. Zamojski, *Carbohydr. Res.*, 132 (1984) 29–38.
15 H.P. Wessel, *J. Carbohydr. Chem.*, 7 (1988) 263–269.
16 S. David and A. Thieffry, *J. Chem. Soc., Perkin Trans. 1*, (1979) 1568–1573.
17 R.R. Schmidt and J. Michel, *Tetrahedron Lett.*, 25 (1984) 821–824.
18 R.M. Evans and L.N. Owen, *J. Chem. Soc.*, (1949) 244–248.
19 K. Dziewiszek and A. Zamojski, *Carbohydr. Res.*, 150 (1986) 163–171.
20 B. Coxon and H.G. Fletcher, Jr., *J. Org. Chem.*, 26 (1961) 2892–2894.