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Synthesis of ω-(methoxycarbonyl)alkyl and 9-(methoxycarbonyl)-3,6-dioxanonyl glycopyranosides for the preparation of carbohydrate–protein conjugates

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ABSTRACT

ω-(Methoxycarbonyl)alkyl glycopyranosides of D-mannose having C_4, C_7, C_9, C_{12}, and C_{15} carbon chains, L-fucose and 2-acetamido-2-deoxy-D-mannose having C_7 and C_9 carbon chains, D-xylose and 2-acetamido-2-deoxy-L-fucose having a C_9 carbon chain, and 9-(methoxycarbonyl)-3,6-dioxanonyl glycopyranosides of D-mannose, 2-acetamido-2-deoxy-D-mannose, and L-fucose were synthesized as intermediates for coupling to human serum albumin in order to examine the effect of chain length and hydrophobicity of the spacer arm on the binding specificity of lectins. 8-(Methoxycarbonyl)octyl glycosides of β-D-Man-(1 → 2)-α-D-Man, α-D-Man-(1 → 2)-α-D-Man, α-D-ManNAc-(1 → 2)-α-D-Man, β-D-GlcNAc-(1 → 2)-α-D-Man, and their 6-*O*-positional isomers, β-D-Man-(1 → 6)-α-D-Man, α-D-Man-(1 → 6)-α-D-Man, α-D-ManNAc-(1 → 6)-α-D-Man, and β-D-GlcNAc-(1 → 6)-α-D-Man, were also synthesized.

INTRODUCTION

Over the past decade an increasing number of studies have demonstrated the existence of carbohydrate-binding proteins or lectins on the cell surface of various normal and malignant animal cells. It has been suggested that such lectin-like

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molecules might be involved in receptor-specific endocytosis of glycoproteins and cell–cell recognitions[1].

Carbohydrate–protein conjugates[2] that contain several types of spacer arms, such as the C_9 carbon chain[3] which frequently have been used, dioxa[4], amide[5], thioether[6], phenylthiourea[7], or *p*-*N*-acryloylphenyl[8], have been prepared for use as tools for studying the role of carbohydrates in biological and biochemical processes.

Chemical modification can produce changes of the overall charge or conformation of protein to obscure the effect of the attached carbohydrates[9]. However, careful selection of both the spacer arm and the sugar density as well as of the methods for coupling to protein can offer variable insights into the study of binding specificity and lectin properties.

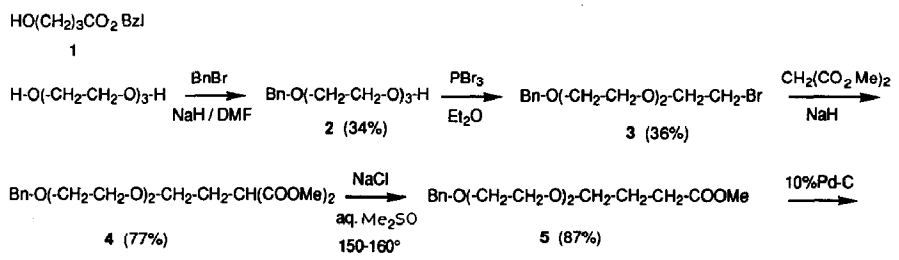
As part of our project of developing carbohydrate sensors as a homing device for cell-specific targeted drug delivery, we synthesized ω-(methoxycarbonyl)alkyl and 9-(methoxycarbonyl)-3,6-dioxanonyl glycopyranosides that can be coupled to proteins and particles in order to examine the effect of chain length and hydrophobicity of the spacer arm on the binding specificity of lectins.

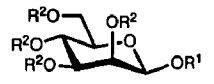
We describe here the details of synthesis of mono- and di-saccharides having C_4, C_7, C_9, C_{12}, and C_{15} carbon chain spacer arms and a C_{10} dioxa-type spacer arm.

RESULTS AND DISCUSSION

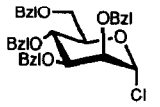
Treatment of triethylene glycol with benzyl bromide in *N*,*N*-dimethylformamide in the presence of an equimolar amount of sodium hydride for 1 h at room temperature gave, after chromatography, a monobenzyl ether **2** in 34% yield. Substitution of the hydroxyl group in **2** with the bromo group by treatment with phosphorus tribromide in anhydrous ether for 1 h at 0° gave 10-phenyl-3,6,9-trioxadecanyl bromide (**3**) in 36% yield. Substitution of the bromo group in **3** with the sodium salt of dimethyl malonate in *N*,*N*-dimethylformamide for 6 h at 40° gave methyl 12-phenyl-2-(methoxycarbonyl)-5,8,11-trioxadodecanoate (**4**) in 77% yield. Demethoxycarbonylation of **4** by treatment with sodium chloride in aqueous dimethyl sulfoxide for 4 h at 150–160° gave methyl 12-phenyl-5,8,11-trioxadodecanoate (**5**) in 87% yield, which was deprotected by catalytic hydrogenolysis over 10% palladium-on-carbon to give the desired 9-(methoxycarbonyl)-3,6-dioxanonanol (**6**) in 99% yield.

Condensation of 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl chloride[10] (**7**) with 3-(benzyloxycarbonyl)propanol (**1**), which was prepared from sodium 4-hydroxybutanoate by treatment with benzyl bromide in *N*,*N*-dimethylformamide for 20 h at room temperature, 11-(methoxycarbonyl)undecanol[11], 14-(methoxylcarbonyl)-tetradecanol[11], and **6** in the presence of silver carbonate and Drierite in dichloromethane, and chromatography of the product on a column of silica gel gave 3-(benzyloxycarbonyl)propyl (**9**), 11-(methoxycarbonyl)undecyl (**12**), 14-





	R^1	R^2
9	$(CH_2)_3CO_2Bzl$	Bzl
10	$(CH_2)_6CO_2Me$	Bzl
11	$(CH_2)_8CO_2Me$	Bzl
12	$(CH_2)_{11}CO_2Me$	Bzl
13	$(CH_2)_{14}CO_2Me$	Bzl
14	$(CH_2)_2O(CH_2)_2O(CH_2)_3CO_2Me$	Bzl
15	$(CH_2)_3CO_2Me$	H
16	$(CH_2)_6CO_2Me$	H
17	$(CH_2)_8CO_2Me$	H
18	$(CH_2)_{11}CO_2Me$	H
19	$(CH_2)_{14}CO_2Me$	H
20	$(CH_2)_2O(CH_2)_2O(CH_2)_3CO_2Me$	H



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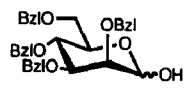

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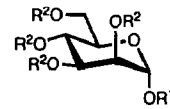


	R^1	R^2
21	$(CH_2)_6CO_2Me$	Bzl
22	$(CH_2)_8CO_2Me$	Bzl
23	$(CH_2)_6CO_2Me$	H
24	$(CH_2)_8CO_2Me$	H

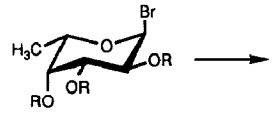
(methoxycarbonyl)tetradecyl (**13**), and 9-(methoxycarbonyl)-3,6-dioxanonyl 2,3,4,6-tetra-*O*-benzyl-β-D-mannopyranosides (**14**) in 63.8, 62.5, 57.8, and 81.2% yields, respectively. ^{1}H-NMR spectra revealed an anomeric proton at δ 4.32 (s) in **9**, at δ 4.35 (s) in **12**, at δ 4.36 (s) in **13**, and at δ 4.46 (s) in **14**. The stereochemical assignment of the glycosidic bond in **9**, **12**, **13**, and **14** was verified by comparison of the specific rotations between both anomers based on Hudson's rules of isorotation[12] and the chemical shift of the anomeric proton in ^{1}H-NMR spectroscopy. Removal of the benzyl groups in **9**, **12**, **13**, and **14** by catalytic hydrogenolysis over 10% palladium-on-carbon gave the 3-(methoxycarbonyl)propyl derivative **15**, which was obtained after esterification with etherial diazomethane, 11-(methoxycarbonyl)undecyl (**18**), 14-(methoxycarbonyl)tetradecyl (**19**), and 9-(methoxycarbonyl)-3,6-dioxa-nonyl β-D-mannopyranosides (**20**) in 80.9, 59.5, 50.5, and 92% yields, respectively.

When **7** was condensed with the C_7 carbon chain spacer arm, 6-(methoxycarbonyl)hexanol[11], in the presence of silver silicate and powdered molecular sieve 4A in toluene and chromatography of the product on a Lobar column, 6-(methoxycarbonyl)hexyl 2,3,4,6-tetra-*O*-benzyl-β-D-mannopyranoside (**10**) and its α anomer (**21**) were obtained in 52.7 and 17.9% yields, respectively. Removal of the benzyl groups from **10** and **21** by catalytic hydrogenolysis over 10% palladium-on-

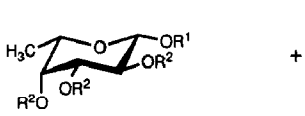
carbon gave 6-(methoxycarbonyl)hexyl β- (**16**) and α-D-mannopyranosides (**23**) in 77 and 73% yields, respectively.

For the synthesis of D-mannopyranosides having a C_9 carbon chain spacer arm, we used the direct 1-*O*-alkylation method reported by Schmidt et al.[13]. Coupling of the sodium salt of 2,3,4,6-tetra-*O*-benzyl-α,β-D-mannopyranose[14] (**8**), prepared by treatment with an equimolar amount of sodium hydride in anhydrous tetrahydrofuran at 0°, with 8-(methoxycarbonyl)octyl trifluoromethanesulfonate[15] gave 8-(methoxycarbonyl)octyl 2,3,4,6-tetra-*O*-benzyl-β-D-mannopyranoside (**11**) and its α anomer (**22**) in 56.7 and 14.9% yields, respectively. Removal of the protecting groups in **11** and **22** by catalytic hydrogenolysis gave 8-(methoxycarbonyl)octyl β-D-mannopyranoside (**17**) and the known α anomer[16] (**24**) in 80.4 and 71% yields, respectively. Synthesis of the anomeric pairs of 8-(ethoxycarbonyl)octyl D-mannopyranosides has also been reported by Ogawa et al.[17].

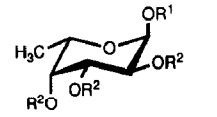
Similarly, condensation of 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide[18] (**25**) with **1**, 6-(methoxycarbonyl)hexanol, 11-(methoxycarbonyl)undecanol, 14-(methoxycarbonyl)tetradecanol, and **6** in the presence of mercuric cyanide in benzene gave 3-(benzyloxycarbonyl)propyl (**27**), 6-(methoxycarbonyl)hexyl (**29**), 11-(methoxycarbonyl)undecyl (**31**), 14-(methoxycarbonyl)tetradecyl (**32**), and 9-(methoxycarbonyl)-3,6-dioxanonyl 2,3,4-tri-*O*-acetyl-β-L-fucopyranosides (**33**) in 64.5, 61.1, 61.7, 75.9, and 58.6% yields, respectively. ^{1}H-NMR spectra revealed a doublet for H-1 at δ 4.38 ($J_{1,2}$ 7.8 Hz) in **27**, at δ 4.42 ($J_{1,2}$ 8.1 Hz) in **29**, at δ 4.42 ($J_{1,2}$ 7.8 Hz) in **31**, at δ 4.42 ($J_{1,2}$ 8 Hz) in **32**, and at δ 4.76 ($J_{1,2}$ 8.1 Hz) in **33**,



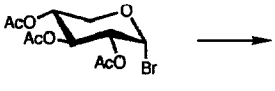
25 R = Ac
26 R = Bzl



	R^1	R^2
27	$(CH_2)_3CO_2Bzl$	Ac
28	$(CH_2)_3CO_2Me$	Ac
29	$(CH_2)_6CO_2Me$	Ac
30	$(CH_2)_8CO_2Me$	Bzl
31	$(CH_2)_{11}CO_2Me$	Ac
32	$(CH_2)_{14}CO_2Me$	Ac
33	$(CH_2)_2O(CH_2)_2O(CH_2)_3CO_2Me$	Ac
34	$(CH_2)_3CO_2Me$	H
35	$(CH_2)_6CO_2Me$	H
36	$(CH_2)_8CO_2Me$	H
37	$(CH_2)_{11}CO_2Me$	H
38	$(CH_2)_{14}CO_2Me$	H
39	$(CH_2)_2O(CH_2)_2O(CH_2)_3CO_2Me$	H



	R^1	R^2
40	$(CH_2)_8CO_2Me$	Bzl
41	$(CH_2)_8CO_2Me$	H



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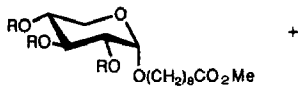
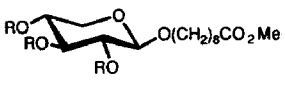


43 R = Ac
44 R = H

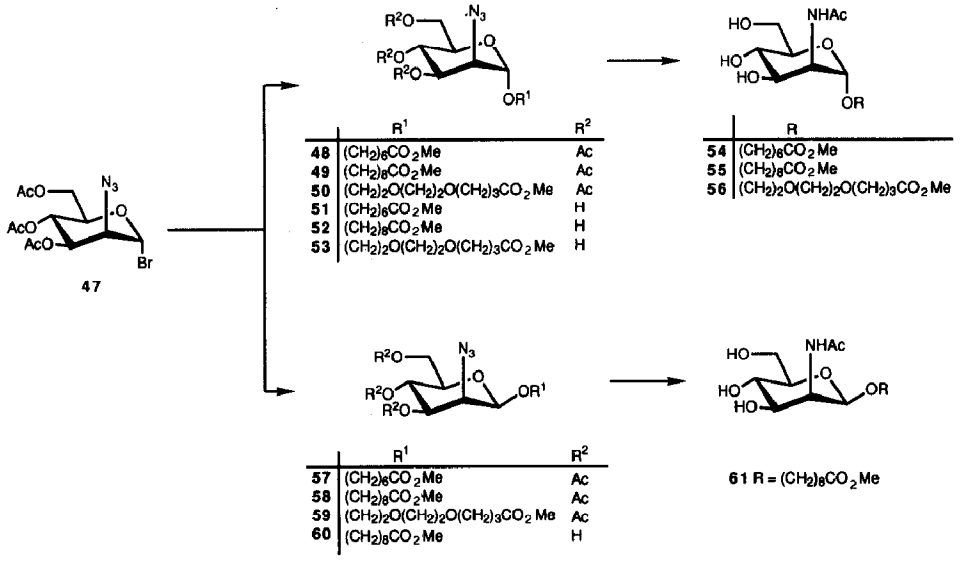


45 R = Ac
46 R = H

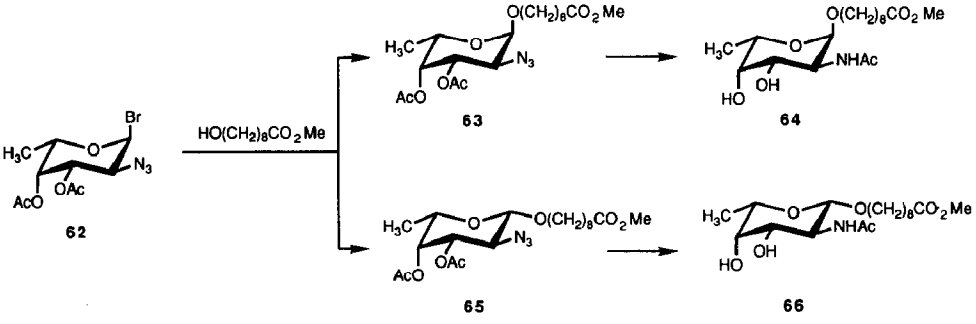
indicating the β-L stereochemistry of the glycosidic bond that had formed in all five compounds. Catalytic hydrogenolysis of the benzyl groups in **27** over 10% palladium-on-carbon, followed by esterification by treatment with ethereal diazomethane, gave 3-(methoxycarbonyl)propyl 2,3,4-tri-*O*-acetyl-β-L-fucopyranoside **28** in 68.9% yield. Removal of the acetyl groups in **28**, **29**, **31**, **32**, and **33** with sodium methoxide in methanol gave 3-(methoxycarbonyl)propyl (**34**), 6-(methoxycarbonyl)hexyl (**35**), 11-(methoxycarbonyl)undecyl (**37**), 14-(methoxycarbonyl)tetradecyl (**38**), and 9-(methoxycarbonyl)-3,6-dioxanonyl β-L-fucopyranosides (**39**) in good yields, respectively. When 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide[19] (**26**) was condensed with 8-(methoxycarbonyl)octanol[3a] in the presence of mercuric cyanide and Drierite, with subsequent chromatography of the product on a column of silica gel, the condensation products **30** and **40** were obtained in 12.6 and 40.1% yields, respectively. Removal of the benzyl groups in both **30** and **40** by catalytic hydrogenolysis over 10% palladium-on-carbon gave 8-(methoxycarbonyl)octyl β- (**36**) and α-L-fucopyranosides (**41**) in 68.6 and 81.3% yields, respectively. ^{1}H-NMR spectra of **36** and **41** showed a doublet for H-1 at δ 4.17 ($J_{1,2}$ 8.1 Hz) for **36** and at δ 4.74 ($J_{1,2}$ 2.7 Hz) for **41**, indicating the stereochemistry of the glycosidic bond formed to be β-L in **36** and α-L in **41**.

Mercuric cyanide-promoted glycosylation of 8-(methoxycarbonyl)octanol with 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide[20] (**42**) in toluene gave 8-(methoxycarbonyl)octyl 2,3,4-tri-*O*-acetyl-α-D-xylopyranoside (**43**) and its β anomer (**45**) in 53.9 and 12.4% yields, respectively. ^{1}H-NMR spectra revealed a doublet for H-1 at δ 4.98 ($J_{1,2}$ 3.4 Hz) in **43** and at δ 4.46 ($J_{1,2}$ 6.8 Hz) in **45**, indicating the stereochemistry of the glycosidic bond formed to be α in **43** and β in **45**. Removal of the acetyl groups in both **43** and **45** with sodium methoxide in methanol gave 8-(methoxycarbonyl)octyl α- (**44**) and β-D-xylopyranosides (**46**) in 82.8 and 80.5% yields, respectively.

For the synthesis of 2-acetamido-2-deoxy-D-mannopyranoside having C_7 and C_9 carbon chain spacer arms and a C_{10} dioxa-type spacer arm, 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-mannopyranosyl bromide[21] (**47**) was coupled with 6-(methoxycarbonyl)hexanol, 8-(methoxycarbonyl)octanol, and **6** in the presence of silver silicate[22] and molecular sieve 4A in toluene with chromatography of the product on a column of silica gel, giving 6-(methoxycarbonyl)hexyl (**48**), 8-(methoxycarbonyl)octyl (**49**), and 9-(methoxycarbonyl)-3,6-dioxanonyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-mannopyranosides (**50**) in 49.9, 45.2, and 43% yields, respectively, together with their β anomers **57**, **58**, and **59** in 1.4, 42.6, and 11.7% yields, respectively. The α anomers **48** ($[\alpha]_D$ + 67.8°), **49** ($[\alpha]_D$ + 67°), and **50** ($[\alpha]_D$ + 58.2°) were dextrorotatory values, whereas the β anomers **57** ($[\alpha]_D$ − 78°), **58** ($[\alpha]_D$ − 75.5°), and **59** ($[\alpha]_D$ − 60.1°) were levorotatory in accord with the stereochemistry assigned. Treatment of **48**, **49**, **50**, and **58** with sodium methoxide in methanol gave the *O*-deacetylated products **51**, **52**, **53**, and **60** in 87, 99, 88.1, and 65.5% yields, respectively. Conversion of the azido group into the acetamido group in **51**, **52**, **53**, and **60** by treatment with sodium borohydride in the presence of a catalytic amount



of nickel chloride[24] in ethanol, followed by *N*-acetylation with acetic anhydride, gave 6-(methoxycarbonyl)hexyl (**54**), 8-(methoxycarbonyl)octyl (**55**), 9-(methoxycarbonyl)-3,6-dioxanonyl 2-acetamido-2-deoxy-α-D-mannopyranosides (**56**), and 8-(methoxycarbonyl)octyl 2-acetamido-2-deoxy-β-D-mannopyranoside (**61**) in 82, 67.4, 95, and 65.1% yields, respectively. ^{1}H-NMR spectra showed a singlet for the *N*-acetyl group at δ 1.99 for **54**, at δ 2.00 for **55**, at δ 2.01 for **56**, and at δ 2.01 for **61**.

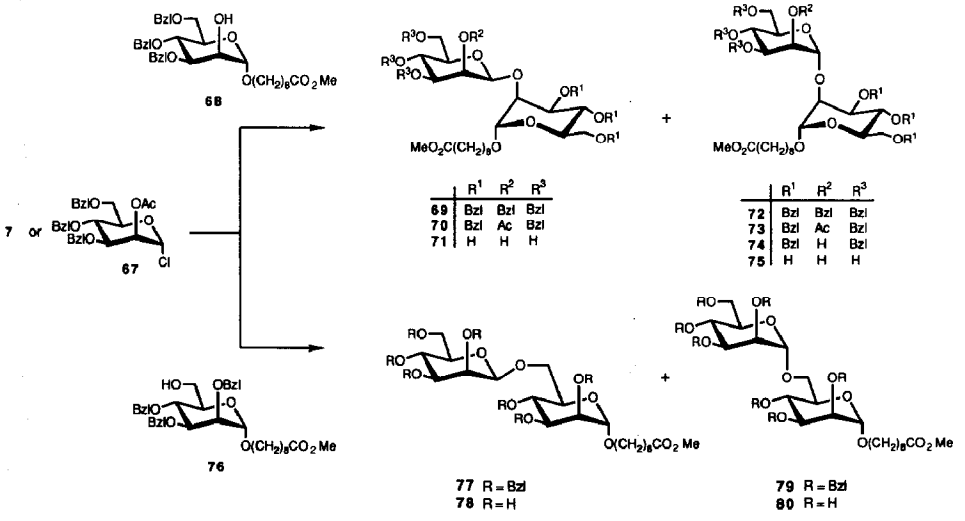


Similarly, mercuric cyanide-promoted glycosylation using 3,4-di-*O*-acetyl-2-azido-2-deoxy-α-L-fucopyranosyl bromide (**62**, prepared from 3,4-di-*O*-acetyl-2-azido-2-deoxy-α-L-fucopyranosyl nitrate[23] by treatment with lithium bromide in acetonitrile for 2 h at room temperature) with 8-(methoxycarbonyl)octanol in benzene, and chromatography of the product on a column of silica gel gave 8-(methoxycarbonyl)octyl 3,4-di-*O*-acetyl-2-azido-2-deoxy-α-L-fucopyranoside (**63**)

and its β anomer (**65**) in 32.3 and 43% yields, respectively. ^{1}H-NMR spectra revealed a H-1 doublet at δ 4.94 ($J_{1,2}$ 3.4 Hz) for **63** and at δ 4.32 ($J_{1,2}$ 8.1 Hz) for **65**, indicating the stereochemistry of the glycosidic bond formed to be α-L for **63** and β-L for **65**. Conversion of the azido group into the acetamido group and simultaneous removal of the acetyl groups of both **63** and **65** by treatment with sodium borohydride in the presence of a catalytic amount of nickel chloride, followed by *N*-acetylation with acetic anhydride in methanol, gave 8-(methoxycarbonyl)octyl 2-acetamido-2-deoxy-α- (**64**) and β-L-fucopyranosides (**66**) in 73 and 69.9% yields, respectively.

Having prepared ω-(methoxycarbonyl)alkyl glycopyranosides of monosaccharides and their dioxa-type derivatives, we then synthesized 8-(methoxycarbonyl)octyl glycosides of β-D-Man-(1→2)-α-D-Man, α-D-Man-(1→2)-α-D-Man, α-D-ManNAc-(1→2)-α-D-Man, β-D-GlcNAc-(1→2)-α-D-Man, and their 6-*O*-positional isomers using the known glycosyl acceptors 8-(methoxycarbonyl)octyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (**68**), readily obtainable [25] by the method reported by Srivastava and Hindsgaul, for the synthesis of (1→2)-linked oligosaccharides and 8-(methoxycarbonyl)octyl 2,3,4-tri-*O*-benzyl (**76**) and 2,4-di-*O*-benzyl-α-D-mannopyranosides (**82**), readily obtainable [26] by the method reported by Srivastava and Hindsgaul, for the synthesis of (1→6)-linked oligosaccharides. Although elegant methods for the synthesis of oligomannosides have been reported by Ogawa et al.[27] and Hindsgaul et al.[25,26], we wanted to synthesize the anomeric pairs of mannobiosides and related compounds having a C_9 carbon chain spacer arm.

Condensation of **68** with **7** in the presence of silver silicate and molecular sieve 4A in benzene gave, after chromatography on a column of silica gel, the (1→2)-linked disaccharides **69** and **72** in 42.3 and 10% yields, respectively. Catalytic

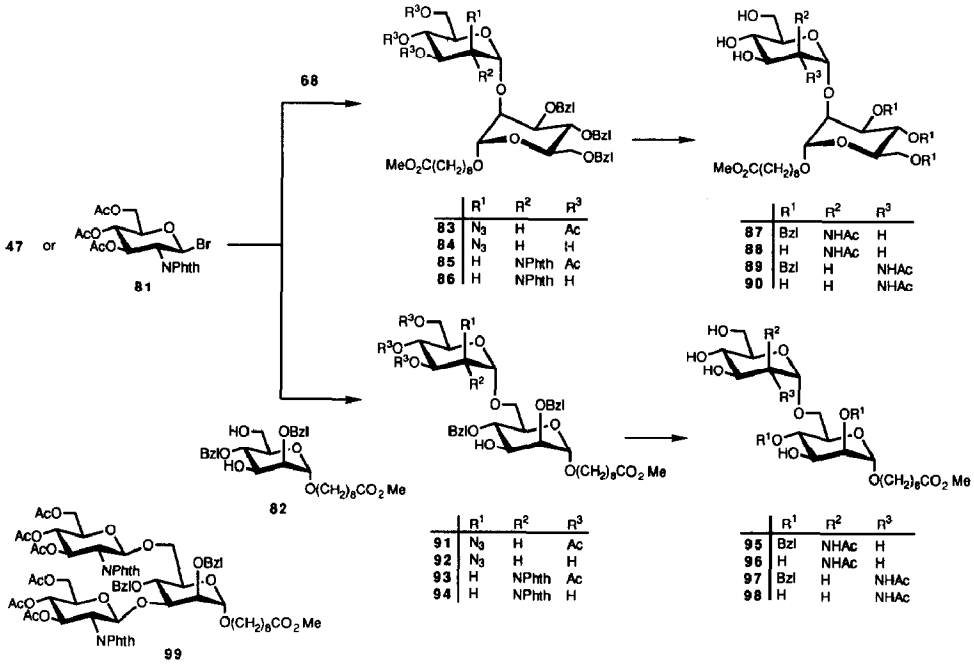


hydrogenolysis of the benzyl groups in **69** and **72** over 10% palladium-on-carbon gave 8-(methoxycarbonyl)octyl 2-*O*-(β-D-mannopyranosyl)-α-D-mannopyranoside (**71**) and the corresponding known α-linked mannobioside[25] (**75**) in 84.2 and 94% yields, respectively. Neighboring-group assisted glycosylation of **68** with 2-*O*-acetyl-3,4-6-tri-*O*-benzyl-α-D-mannopyranosyl chloride[28] (**67**) in the presence of silver triflate and *N,N,N',N'*-tetramethylurea in dichloromethane gave the condensation products **70** and **73** in 7.4 and 55.4% yields, respectively. Treatment of the main condensation product **73** with sodium methoxide in methanol gave the *O*-deacetylated product **74** in 88.4% yield. Debenzylation of **74** by catalytic hydrogenolysis over 10% palladium-on-carbon gave the α-linked mannobioside **75** in 94% yield.

Similar silver silicate-promoted glycosylation[22] of **7** with **76** in 1,2-dichloroethane gave the (1→6)-linked disaccharides **77** and **79** in 55.9 and 23.9% yields, respectively, while silver triflate-promoted glycosylation of **7** with **76** in benzene and dichloromethane gave **77** and **79** in 27.3 and 42.9% yields, respectively. ^{1}H-NMR spectra revealed two signals for the anomeric protons H-1 and H-1′ at δ 4.70 ($J_{1,2}$ 1 Hz) and δ 4.65 (s) in **77**, respectively, and at δ 4.70 ($J_{1,2}$ 1.8 Hz) and δ 4.59 (s) in **79**, respectively. These results indicated the stereochemistry of the newly formed glycosidic bond to be β in **77** and α in **79**. Removal of the benzyl groups in both **77** and **79** by catalytic hydrogenolysis over 10% palladium-on-carbon gave 8-(methoxycarbonyl)octyl 6-*O*-(β-D-mannopyranosyl)-α-D-mannopyranoside (**78**) and the α-linked mannobioside **80** in 86.3 and 47% yields, respectively.

To obtain analogs of the (1→2)- and (1→6)-linked mannobiosides, we then synthesized the (1→2)- and (1→6)-linked ManNAc-Man derivatives. Condensation of **47** and **68** in the presence of silver silicate and molecular sieve 4A in toluene gave the α-(1→2)-linked disaccharide **83** in 59.7% yield. The ^{1}H-NMR spectrum of **83** revealed the characteristic signal for H-3′ at δ 5.43 ($J_{2',3'}$ 3.7 and $J_{3',4'}$ 9.4 Hz) deshielded, together with the anomeric protons, for H-1 and H-1′, at δ 4.85 ($J_{1,2}$ 1.7 Hz) and δ 4.98 ($J_{1',2'}$ 1.8 Hz), respectively, indicating the stereochemistry of the newly formed glycosidic bond to be α. Treatment of **83** with sodium methoxide in methanol gave the *O*-deacetylated product **84** in 93% yield. Compound **84** was converted into the acetamido derivative **87** in 58.2% yield as described for the preparation of **54**. Removal of the benzyl groups in **87** by catalytic hydrogenolysis over 10% palladium-on-carbon gave the desired 8-(methoxycarbonyl)octyl 2-*O*-(2-acetamido-2-deoxy-α-D-mannopyranosyl)-α-D-mannopyranoside (**88**) in 75.4% yield.

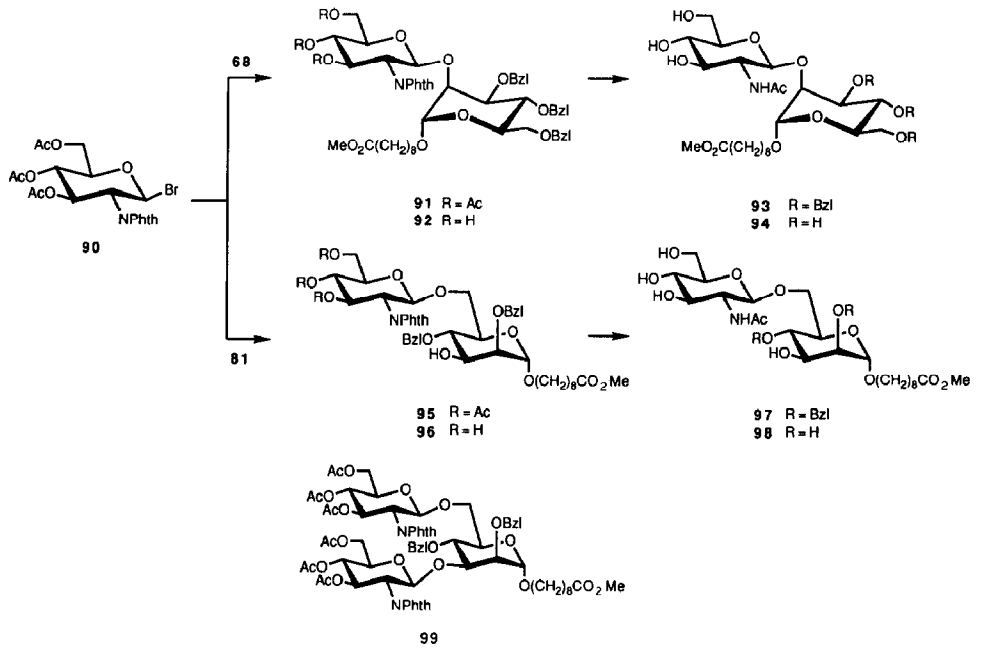
Condensation of **47** with the glycosyl acceptor **82**, in which both 3- and 6-hydroxyl groups had been unprotected so that the sugar sequence could be introduced at the 3-hydroxyl group of **82**, in the presence of silver triflate and *N,N,N',N'*-tetramethylurea gave the (1→6)-linked disaccharide **91** in 43% yield. The structural assignment was verified by conversion of a small quantity of **91** into the tetraacetate by treatment with acetic anhydride in pyridine and observing the characteristic signal for H-3 at δ 5.08 ($J_{2,3}$ 3.2 and $J_{3,4}$ 8.8 Hz) deshielded in the ^{1}H-NMR spectrum. Treatment of **91** with sodium methoxide in methanol gave the



O-deacetylated product **92** in 83.2% yield. Conversion of **92** into the acetamido derivative **95** as described for the preparation of **54**, led to a yield of 71.5%. Removal of the benzyl groups in **95** by catalytic hydrogenolysis over 10% palladium-on-carbon gave 8-(methoxycarbonyl)octyl 6-*O*-(2-acetamido-2-deoxy-α-D-mannopyranosyl)-α-D-mannopyranoside (**96**) in 68.3% yield.

Finally, the syntheses of 8-(methoxycarbonyl)octyl glycoside of β-D-GlcNAc-(1→2)- and -(1→6)-α-D-Man were carried out using the glycosyl donor 3,4,6-tri-*O*-acetyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl bromide[29] (**81**). Condensation of **81** with **68** in the presence of silver silicate and molecular sieve 4A in dichloromethane gave the β-(1→2)-linked disaccharide **85** in 58.3% yield. The ^{1}H-NMR spectrum of **85** contained two doublets for H-1 and H-1′ at δ 4.54 (s) and δ 5.51 ($J_{1',2'}$ 8.5 Hz), respectively, indicating the stereochemistry of the newly formed glycosidic bond to be β. Treatment of **85** with sodium methoxide in methanol gave the *O*-deacetylated product **86** in 82.6% yield. Dephthaloylation of **86** by treatment with hydrazine acetate in methanol, followed by *N*-acetylation with acetic anhydride in methanol, gave the acetamido derivative **89** in 74.4% yield. The ^{1}H-NMR spectrum of **89** contained a singlet for the *N*-acetyl group at δ 1.94. Removal of the benzyl groups in **89** by catalytic hydrogenolysis over 10% palladium-on-carbon gave 8-(methoxycarbonyl)octyl 2-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-α-D-mannopyranoside (**90**) in 87.5% yield.

When two molar equivalents of the glycosyl donor **81** were coupled with **82** in the presence of silver silicate and molecular sieve 4A in benzene, the (1→6)-linked



disaccharide **93** was obtained in 18.9% yield, together with the trisaccharide **99** in 48.9% yield. ^{1}H-NMR spectra revealed two anomeric protons for H-1 and H-1′ at δ 4.40 (s) and δ 5.45 ($J_{1',2'}$ 8.6 Hz) in **93**, respectively, and two of the three anomeric protons, for H-1′ and H-1″, at δ 5.47 ($J_{1',2' \text{ or } 1'',2''}$ 8.4 Hz) and δ 5.35 ($J_{1'',2'' \text{ or } 1',2'}$ 8 Hz) in **99**, respectively, indicating the newly formed glycosidic bond to be β in both **93** and **99**. Treatment of **93** with sodium methoxide in methanol gave the *O*-deacetylated product **94** in 80% yield. Conversion of **94** into the acetamido derivative **97** as described for the preparation of **89**, gave a yield of 71.1%. Debenzylation of **97** by catalytic hydrogenolysis over 10% palladium-on-carbon gave the desired 8-(methoxycarbonyl)octyl 6-*O*-(acetamido-2-deoxy-β-D-glucopyranosyl)-α-D-mannopyranoside (**98**) in 78% yield.

EXPERIMENTAL

General methods.—Melting points were measured with a Yanagimoto micro-melting-point apparatus and were not corrected. Evaporations were conducted under diminished pressure. Column chromatography was performed on columns of silica gel (Merck, 230–400 mesh) or pre-packed LiChroprep Si 60 (Merck, 40–63 μm). Optical rotations were measured in chloroform with a Perkin–Elmer Model 141 polarimeter, unless otherwise noted. IR spectra were recorded with a Hitachi 215 spectrometer, ^{1}H-NMR spectra were recorded with a Varian VXR-200 or VXR-500 FT NMR spectrometer, for solutions in $CDCl_3$, unless otherwise noted.

The values of δ_H are expressed in ppm downfield from the signal for internal Me_4Si, unless otherwise noted. Secondary-ion mass spectra (SIMS), high-resolution liquid secondary-ion mass spectra (HRL-SIMS), and fast-atom-bombardment mass spectra (FABMS) were measured with a Hitachi M-90 mass spectrometer, with Xe as the primary ion gas, using *m*-nitrobenzyl alcohol or glycerol as the matrix and polyethyleneglycol 300 with or without KI or NaI as internal standard.

3-(Benzyloxycarbonyl)propanol (**1**).—A mixture of sodium 4-hydroxybutanoate (7.15 g, 56.7 mmol) and benzyl bromide (10.2 g, 59 mmol) in dry *N*,*N*-dimethylformamide (40 mL) was stirred for 20 h at room temperature. The mixture was concentrated to a low volume and then partitioned between EtOAc and water. The organic phase was washed with water, dried ($MgSO_4$), and evaporated. Chromatography of the residue on a column of SiO_2 with 2:1 hexane–EtOAc gave **1** (8.19 g, 74.4%) as an oil, ν_{max}^{film} 3350 and 1730 cm^{-1}; ^{1}H-NMR: δ_H 7.40–7.30 (m, 5 H, Ph), 5.11 (s, 2 H, PhCH_2), 3.67 (t, 2 H, CH_2OH), 2.48 (t, 2 H, *J* 7.2 Hz, –CH_2CO–), and 1.95–1.81 (m, 2 H, –CH_2–); FABMS: *m/z* 194 $[M]^+$.

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.73, H, 7.37.

10-Phenyl-3,6,9-trioxadecanol (**2**).—Sodium hydride (13.5 g, 0.338 mol, 60% dispersion in oil) was added to an ice-cooled solution of triethylene glycol (50 g, 0.33 mol) in *N*,*N*-dimethylformamide (300 mL) in an N_2 atmosphere, with stirring. After stirring until the evolution of hydrogen gas had ceased, benzyl bromide (56 g, 0.33 mol) was added dropwise to the mixture and stirring was continued for 4 h at 0°. The mixture was partitioned between EtOAc and water. The organic layer was washed with water, dried ($MgSO_4$), and evaporated. Chromatography of the residue on a column of SiO_2 with 1:1 hexane–EtOAc gave **2** (27.5 g, 34%) as an oil, ν_{max}^{film} 3450 and 1099 cm^{-1}; ^{1}H-NMR: δ_H 7.26–7.35 (m, 5 H, Ph), 4.57 (s, 2 H, PhCH_2), 3.73–3.62 (m, 12 H, CH_2O), and 2.25 (br, 1 H, OH); HRL-SIMS *m/z* 241.1437 (Obsd), *m/z* 241.1438 (Calcd for $C_{13}H_{21}O_4$, $[M + H]^+$).

Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.79; H, 8.40. Found: C, 64.20; H, 8.39.

10-Phenyl-3,6,9-trioxadecanyl bromide (**3**).—Phosphorus tribromide (14 g, 52 mmol) was added dropwise to an ice-cooled solution of **2** (36 g, 150 mmol) in anhydrous ether (100 mL) with stirring. The mixture was stirred for 1 h at the same temperature. The cooling bath was removed and stirring was continued for 1 h at ambient temperature. The mixture was partitioned between EtOAc and water. The organic phase was washed with water, dried ($MgSO_4$), and evaporated. Chromatography of the residue on a column of SiO_2 with 9:1 hexane–EtOAc gave **3** (13.6 g, 36%) as an oil, ν_{max}^{film} 1112 cm^{-1}; ^{1}H-NMR: δ_H 7.26–7.35 (m, 5 H, Ph), 4.58 (s, 2 H, PhCH_2), 3.81 (t, 2 H, *J* 7 Hz, –CH_2Br), and 3.66–3.61 (m, 8 H, CH_2O), and 3.47 (t, 2 H, *J* 6.4 Hz, CH_2O); HRL-SIMS: *m/z* 303.0595 (Obsd), *m/z* 303.0595 (Calcd for $C_{13}H_{20}O_3Br$, $[M + H]^+$).

Anal. Calcd for $C_{13}H_{19}O_3Br$: C, 51.49; H, 6.32; Br, 26.36. Found: C, 51.26; H, 6.30; Br, 26.64.

Methyl 2-(methoxycarbonyl)-12-phenyl-5,8,11-trioxadodecanoate (**4**).—Sodium hydride (10 g, 250 mmol, 60% dispersion in oil) was added to a solution of

dimethyl malonate (33 g, 250 mmol) in *N,N*-dimethylformamide (300 mL) in an N_2 atmosphere. The mixture was stirred for 1 h at 40°. To this mixture was added **3** (41.1 g, 136 mmol) and stirring was continued for 6 h at 40°. After being cooled to room temperature, the mixture was partitioned between EtOAc and water. The organic phase was washed with water, dried ($MgSO_4$), and evaporated. Chromatography of the residue on a column of SiO_2 with 2:1 hexane–EtOAc gave **4** (36.8 g, 77%) as an oil, ν_{max}^{film} 1754 and 1735 cm^{-1}; ^{1}H-NMR: δ_H 7.26–7.35 (m, 5 H, Ph), 4.56 (s, 2 H, PhCH_2), 3.72 (s, 6 H, OCH_3), 3.52 (t, 2 H, *J* 5.9 Hz, CH_2O), 3.45–3.7 [m, 9 H, CH_2O and CH(COOMe)$_2$], and 2.18 (m, 2 H, –CH_2–); HRL-SIMS: *m/z* 355.1754 (Obsd), *m/z* 355.1755 (Calcd for $C_{18}H_{27}O_7$, $[M + H]^+$).

Anal. Calcd for $C_{18}H_{26}O_7$: C, 61.00; H, 7.40. Found: C, 60.60; H, 7.36.

Methyl 12-phenyl-5,8,11-trioxadodecanoate (**5**). —A mixture of **4** (23.2 g, 65.5 mmol) and NaCl (4.5 g, 76.9 mmol) in Me_2SO (80 mL) and water (4 mL) was heated for 4 h at 150–160°. After being cooled to room temperature, the mixture was evaporated. The residue was partitioned between EtOAc and water. The organic phase was washed with water, dried ($MgSO_4$), and evaporated. Chromatography of the residue on a column of SiO_2 with 5:1 hexane–EtOAc gave **5** (17 g, 87%) as an oil, ν_{max}^{film} 1738 and 1113 cm^{-1}; ^{1}H-NMR: δ_H 7.24–7.33 (m, 5 H, Ph), 4.57 (s, 2 H, PhCH_2), 3.66 (s, 3 H, OCH_3), 3.63–3.50 (m, 10 H, CH_2O), 2.42 (t, 2 H, *J* 7.3 Hz, –CH_2CO–), and 1.90 (m, 2 H, –CH_2–); HRL-SIMS *m/z* 297.1704 (Obs.), *m/z* 297.1701 (Calc. for $C_{16}H_{25}O_5$, $[M + H]^+$).

Anal. Calc. for $C_{16}H_{24}O_5$: C, 64.84; H, 8.16. Found: C, 64.54; H, 8.20.

9-(Methoxycarbonyl)-3,6-dioxanonanol (**6**).—A solution of **5** (16.6 g, 56 mmol) in MeOH (20 mL) was hydrogenolyzed over 10% Pd–C (2 g) for 4 h at room temperature. After removal of the catalyst by filtration, the filtrate was evaporated to give **6** (11.3 g, 99%) as an oil, ν_{max}^{film} 3450, 1738 and 1119 cm^{-1}; ^{1}H-NMR: δ_H 3.73 (t, 2 H, CH_2OH), 3.68 (s, 3 H, OCH_3), 3.63–3.50 (m, 10 H, CH_2O-), 2.42 (t, 2 H, *J* 7.3 Hz, –CH_2CO–), 1.92 (m, 2 H, –CH_2–), and 1.70 (br. 1 H, OH); HRL-SIMS: *m/z* 207.1223 (Obsd), *m/z* 207.1231 (Calcd for $C_9H_{19}O_5$, $[M + H]^+$).

Anal. Calcd for $C_9H_{18}O_5$: C, 52.41; H, 8.80. Found: C, 52.11, H, 8.77.

*3-(Benzyloxycarbonyl)propyl 2,3,4,6-tetra-O-benzyl-β-*D*-mannopyranoside* (**9**). —A solution of 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl chloride[10] (**7**, 580 mg, 1.04 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a mixture of **1** (544 mg, 2.8 mmol), Ag_2CO_3 (500 mg), and Drierite (500 mg) in CH_2Cl_2 (10 mL), with stirring, in an N_2 atmosphere. The mixture was stirred for 8 h at room temperature. The insoluble material was removed by filtration and the filtrate was evaporated. Chromatography of the residue on a column of silica gel with 6:1 hexane–EtOAc gave **9** (462 mg, 63.8%); $[\alpha]_D^{25}$ –41.7° (*c* 0.95); $\nu_{max}^{CHCl_3}$ 1740 cm^{-1}; ^{1}H-NMR: δ_H 7.5–7.1 (m, 25 H, Ph), 5.10 (s, 2 H, PhCH_2), 4.32 (s, 1 H, H-1), 3.97 (dt, 1 H, *J* 6.8 and 9.6 Hz, CH_2O), 3.87 (dd, 1 H, $J_{2,3}$ 3 Hz, H-3), 3.84 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.5 Hz, H-4), 3.76 (dd, 1 H, $J_{6a,6b}$ 10.8 Hz, $J_{5,6a}$ 1.7 Hz, H-6a), 3.71 (dd, $J_{5,6b}$ 6.1 Hz, H-6b), 3.65 (s, 3 H, OCH_3), 3.48 (dd, $J_{2,3}$ 3 Hz, $J_{3,4}$ 9.5 Hz, H-3), 3.45 (ddd, 1 H, H-5), 3.41 (dt, 1 H, *J* 6.2 and 9.6 Hz, CH_2O), 2.45 (m, 2 H, –CH_2CO–), and 1.95 (m, 2 H, –CH_2–).

Anal. Calcd for $C_{45}H_{48}O_8 \cdot 0.3\ H_2O$: C, 74.83; H, 6.78. Found: C, 75.11; H, 6.66.

6-(Methoxycarbonyl)hexyl 2,3,4,6-tetra-O-benzyl-β-D-mannopyranoside (**10**) *and its α anomer* (**21**).—A mixture of **7** (608 mg, 1.08 mmol), 6-(methoxycarbonyl)hexanol[11] (159 mg, 1.08 mmol), and powdered molecular sieve 4A (750 mg) in toluene (20 mL) was stirred for 30 min at room temperature in an N_2 atmosphere. To this mixture was added silver silicate (500 mg) and stirring was continued for 72 h. The mixture was filtered through Celite, and the filtrate evaporated. Chromatography of the residue on a Lobar column with 4:1 hexane–EtOAc gave **10** (380 mg, 52.7%) and **21** (130 mg, 17.9%).

Compound **10** had $[\alpha]_D^{22.5}$ −47.1° (*c* 0.55); ν_{max}^{film} 1740, 1440, 1365, and 1105 cm^{-1}; ^{1}H-NMR: δ_H 7.5–7.1 (m, 20 H, Ph), 4.36 (s, 1 H, H-1), 3.65 (s, 3 H, OCH_3), 2.29 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.65–1.2 (m, 8 H, $-CH_2-$).

Anal. Calcd for $C_{42}H_{50}O_8$: C, 73.87; H, 7.38. Found: C, 73.66; H, 7.08.

Compound **21** had $[\alpha]_D^{22.5}$ +21.1° (*c* 1.05); ν_{max}^{film} 1738, 1455, 1275, and 1105 cm^{-1}; ^{1}H-NMR: δ_H 7.4–7.2 (m, 20 H, Ph), 4.62 (s, 1 H, H-1), 3.64 (s, 3 H, OCH_3), 2.29 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.8–1.2 (m, 8 H, $-CH_2-$).

Anal. Calcd for $C_{42}H_{50}O_8$: C, 73.87; H, 7.38. Found: C, 73.59; H, 7.11.

8-(Methoxycarbonyl)octyl 2,3,4,6-tetra-O-benzyl-β-D-mannopyranoside (**11**) *and its α anomer* (**22**).—Sodium hydride (90 mg, 50% dispersion in oil) was added to an ice-cooled solution of 2,3,4,6-tetra-*O*-benzyl-α,β-D-mannopyranose[14] (**8**, 1 g, 1.85 mmol) in anhydrous tetrahydrofuran (20 mL) in an N_2 atmosphere. After stirring for 40 min, a solution of 8-(methoxycarbonyl)octyl trifluoromethanesulfonate[15] (600 mg, 1.87 mmol) in anhydrous tetrahydrofuran (4 mL) was added, and stirring was continued for 2 h. The mixture was partitioned between EtOAc and water. The organic phase was washed with water, dried ($MgSO_4$), and evaporated. Chromatography of the residue on a Lobar column with 6:1 hexane–EtOAc gave **11** (650 mg, 56.7%), which crystallized from EtOAc–hexane, and **22** (170 mg, 14.9%).

Compound **11** had mp 54.5–55°, $[\alpha]_D^{25}$ −46.7° (*c* 0.85); $\nu_{max}^{CHCl_3}$ 1732, 1497, 1454, 1362, and 1100 cm^{-1}; ^{1}H-NMR: δ_H 7.6–7.1 (m, 20 H, Ph), 4.36 (s, 1 H, H-1), 3.66 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.8–1.2 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{44}H_{54}O_8$: C, 74.38; H, 7.66. Found: C, 74.31; H, 7.62.

Compound **22** had $[\alpha]_D^{25}$ +21.6° (*c* 1.1); $\nu_{max}^{CHCl_3}$: 1732, 1497, 1454, and 1100 cm^{-1}; ^{1}H-NMR: δ_H 7.6–7.1 (m, 20 H, Ph), 4.73 (s, 1 H, H-1), 3.66 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.7–1.2 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{44}H_{54}O_8$: C, 74.38; H, 7.66. Found: C, 73.95; H, 7.65.

11-(Methoxycarbonyl)undecyl 2,3,4,6-tetra-O-benzyl-β-D-mannopyranoside (**12**).—Condensation of **7** (580 mg, 1.04 mmol) with 11-(methoxycarbonyl)undecanol[11] (645 mg, 2.8 mmol) in the presence of Ag_2CO_3 (500 mg) and Drierite (500 mg) as described for the preparation of **9**, and chromatography of the product on a column of silica gel with 6:1 hexane–EtOAc gave **12** (485 mg, 62.5%), $[\alpha]_D^{25}$ −41.8° (*c* 1.2); $\nu_{max}^{CHCl_3}$ 1740 cm^{-1}; ^{1}H-NMR: δ_H 7.6–7.1 (m, 20 H, Ph), 4.35 (s, 1 H, H-1),

3.65 (s, 3 H, OCH_3), 2.28 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.65–1.2 (m, 18 H, $-CH_2-$).

Anal. Calcd for $C_{47}H_{60}O_8$: C, 74.97; H, 8.03. Found: C, 74.66; H, 7.96.

14-(Methoxycarbonyl)tetradecyl 2,3,4,6-tetra-O-benzyl-β-D-mannopyranoside (**13**). —Condensation of **7** (580 mg, 1.04 mmol) with 14-(methoxycarbonyl)tetradecanol[11] (763 mg, 2.8 mmol) in the presence of Ag_2CO_3 (500 mg) and Drierite (500 mg) as described for the preparation of **9**, and chromatography of the product gave **13** (478 mg, 57.8%); $[\alpha]_D^{25}$ −38.9° (*c* 1.1); $\nu_{max}^{CHCl_3}$ 1740 cm^{-1}; ^{1}H-NMR: δ_H 7.6–7.1 (m, 20 H, Ph), 4.35 (s, 1 H, H-1), 3.65 (s, 3 H, OCH_3), 2.28 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.65–1.2 (m, 24 H, $-CH_2-$).

Anal. Calcd for $C_{50}H_{66}O_8$: C, 75.53; H, 8.37. Found: C, 75.32; H, 8.49.

9-(Methoxycarbonyl)-3,6-dioxanonyl 2,3,4,6-tetra-O-benzyl-β-D-mannopyranoside (**14**).—Condensation of **7** (580 mg, 0.84 mmol) with **5** (577 mg, 2.8 mmol) in the presence of Ag_2CO_3 (500 mg) and Drierite (500 mg) as described for the preparation of **9**, and chromatography of the product on a column of SiO_2 with 3:2 hexane–EtOAc gave **14** (520 mg, 81.2%).

Compound **14** had $[\alpha]_D^{24}$ −44.6° (*c* 0.67); $\nu_{max}^{CHCl_3}$ 1726 cm^{-1}; ^{1}H-NMR: δ_H 7.5–7.18 (m, 20 H, Ph), 4.46 (s, 1 H, H-1), 3.63 (s, 3 H, OCH_3), 2.37 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.90 (m, 2 H, $-CH_2-$).

Anal. Calcd for $C_{43}H_{52}O_{10}$: C, 70.86; H, 7.19. Found: C, 70.55; H, 7.03.

3-(Methoxycarbonyl)propyl β-D-mannopyranoside (**15**).—A solution of **9** (758 mg, 1.05 mmol) in MeOH (10 mL)–EtOAc (10 mL) was hydrogenolyzed over 10% Pd–C (530 mg) for 7 h at room temperature and 5 kg/cm^2. After removal of the catalyst by filtration, the filtrate was evaporated. The residue was dissolved in MeOH (20 mL) and an excess of ethereal CH_2N_2 was added. The solution was kept for 30 min at room temperature. The excess of reagent was decomposed by addition of a small amount of AcOH. Evaporation of the solvent gave **15** (238 mg, 80.9%), which crystallized from isopropyl ether, mp 102–108°, $[\alpha]_D^{14}$ −46.2° (*c* 1, MeOH), ν_{max}^{KBr} 1730 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.48 (d, 1 H, $J_{1,2}$ 0.7 Hz, H-1), 3.92 (dt, 1 H, CH_2O), 3.85 (dd, 1 H, $J_{5,6a}$ 2.4 Hz, $J_{6a,6b}$ 12 Hz, H-6a), 3.82 (dd, 1 H, $J_{2,3}$ 2.9 Hz, H-2), 3.67 (dd, 1 H, $J_{5,6b}$ 5.9 Hz, H-6b), 3.64 (s, 3 H, OCH_3), 3.54 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.5 Hz, H-4), 3.52 (dt, 1 H, *J* 6.2 and 9.6 Hz, CH_2O), 3.41 (dd, 1 H, H-3), 3.16 (ddd, 1 H, H-5), 2.45 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.87 (m, 2 H, $-CH_2-$); FABMS: *m/z* 303 $[M + Na]^+$.

Anal. Calcd for $C_{11}H_{20}O_8$: C, 47.48; H, 7.24. Found: C, 47.56; H, 7.02.

6-(Methoxycarbonyl)hexyl β-D-mannopyrasonide (**16**).—A solution of **10** (350 mg, 0.523 mmol) in a mixture of MeOH (15 mL) and AcOH (5 mL) was hydrogenolyzed over 10% Pd–C (200 mg) for 24 h at room temperature and 4.5 kg/cm^2. After removal of the catalyst by filtration, the filtrate was evaporated. Chromatography of the residue on a column of silica gel with 10: 1 $CHCl_3$–MeOH gave **16** (130 mg, 77%), which crystallized from EtOAc, mp 113–114°, $[\alpha]_D^{23}$ −44.4° (*c* 0.54); ν_{max}^{KBr} 1732, 1084, and 1026 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.48 (d, 1 H, $J_{1,2}$ 0.5 Hz, H-1), 3.64 (s, 3 H, OCH_3), 2.33 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.7–1.25 (m, 8 H, $-CH_2-$).

Anal. Calcd for $C_{14}H_{26}O_8 \cdot 0.5H_2O$: C, 50.74; H, 8.21. Found: C, 50.60; H, 7.94.

6-(Methoxycarbonyl)hexyl α-D-mannopyranoside (**23**).—A solution of **21** (130 mg, 0.194 mmol) in MeOH–AcOH was hydrogenolyzed over 10% Pd–C (50 mg) as described for the preparation of **16**, giving **23** (46 mg, 73%), $[\alpha]_D^{23}$ + 50° (*c* 0.5, MeOH); ν_{max}^{film}: 3446, 1728, 1438, and 1060 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.73 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 3.65 (s, 3 H, OCH_3), 2.33 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.7–1.35 (m, 8 H, $-CH_2-$).

Anal. Calcd for $C_{14}H_{26}O_8 \cdot 0.5\ H_2O$: C, 50.74; H, 8.21. Found: C, 50.99; H, 8.01.

8-(Methoxycarbonyl)octyl β-D-mannopyranoside (**17**).—A solution of **11** (581 mg, 0.817 mmol) in MeOH (20 mL) was hydrogenolyzed over 10% Pd–C (54 mg) as described for the preparation of **16**, giving **17** (240 mg, 80.4%), which crystallized from EtOAc–ether, mp 96.5–97.5°, $[\alpha]_D^{25}$ –41.1° (*c* 1.1, MeOH); ν_{max}^{KBr} 1738 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.46 (d, 1 H, $J_{1,2}$ 1.0 Hz, H-1), 3.65 (s, 3 H, OCH_3), 2.32 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.7–1.2 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{16}H_{30}O_8$: C, 54.84; H, 8.63. Found: C, 54.61; H, 8.42.

8-(Methoxycarbonyl)octyl α-D-mannopyranoside (**24**).—A solution of **22** (300 mg, 0.483 mmol) in MeOH (15 mL) was hydrogenolyzed over 10% Pd–C (54 mg) as described for the preparation of **16**, and crystallization of the product from EtOAc–ether gave **24** (120 mg, 71%), mp 76–77°, $[\alpha]_D^{25}$ + 52.7° (*c* 0.4, MeOH); ^{1}H-NMR (CD_3OD): δ_H 4.73 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 3.65 (s, 3 H, OCH_3), 2.33 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.7–1.35 (m, 12 H, $-CH_2-$); [lit.[16b] mp 81–82°, $[\alpha]_D^{25}$ + 48°].

11-(Methoxycarbonyl)undecyl β-D-mannopyranoside (**18**).—A solution of **12** (631 mg) in MeOH (20 mL) was hydrogenolyzed over 10% Pd–C (500 mg) as described for the preparation of **16**, giving **18** (196 mg, 59.5%), which crystallized from isopropyl ether, mp 124.5–125°, $[\alpha]_D^{18}$ –32.6° (*c* 1.1, MeOH); ν_{max}^{KBr} 1735 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.48 (d, 1 H, $J_{1,2}$ 0.8 Hz, H-1), 3.64 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.65–1.26 (m, 18 H, $-CH_2-$); FABMS: *m/z* 415 $[M + Na]^+$ and *m/z* 393 $[M + H]^+$.

Anal. Calcd for $C_{19}H_{36}O_8$: C, 58.14; H, 9.25. Found: C, 58.00; H, 9.14.

14-(Methoxycarbonyl)tetradecyl β-D-mannopyranoside (**19**).—A solution of **13** (620 mg) in MeOH (20 mL)–EtOAc (5 mL) was hydrogenolyzed over 10% Pd–C (500 mg) as described for the preparation of **16**, giving **19** (171 mg, 50.5%), $[\alpha]_D^{18}$ –26.2° (*c* 1.1, MeOH); ν_{max}^{KBr} 1730 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.48 (d, 1 H, $J_{1,2}$ 0.7 Hz, H-1), 3.64 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.65–1.26 (m, 24 H, $-CH_2-$); FABMS: *m/z* 457 $[M + Na]^+$ and *m/z* 435 $[M + H]^+$.

Anal. Calcd for $C_{22}H_{42}O_8 \cdot 0.5H_2O$: C, 59.75; H, 9.73. Found: C, 59.56; H, 9.64.

9-(Methoxycarbonyl)-3,6-dioxanonyl β-D-mannopyranoside (**20**). —A solution of **14** (500 mg) in MeOH (10 mL) was hydrogenolyzed over 10% Pd–C (500 mg) as described for the preparation of **16**, giving **20** (232 mg, 92%), $[\alpha]_D^{23}$ –22.3°, (*c* 2.2, MeOH); ν_{max}^{KBr} 1730 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.53 (s, 1 H, H-1), 3.62 (s, 3 H,

OCH_3), 2.38 (t, 2 H, *J* 7.3 Hz, $-CH_2CO-$), and 1.83 (m, 2 H, $-CH_2-$); FABMS: *m/z* 391 $[M + Na]^+$.

Anal. Calcd for $C_{15}H_{28}O_{10}$: C, 48.90; H, 7.66. Found: C, 48.99; H, 7.65.

3-(Benzylocarbonyl)propyl 2,3,4-tri-O-acetyl-β-L-fucopyranoside (**27**).—Compound **1** (263 mg, 1.36 mmol), $Hg(CN)_2$ (342 mg, 1.36 mmol), and Drierite (900 mg) were added, with stirring, to a solution of 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide[18] (**25**, 900 mg, 2.71 mmol) in benzene (9 mL) in an Ar atmosphere. The mixture was stirred for 20 h at room temperature. After filtration of the mixture to remove the insoluble material, the filtrate was partitioned between EtOAc and water. The organic phase was successively washed with aq $NaHCO_3$ and water, dried ($MgSO_4$), and evaporated. Chromatography of the residue on a column of SiO_2 with 15:1 toluene–EtOAc gave **27** (408 mg, 64.5%) as a syrup, $[\alpha]_D^{24}$ +8.2° (*c* 1.1); ν_{max}^{film} 1750, 1230, and 1070 cm^{-1}; ^{1}H-NMR: δ_H 7.4–7.3 (m, 5 H, Ph), 5.22 (d, 1 H, $J_{3,4}$ 3.7 Hz, H-4), 5.18 (dd, 1 H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 10.5 Hz, H-2), 5.10 (s, 2 H, $PhCH_2$), 4.99 (dd, 1 H, $J_{3,4}$ 3.6 Hz, H-3), 4.38 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 3.87 (dt, 1 H, *J* 6.2 and 9.6 Hz, CH_2O), 3.76 (q, $J_{5,6}$ 6.4 Hz, H-5), 3.44 (dt, *J* 6.8 and 9.6 Hz, CH_2O), 2.43 (t, 2 H, *J* 7.6 Hz, $-CH_2CO-$), 1.99 (s, 3 H, OAc), 2.05 (s, 3 H, OAc), 2.17 (s, 3 H, OAc), 1.93 (m, 2 H, $-CH_2-$), and 1.22 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6).

Anal. Calcd for $C_{23}H_{30}O_{10}$: C, 82.04; H, 8.98. Found: C, 82.26; H, 8.55.

3-(Methoxycarbonyl)propyl 2,3,4-tri-O-acetyl-β-L-fucopyranoside (**28**).—A solution of **27** (392 mg, 0.84 mmol) in MeOH (10 mL) was hydrogenolyzed over 10% Pd–C for 5 h at room temperature. After removal of the catalyst by filtration, the filtrate was evaporated. To the residue was added an excess of ethereal CH_2N_2. The mixture was kept for 20 min at room temperature and then evaporated. Chromatography of the residue on a column of SiO_2 with 15:1 toluene–EtOAc gave **28** (226 mg, 68.9%) as a syrup, $[\alpha]_D^{23}$ +3.1° (*c* 1); ν_{max}^{film} 1750, 1220, and 1060 cm^{-1}; ^{1}H-NMR: δ_H 5.21 (dd, 1 H, $J_{3,4}$ 3.7 Hz, $J_{4,5}$ 0.7 Hz, H-4), 5.16 (dd, 1 H, $J_{2,3}$ 10.5 Hz, H-2), 4.99 (dd, 1 H, H-3), 4.39 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 3.87 (dt, 1 H, *J* 6.2 and 9.6 Hz, CH_2O), 3.77 (dq, 1 H, $J_{4,5}$ 0.7 Hz, $J_{5,6}$ 6.5 Hz, H-5), 3.44 (dt, 1 H, *J* 6.8 and 9.6 Hz, CH_2O), 2.37 (t, 2 H, *J* 7.3 Hz, $-CH_2CO-$), 1.97 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), 2.16 (s, 3 H, OAc), 1.93 (m, 2 H, $-CH_2-$), and 1.22 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6).

Anal. Calcd for $C_{17}H_{26}O_{10}$: C, 52.30; H, 6.71. Found: C, 52.29; H, 6.45.

6-(Methoxycarbonyl)hexyl 2,3,4-tri-O-acetyl-β-L-fucopyranoside (**29**). —Condensation of **25** (1.0 g, 3.01 mmol) with 6-(methoxycarbonyl)hexanol (241 mg, 1.5 mmol) in the presence of $Hg(CN)_2$ (380 mg) and Drierite (900 mg) in benzene (10 mL) as described for the preparation of **27**, and chromatography of the residue on a column of SiO_2 with 8:1 toluene–EtOAc gave **29** (401 mg, 61.6%) as a syrup, $[\alpha]_D^{23}$ +1.7° (*c* 1.0); ν_{max}^{film} 1740 cm^{-1}; ^{1}H-NMR: δ_H 4.42 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 3.67 (s, 3 H, OCH_3), 2.31 (t, 2 H, *J* 7.6 Hz, $-CH_2CO-$), 2.17 (s, 3 H, OAc), 2.05 (s, 3 H, OAc), 1.99 (s, 3 H, OAc), 1.7–1.35 (m, 8 H, $-CH_2-$), and 1.22 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6).

Anal. Calcd for $C_{20}H_{32}O_{10}$: C, 55.54; H, 7.46. Found: C, 55.29; H, 7.45.

8-(Methoxycarbonyl)octyl 2,3,4-tri-O-benzyl-β-L-fucopyranoside (**30**) *and its α anomer* (**40**).—Condensation of 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide[19] (**26**, 4 g, 6.85 mmol) with 8-(methoxycarbonyl)octanol (1.29 g, 6.85 mmol) in the presence of $Hg(CN)_2$ (1.73 g, 6.85 mmol) and Drierite (3.6 g) in benzene (40 mL) as described for the preparation of **27**, and chromatography of the product on a column of SiO_2 with 15:1 hexane–EtOAc gave **30** (534 mg, 12.6%) and **40** (1.69 g, 40.1%).

Compound **30** had $[\alpha]_D^{24}$ +6.2° (*c* 1); ν_{max}^{film} 1725 cm^{-1}; ^{1}H-NMR: δ_H 7.4–7.2 (m, 15 H, Ph), 4.32 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1), 3.65 (s, 3 H, OCH_3), 2.28 (t, 2 H, *J* 7.6 Hz, $-CH_2CO-$), 1.4–1.2 (m, 12 H, $-CH_2-$), and 1.15 (d, 3 H, $J_{5,6}$ 7.5 Hz, H-6).

Anal. Calcd for $C_{38}H_{50}O_7$: C, 73.75; H, 8.15. Found: C, 73.65; H, 8.34.

Compound **40** had $[\alpha]_D^{24}$ −34° (*c* 1); ν_{max}^{film} 1725 cm^{-1}; ^{1}H-NMR: δ_H 7.4–7.2 (m, 15 H, Ph), 3.65 (s, 3 H, OCH_3), 3.60 (dt, 1 H, *J* 6.8 and 9.6 Hz, $-CH_2O$), 3.42 (dt, 1 H, *J* 6.8 and 9.6 Hz, $-CH_2O$), 2.28 (t, 2 H, *J* 7.6 Hz, $-CH_2CO-$), 1.7–1.35 (m, 12 H, $-CH_2-$), and 1.10 (d, 3 H, $J_{5,6}$ 7.5 Hz, H-6).

Anal. Calcd for $C_{38}H_{50}O_7$: C, 73.75; H, 8.15. Found: C, 73.78; H, 8.53.

11-(Methoxycarbonyl)undecyl 2,3,4-tri-O-acetyl-β-L-fucopyranoside (**31**).—Condensation of **25** (731 mg, 2.2 mmol) with 11-(methoxycarbonyl)undecanol (253 mg, 1.1 mmol) in the presence of $Hg(CN)_2$ (278 mg) and Drierite (800 mg) in benzene (8 mL) as described for the preparation of **27**, and chromatography of the residue on a column of SiO_2 with 15:1 toluene–EtOAc gave **31** (341 mg, 61.7%) as a syrup, $[\alpha]_D^{23}$ −12° (*c* 1.1); ν_{max}^{film} 1750, 1220, and 1080 cm^{-1}; ^{1}H-NMR: δ_H 4.42 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 3.67 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7.6 Hz, $-CH_2CO-$), 2.17 (s, 3 H, OAc), 2.05 (s, 3 H, OAc), 1.99 (s, 3 H, OAc), 1.7–1.35 (m, 18 H, $-CH_2-$), and 1.22 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6).

Anal. Calcd for $C_{25}H_{42}O_{10}$: C, 59.74; H, 8.42. Found: C, 59.63; H, 8.33.

14-(Methoxycarbonyl)tetradecyl 2,3,4-tri-O-acetyl-β-L-fucopyranoside (**32**).—Condensation of **25** (889 mg, 2.68 mmol) with 14-(methoxycarbonyl)tetradecanol (365 mg, 1.34 mmol) in the presence of $Hg(CN)_2$ (339 mg) and Drierite (900 mg) in benzene (9 mL) as described for the preparation of **27**, and chromatography of the residue on a column of SiO_2 with 15:1 toluene–EtOAc gave **32** (554 mg, 75.9%) as a syrup, $[\alpha]_D^{24}$ +4.4° (*c* 1.1); ν_{max}^{film} 1740 and 1070 cm^{-1}; ^{1}H-NMR: δ_H 4.42 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 3.67 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7.6 Hz, $-CH_2CO-$), 2.17 (s, 3 H, OAc), 2.05 (s, 3 H, OAc), 1.99 (s, 3 H, OAc), 1.7–1.35 (m, 18 H, $-CH_2-$), and 1.22 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6).

Anal. Calcd for $C_{28}H_{48}O_{10} \cdot H_2O$: C, 59.77; H, 8.96. Found: C, 59.25; H, 8.75.

9-(Methoxycarbonyl)-3,6-dioxanonyl 2,3,4-tri-O-acetyl-β-L-fucopyranoside (**33**).—Condensation of **25** (166 mg, 0.469 mmol) with **6** (100 mg, 0.485 mmol) in the presence of $Hg(CN)_2$ (123 mg) and Drierite (350 mg) in benzene (10 mL) as described for the preparation of **27**, and chromatography of the product on a column of SiO_2 with 200:1 $CHCl_3$–MeOH gave **33** (136 mg, 58.6%), $[\alpha]_D^{24}$ −2.9° (*c* 1.1); ν_{max}^{film} 1750 and 1070 cm^{-1}; ^{1}H-NMR: δ_H 5.23 (dd, 1 H, $J_{3,4}$ 4.8 Hz, $J_{4,5}$ 1 Hz, H-4), 5.20 (dd, 1 H, $J_{2,3}$ 10.5 Hz, H-2), 5.01 (dd, 1 H, $J_{2,3}$ 3.4 Hz, H-3), 4.76 (d, 1 H,

$J_{1,2}$ 8.1 Hz, H-1), 3.98 (dt, 1 H, J 6.8 and 9.6 Hz, CH_2O), 3.81 (dq, 1 H, H-5), 3.68 (s, 3 H, OCH_3), 2.42 (t, 2 H, J 7.3 Hz, –CH_2CO–), 2.18 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 1.99 (s, 3 H, OAc), 1.90 (m, 2 H, –CH_2–), and 1.22 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6).

Anal. Calcd for $C_{23}H_{38}O_{13}$: C, 52.86; H, 7.33. Found: C, 52.56; H, 7.45.

3-(Methoxycarbonyl)propyl β-L-fucopyranoside (**34**).—A solution of **28** (220 mg, 0.564 mmol) in MeOH (3 mL) containing 28% NaOMe in MeOH (0.06 mL) was kept for 3 h at room temperature. The solution was neutralized with Amberlite IR-120B (H^+) resin. The resin was filtered off and washed with MeOH. The filtrate and washings were combined, and evaporated to give **34** (134 mg, 90%) as a hygroscopic powder, $[\alpha]_D^{23}$ +16.3° (*c* 1, MeOH); ν_{max}^{film} 3420, 1740, and 1070 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.15 (d, 1 H, $J_{1,2}$ 6.6 Hz, H-1), 3.85 (dt, 1 H, J 6.8 and 9.6 Hz, CH_2O), 3.64 (s, 3 H, OCH_3), 3.53 (dt, 1 H, J 6.8 and 9.6 Hz, CH_2O), 2.46 (t, 2 H, J 7.3 Hz, –CH_2CO–), 1.88 (m, 2 H, –CH_2–), and 1.23 (d, 3 H, $J_{5,6}$ 6.6 Hz, H-6).

Anal. Calcd for $C_{11}H_{20}O_7$: C, 49.99; H, 7.63. Found: C, 50.14; H, 7.31.

6-(Methoxycarbonyl)hexyl β-L-fucopyranoside (**35**). —Compound **29** (389 mg, 0.899 mmol) was *O*-deacetylated with NaOMe in MeOH as described for the preparation of **34**, giving **35** (268 mg, 97.3%) as a hygroscopic powder, $[\alpha]_D^{23}$ +3.3° (*c* 0.6, MeOH); ν_{max}^{film} 3450 and 1725 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.19 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 3.67 (s, 3 H, OCH_3), 2.37 (t, 2 H, J 7.6 Hz, –CH_2CO–), 1.75–1.2 (m, 8 H, –CH_2–), and 1.23 (d, 3 H, $J_{5,6}$ 6.6 Hz, H-6).

Anal. Calcd for $C_{14}H_{26}O_7 \cdot 0.4H_2O$: C, 53.62; H, 8.62. Found: C, 53.87; H, 8.57.

8-(Methoxycarbonyl)octyl β-L-fucopyranoside (**36**).—A solution of **30** (596 mg, 0.985 mmol) in AcOH (20 mL) was hydrogenolyzed over 10% Pd–C (100 mg) as described for the preparation of **16**, and chromatography of the product on a column of SiO_2 with 30:1 $CHCl_3$–MeOH gave **36** (226 mg, 68.6%) as a hygroscopic powder, $[\alpha]_D^{23}$ +4.5° (*c* 1, MeOH); ν_{max}^{film} 3350 and 1740 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.17 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 3.65 (s, 3 H, OCH_3), 2.31 (t, 2 H, J 7.6 Hz, –CH_2CO–), 1.75–1.2 (m, 12 H, –CH_2–), and 1.21 (d, 3 H, $J_{5,6}$ 7.5 Hz, H-6).

Anal. Calcd for $C_{16}H_{30}O_7 \cdot 0.6H_2O$: C, 55.66; H, 9.11. Found: C, 55.48; H, 8.91.

8-(Methoxycarbonyl)octyl α-L-fucopyranoside (**41**). —A solution of **40** (1.89 g, 3.12 mmol) in AcOH (50 mL) was hydrogenolyzed over 10% Pd–C (1 g) as described for the preparation of **16**, and chromatography of the product on a column of SiO_2 with 30:1 $CHCl_3$–MeOH gave **41** (949 mg, 81.3%) as a hygroscopic powder, $[\alpha]_D^{23}$ –110° (*c* 1, MeOH); ν_{max}^{film} 3350 and 1740 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.74 (d, 1 H, $J_{1,2}$ 2.7 Hz, H-1), 3.65 (s, 3 H, OCH_3), 2.31 (t, 2 H, J 7.6 Hz, –CH_2CO–), 1.75–1.2 (m, 12 H, –CH_2–), and 1.18 (d, 3 H, $J_{5,6}$ 7.5 Hz, H-6).

Anal. Calcd for $C_{16}H_{30}O_7 \cdot 0.6H_2O$: C, 55.66; H, 9.11. Found: C, 55.39; H, 8.97.

11-(Methoxycarbonyl)undecyl β-L-fucopyranoside (**37**).—Compound **31** (120 mg, 0.239 mmol) was *O*-deacetylated with NaOMe in MeOH as described for the

preparation of **34**, giving **37** (86 mg, 95.5%), which crystallized from isopropyl ether, mp 67°, $[\alpha]_D^{23}$ −4.1°, (*c* 1.1, MeOH); ν_{max}^{film} 3460 and 1740 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.15 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 3.64 (s, 3 H, OCH_3), 2.29 (t, 2 H, *J* 7.6 Hz, $-CH_2CO-$), 1.6–1.2 (m, 18 H, $-CH_2-$), and 1.25 (d, 3 H, $J_{5,6}$ 6.6 Hz, H-6).

Anal. Calcd for $C_{19}H_{36}O_7$: C, 60.61; H, 9.64. Found: C, 60.44; H, 9.31.

*14-(Methoxycarbonyl)tetradecyl β-*L*-fucopyranoside* (**38**).—Compound **32** (340 mg, 0.624 mmol) was *O*-deacetylated with NaOMe in MeOH as described for the preparation of **34**, giving **38** (246 mg, 94.2%), which crystallized from isopropyl ether, mp 67°, $[\alpha]_D^{23}$ +10.6° (*c* 1, MeOH); ν_{max}^{film} 3400 and 1740 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.15 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 3.64 (s, 3 H, OCH_3), 2.29 (t, 2 H, *J* 7.6 Hz, $-CH_2CO-$), 1.6–1.2 (m, 24 H, $-CH_2-$), and 1.25 (d, 3 H, $J_{5,6}$ 6.6 Hz, H-6).

Anal. Calcd for $C_{22}H_{42}O_7$: C, 63.13; H, 10.12. Found: C, 62.89; H, 10.31.

*9-(Methoxycarbonyl)-3,6-dioxanonyl β-*L*-fucopyranosnide* (**39**).—Compound **33** (180 mg) was *O*-deacetylated with NaOMe in MeOH as described for the preparation of **34**, giving **39** (109 mg, 82.3%) as a syrup, $[\alpha]_D^{26}$ −2.1° (*c* 1, MeOH); ν_{max}^{film} 3350 and 1740 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.19 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 3.67 (s, 3 H, OCH_3), 2.37 (t, 2 H, *J* 7.6 Hz, $-CH_2CO-$), 2.32 (m, 2 H, $-CH_2-$), and 1.23 (d, 3 H, $J_{5,6}$ 6.6 Hz, H-6).

Anal. Calcd for $C_{17}H_{32}O_{10} \cdot H_2O$: C, 49.26; H, 8.27. Found: C, 49.56; H, 8.33.

*8-(Methoxycarbonyl)octyl 2,3,4-tri-*O*-acetyl-α-*D*-xylopyranoside* (**43**) *and its β anomer* (**45**).—Condensation of 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide[20] (**42**, 1.2 g, 3.54 mmol) with 8-(methoxycarbonyl)octanol (333 mg, 1.77 mmol) in the presence of $Hg(CN)_2$ (447 mg) and Drierite (1 g) in benzene (10 mL) as described for the preparation of **27**, and chromatography of the product on a column of silica gel with 8:1 toluene–EtOAc gave **43** (426 mg, 53.9%) and **45** (98 mg, 12.4%).

Compound **43** had $[\alpha]_D^{23}$ +92.4° (*c* 1.1); ν_{max}^{film} 1760 and 1230 cm^{-1}; ^{1}H-NMR: δ_H 5.48 (t, 1 H, $J_{2,3} = J_{3,4}$ 9.8 Hz, H-3), 4.98 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.78 (dd, 1 H, H-2), 3.74 (dd, 1 H, $J_{4,5a}$ 6.2 Hz, $J_{5a,5b}$ 11 Hz, H-5a), 3.67 (s, 3 H, OCH_3), 3.61 (t, 1 H, $J_{4,5b} = J_{5a,5b}$ 11 Hz, H-5b), 3.38 (m, 1 H, CH_2O), 2.31 (t, 2 H, *J* 7.6 Hz, $-CH_2CO-$), 2.06 (s, 6 H, OAc), 2.03 (s, H, OAc), and 1.75–1.25 (m, 12 H, $-CH_2$).

Anal. Calcd for $C_{21}H_{34}O_{10}$: C, 56.49; H, 7.68. Found: C, 55.98; H, 7.97.

Compound **45** had $[\alpha]_D^{22}$−19.5° (*c* 0.9); ν_{max}^{film} 1760 and 1220 cm^{-1}; ^{1}H-NMR: δ_H 5.16 (t, 1 H, $J_{2,3} = J_{3,4}$ 8.6 Hz, H-3), 4.46 (d, 1 H, $J_{1,2}$ 6.8 Hz, H-1), 4.11 (dd, 1 H, $J_{4,5a}$ 4 Hz, $J_{5a,5b}$ 11.8 Hz, H-5a), 3.80 (dt, 1 H, *J* 6.4 and 9.4 Hz, CH_2O), 3.67 (s, 3 H, OCH_3), 3.45 (dt, 1 H, *J* 6.4 and 9.4 Hz, CH_2O), 3.35 (dd, 1 H, $J_{5a,5b}$ 11.8 Hz, H-5b), 2.30 (t, 2 H, *J* 7.4 Hz, $-CH_2CO-$), 2.03 (s, 3 H, OAc), 2.05 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), and 1.7–1.2 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{21}H_{34}O_{10}$: C, 56.49; H, 7.68. Found: C, 56.12; H, 7.91.

*8-(Methoxycarbonyl)octyl α-*D*-xylopyranoside* (**44**).—Compound **43** (410 mg, 0.918 mmol) was *O*-deacetylated with NaOMe in MeOH as described for the preparation of **34**, and chromatography of the product on a column of SiO_2 with 30:1 $CHCl_3$–MeOH gave **44** (243 mg, 82.8%) as a hygroscopic powder, $[\alpha]_D^{25}$ +90.9° (*c* 1.1 MeOH); ν_{max}^{film} 1740 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.69 (d, 1 H, $J_{1,2}$ 3.9 Hz,

H-1), 3.64 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7.4 Hz, $-CH_2CO-$), and 1.7–1.2 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{15}H_{28}O_7 \cdot 0.1H_2O$: C, 55.92; H, 8.82. Found: C, 55.80; H, 8.81.

8-(Methoxycarbonyl)octyl β-D-xylopyranoside (**46**).—Compound **45** (101 mg, 0.226 mmol) was *O*-deacetylated with NaOMe in MeOH as described for the preparation of **34**, and chromatography of the product on a column of SiO_2 with 30:1 $CHCl_3$–MeOH gave **46** (58 mg, 80.5%) as a hygroscopic powder, $[\alpha]_D^{24}$ −10.3° (*c* 1 MeOH); ν_{max}^{film} 1740 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.17 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 3.78 (t, 1 H, $J_{2,3} = J_{3,4}$ 7 Hz, H-3), 3.65 (s, 3 H, OCH_3), 3.50 (m, 2 H, CH_2O), 2.31 (t, 2 H, *J* 7.4 Hz, $-CH_2CO-$), and 1.7–1.2 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{15}H_{28}O_7 \cdot 0.1H_2O$: C, 55.92; H, 8.82. Found: C, 55.77; H, 8.87.

6-(Methoxycarbonyl)hexyl 3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-mannopyranoside (**48**) *and its β anomer* (**57**).—A solution of 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-mannopyranosyl bromide[21] (**47**, 730 mg, 1.85 mmol) in toluene (8 mL) was added dropwise to an ice-cooled mixture of 6-(methoxycarbonyl)hexanol (271 mg, 1.85 mmol), silver silicate (750 mg)[22], and powdered molecular sieve 4A (750 mg) in toluene (25 mL), with stirring, in an N_2 atmosphere. The mixture was stirred for 18 h at 0°. The mixture was filtered through Celite and the filtrate evaporated. Chromatography of the residue on a column of silica gel with 3:1 hexane–EtOAc gave **48** (424 mg, 49.9%) and **57** (8 mg, 1.4%).

Compound **48** had $[\alpha]_D^{23}$ +67.8° (*c* 0.7); ν_{max}^{film} 2110, 1747, 1436, 1369, 1228, and 1053 cm^{-1}; ^{1}H-NMR: δ_H 5.39 (dd, 1 H, $J_{2,3}$ 4, $J_{3,4}$ 9 Hz, H-3), 5.31 (t, 1 H, $J_{3,4} = J_{4,5}$ 9 Hz, H-4), 4.82 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 4.24 (dd, 1 H, $J_{5,6a}$ 4.5, $J_{6a,6b}$ 10 Hz, H-6a), 4.08 (dd, 1 H, $J_{5,6b}$ 2.5 Hz, H-6b), 4.00 (dd, 1 H, H-2), 3.86 (ddd, 1 H, H-5), 3.67 (m, 1 H, CH_2O), 3.67 (s, 3 H, OCH_3), 3.42 (dt, 1 H, *J* 6.8 and 9.6 Hz, CH_2O), 2.32 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), 2.09 (s, 6 H, OAc), 2.04 (s, 3 H, OAc), and 1.7–1.25 (m, 8 H, $-CH_2-$).

Anal. Calcd for $C_{19}H_{29}N_3O_{10}$: C, 49.67; H, 6.36; N, 9.15. Found: C, 49.33; H, 6.05; N, 9.01.

Compound **57** had $[\alpha]_D^{23}$ −78° (*c* 0.7); ν_{max}^{film} 2110, 1747, 1436, 1369, 1228, and 1053 cm^{-1}; ^{1}H-NMR: δ_H 5.25 (t, 1 H, $J_{3,4} = J_{4,5}$ 10 Hz, H-4), 4.97 (dd, $J_{2,3}$ 4 Hz, H-3), 4.67 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 4.24 (dd, 1 H, $J_{5,6a}$ 4.5, $J_{6a,6b}$ 12 Hz, H-6a), 4.12 (dd, 1 H, $J_{5,6b}$ 2.5 Hz, H-6b), 4.10 (dd, 1 H, H-2), 3.87 (dt, 1 H, *J* 6.8 and 9.6 Hz, CH_2O), 3.60 (ddd, 1 H, H-5), 3.67 (s, 3 H, OCH_3), 3.50 (dt, 1 H, *J* 6.8 and 9.6 Hz, CH_2O), 2.32 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), 2.11 (s, 3 H, OAc), 2.11 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), and 1.7–1.25 (m, 8 H, $-CH_2-$).

Anal. Calcd for $C_{19}H_{29}N_3O_{10}$: C, 49.67; H, 6.36; N, 9.15. Found: C, 49.53; H, 6.11; N, 9.34.

8-(Methoxycarbonyl)octyl 3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-mannopyranoside (**49**) *and its β anomer* (**58**).—Condensation of **47** (505 mg, 1.27 mmol) with 8-(methoxycarbonyl)octanol (241 mg, 1.27 mmol) in the presence of silver silicate (500 mg) and powdered molecular sieve 4A (500 mg) in toluene (15 mL) as described for the preparation of **48** and **57**, and chromatography of the product on

a Lobar column with 3:1 hexane–EtOAc gave **49** (250 mg, 45.2%) and **58** (273 mg, 42.6%).

Compound **49** had $[\alpha]_D^{23}$ +67° (*c* 1.3); $\nu_{max}^{CHCl_3}$ 2028, 1745, 1439, 1370, and 1053 cm^{-1}; ^{1}H-NMR: 4.83 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 3.67 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 6 Hz, –CH_2CO–), 2.10 (s, 6 H, OAc), 2.05 (s, 3 H, OAc), and 1.7–1.2 (m, 12 H, –CH_2–).

Anal. Calcd for $C_{22}H_{35}N_3O_{10}$: C, 52.68; H, 7.03; N, 8.38. Found: C, 52.68; H, 6.90; N, 8.47.

Compound **58** had $[\alpha]_D^{23}$ −75.5° (*c* 0.8); $\nu_{max}^{CHCl_3}$ 2028, 1745, 1439, 1370, and 1053 cm^{-1}; ^{1}H-NMR: δ_H 4.66 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 3.67 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 6 Hz, –CH_2CO–), 2.11 (s, 3 H, OAc), 2.10 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), and 1.7–1.2 (m, 12 H, –CH_2–).

Anal. Calcd for $C_{22}H_{35}N_3O_{10}$: C, 52.68; H, 7.03; N, 8.38. Found: C, 52.55; H, 7.08; N, 8.39.

*9-(Methoxycarbonyl)-3,6-dioxanonyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-*D*-mannopyranoside* (**50**) *and its β anomer* (**59**).—Condensation of **47** (930 mg, 2.35 mmol) with **6** (485 mg, 2.35 mmol) in the presence of silver silicate (700 mg) and molecular sieve 4A (500 mg) in toluene (20 mL) as described for the preparation of **48** and **57**, and chromatography of the product on a Lobar column with 1:1 hexane–EtOAc gave **50** (525 mg, 43%) and **59** (143 mg, 11.7%).

Compound **50** had $[\alpha]_D^{24}$ +58.2° (*c* 0.6); ν_{max}^{film} 2110, 1747, 1438, 1369, 1230 and 1049 cm^{-1}; ^{1}H-NMR: δ_H 5.39 (dd, 1 H, $J_{3,4}$ 10, $J_{2,3}$ 4 Hz, H-3), 5.32 (t, 1 H, $J_{3,4} = J_{4,5}$ 10 Hz, H-4), 4.91 (s, 1 H, H-1), 4.25 (dd, 1 H, $J_{5,6a}$ 4.5 Hz, $J_{6a,6b}$ 12 Hz, H-6a), 4.02 (ddd, 1 H, H-5), 3.67 (s, 3 H, OCH_3), 2.40 (t, 2 H, *J* 7.5 Hz, –CH_2CO–), 2.10 (s, 3 H, OAc), 2.08 (s, 3 H, OAc), 2.03 (s, 3 H, OAc), and 1.90 (m, 2 H, –CH_2–).

Anal. Calcd for $C_{21}H_{33}N_3O_{12}$: C, 48.55; H, 6.40; N, 8.09. Found: C, 48.35; H, 6.13; N, 7.9.

Compound **59** had $[\alpha]_D^{24}$ −60.1° (*c* 0.9); ν_{max}^{film} 2112, 1743, 1371, 1236, and 1055 cm^{-1}; ^{1}H-NMR: δ_H 5.24 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.5 Hz, H-4), 4.99 (dd, 1 H, $J_{2,3}$ 3.5Hz, H-3), 4.79 (s, 1 H, H-1), 4.25 (dd, 1 H, $J_{5,6a}$ 5.5 Hz, $J_{6a,6b}$ 12 Hz, H-6a), 4.00 (ddd, 1 H, H-5), 3.80 (m, 1 H, CH_2O), 3.67 (s, 3 H, OCH_3), 2.40 (t, 2 H, *J*7.5 Hz, –CH_2CO–), 2.10 (s, 3 H, OAc), 2.08 (s, 3 H, OAc), 2.03 (s, 3 H, OAc), and 1.90 (m, 2 H, –CH_2–).

Anal. Calcd for $C_{21}H_{33}N_3O_{12}$: C, 48.55; H, 6.40; N, 8.09. Found: C, 48.40; H, 6.55; N, 7.99.

*6-(Methoxycarbonyl)hexyl 2-azido-2-deoxy-α-*D*-mannopyranoside* (**51**).—Compound **48** (420 mg, 0.914 mmol) was *O*-deacetylated with NaOMe in MeOH as described for the preparation of **34**, giving **51** (265 mg, 87%), $[\alpha]_D^{22.5}$ +75.8° (*c* 0.9, MeOH), ν_{max}^{film} 3400, 2120, and 1735 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.77 (s, 1 H, H-1), 3.93 (dd, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 9.5 Hz, H-3), 3.80 (m, 2 H, H-2 and 6a), 3.73 (dt, 1 H, *J* 6.5 and 8.6 Hz, –CH_2O), 3.65 (s, 3 H, OCH_3), 3.55 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.5 Hz, H-4), 3.48 (ddd, 1 H, H-5), 3.42 (dt, 1 H, *J* 6.5 and 8.6 Hz, CH_2O), 2.33 (t, 2 H, *J* 7.5 Hz, –CH_2CO–), and 1.7–1.28 (m, 8 H, –CH_2–).

Anal. Calcd for $C_{14}H_{25}N_3O_7$: C, 48.40; H, 7.31; N, 12.10. Found: C, 48.55; H, 7.35; N, 12.01.

8-(Methoxycarbonyl)octyl 2-azido-2-deoxy-α-D-mannopyranoside (**52**).—Compound **49** (283 mg, 0.564 mmol) was *O*-deacetylated with NaOMe in MeOH as described for the preparation of **34**, giving **52** (210 mg, 99%), $[\alpha]_D^{24}$ +68.6° (*c* 0.6, MeOH), $\nu_{max}^{CHCl_3}$ 3600, 2028, and 1730 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.77 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 3.65 (s, 3 H, OCH_3), 2.32 (t, 2 H, *J* 7 Hz, $-CH_2CO-$), and 1.7–1.2 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{16}H_{29}N_3O_7$: C, 51.19; H, 7.79; N, 11.19. Found: C, 50.87; H, 7.66; N, 11.02.

8-(Methoxycarbonyl)octyl 2-azido-2-deoxy-β-D-mannopyranoside (**60**).—Compound **58** (273 mg, 0.54 mmol) was *O*-deacetylated with NaOMe in MeOH as described for the preparation of **34**, giving **60** (133 mg, 65.5%), which crystallized from ether–hexane, mp 47–49°, $[\alpha]_D^{24}$ −83.8° (*c* 0.8), $\nu_{max}^{CHCl_3}$ 3620, 2028, and 1732 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.68 (d, 1 H, $J_{1,2}$ 1.0 Hz, H-1), 3.65 (s, 3 H, OCH_3), 3.42 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.5 Hz, H-4), 3.18 (ddd, 1 H, H-5), 2.31 (t, 2 H, *J* 7 Hz, $-CH_2CO-$), and 1.7–1.2 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{16}H_{29}N_3O_7$: C, 51.19; H, 7.79; N, 11.19. Found: C, 51.00; H, 7.79; N, 11.19.

9-(Methoxycarbonyl)-3,6-dioxanonyl 2-azido-2-deoxy-α-D-mannopyranoside (**53**).—Compound **50** (525 mg, 1.01 mmol) was *O*-deacetylated with NaOMe in MeOH as described for the preparation of **34**, giving **53** (350 mg, 88.1%), $[\alpha]_D^{24}$ +67.6° (*c* 0.7, MeOH), $\nu_{max}^{CHCl_3}$ 3600, 2028, and 1730 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.84 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 3.65 (s, 3 H, OCH_3), 2.32 (t, 2 H, *J* 7 Hz, $-CH_2CO-$), and 1.95 (m, 2 H, $-CH_2-$).

Anal. Calcd for $C_{15}H_{27}N_3O_9$: C, 45.79; H, 6.92; N, 10.68. Found: C, 45.68; H, 6.79; N, 10.09.

6-(Methoxycarbonyl)hexyl 2-acetamido-2-deoxy-α-D-mannopyranoside (**54**).—A solution of $NaBH_4$ (90 mg, 2.39 mmol) in EtOH (6 mL) was added dropwise to a solution of **51** (265 mg, 0.795 mmol) in EtOH (7 mL) containing 0.16 mM solution of $NiCl_2 \cdot 6H_2O$ in EtOH (0.14 mL). The mixture was stirred for 30 min at room temperature. After neutralization of the mixture with a small amount of AcOH, Ac_2O (0.2 mL) was added. The mixture was kept for 1 h at room temperature and then evaporated. Chromatography of the residue on a column of SiO_2 with 10:1 $CHCl_3$–MeOH gave **54** (228 mg, 82%), $[\alpha]_D^{23.5}$ +38.3° (*c* 0.5, MeOH), ν_{max}^{KBr} 1730, 1650, 1552, 1438, and 1377 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.65 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1), 4.27 (dd, 1 H, $J_{2,3}$ 4.5 Hz, H-2), 3.90 (dd, $J_{3,4}$ 10 Hz, H-3), 3.68 (dt, 1 H, *J* 6.5 and 10 Hz, CH_2O), 3.56 (t, 1 H, $J_{3,4} = J_{4,5}$ 10 Hz, H-4), 3.65 (s, 3 H, OCH_3), 3.40 (dt, 1 H, *J* 6.5 and 10 Hz, CH_2O), 2.33 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), 1.99 (s, 3 H, NAc), and 1.7–1.35 (m, 8 H, $-CH_2-$).

Anal. Calcd for $C_{15}H_{27}NO_8 \cdot H_2O$: C, 49.04; H, 7.96; N, 3.81. Found: C, 49.34; H, 8.02; H, 3.65.

8-(Methoxycarbonyl)octyl 2-acetamido-2-deoxy-α-D-mannopyranoside (**55**).

—Compound **52** (210 mg, 0.559 mmol) was reduced with $NaBH_4$ (63 mg, 1.677 mmol) in EtOH (5 mL) containing 0.16 mM $NiCl_2 \cdot 6H_2O$ in EtOH (0.1 mL), followed by *N*-acetylation with Ac_2O (0.2 mL), as described for the preparation of **54**, and chromatography of the product on a column of SiO_2 with 10:1 $CHCl_3$–MeOH gave **55** (147 mg, 67.4%), $[\alpha]_D^{25}$ +37.1° (*c* 0.4, MeOH), $\nu_{max}^{CHCl_3}$ 1732, 1655, 1439, 1375, 1100, and 1070 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.66 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 4.28 (dd, 1 H, $J_{2,3}$ 4.8 Hz, H-2), 3.65 (s, 3 H, OCH_3), 2.32 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), 2.00 (s, 3 H, NAc), and 1.7–1.28 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{18}H_{33}NO_8 \cdot 0.2H_2O$: C, 54.72; H, 8.52; N, 3.55. Found: C, 54.60; H, 8.41; H, 3.72.

*8-(Methoxycarbonyl)octyl 2-acetamido-2-deoxy-β-*D*-mannopyranoside* (**61**). —Compound **60** (149 mg, 0.396 mmol) was reduced with $NaBH_4$ (45 mg) in EtOH (4 mL) containing 0.16 mM $NiCl_2 \cdot 6H_2O$ in EtOH (0.07 mL), followed by *N*-acetylation with Ac_2O (0.2 mL), as described for the preparation of **54**, and chromatography of the product on a column of SiO_2 with 10:1 $CHCl_3$–MeOH gave **61** (101 mg, 65.1%), $[\alpha]_D^{24}$ −49.4° (*c* 0.8, MeOH), ν_{max}^{KBr} 1740, 1645, 1550, and 1100 cm^{-1}; ^{1}H-NMR (CD_3OD): 4.60 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 4.42 (dd, 1 H, $J_{2,3}$ 4.2 Hz, H-2), 3.64 (s, 3 H, OCH_3), 3.50 (dt, 1 H, *J* 6.5 and 9.5 Hz, CH_2O), 3.20 (ddd, 1 H, H-5), 2.30 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), 2.01 (s, 3 H, NAc), and 1.7–1.28 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{18}H_{33}NO_8 \cdot 0.3\ H_2O$: C, 54.47; H, 8.53; N, 3.53. Found: C, 54.55; H, 8.36; N, 3.59.

*9-(Methoxycarbonyl)-3,6-dioxanonyl 2-acetamido-2-deoxy-α-*D*-mannopyranoside* (**56**).—Compound **53** (150 mg, 0.381 mmol) was reduced with $NaBH_4$ (43 mg) in EtOH (4 mL) containing 0.16 mM $NiCl_2 \cdot 6H_2O$ in EtOH (0.07 mL), followed by *N*-acetylation with Ac_2O (0.5 mL), as described for the preparation of **54**, and chromatography of the product on a column of SiO_2 with 7:1 $CHCl_3$–MeOH gave **56** (157 mg, 95%), $[\alpha]_D^{25}$ +26.4° (*c* 0.6, MeOH), ν_{max}^{KBr} 1730, 1660, 1550, 1132, and 1068 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.72 (d, 1 H, $J_{1,2}$ 1 Hz, H-1), 4.31 (dd, 1 H, $J_{2,3}$ 4.7 Hz, H-2), 3.92 (dd, 1 H, $J_{3,4}$ 9 Hz, H-3), 3.78 (m, 2 H, CH_2O), 3.65 (s, 3 H, OCH_3), 2.32 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), 2.01 (s, 3 H, NAc) and 1.85 (m, 2 H, $-CH_2-$).

Anal. Calcd for $C_{17}H_{31}NO_{10} \cdot H_2O$: C, 47.77; H, 7.31; N, 3.28. Found: C, 47.89; H, 7.05; N, 3.54.

*3,4-Di-*O*-acetyl-2-azido-2-deoxy-α-*L*-fucopyranosyl* bromide (**62**).—A mixture of 3,4-di-*O*-acetyl-2-azido-2-deoxy-α-L-fucopyranosyl nitrate[23] (830 mg, 2.61 mmol) and LiBr (907 mg, 10.4 mmol) in MeCN (80 mL) was stirred for 2 h at room temperature. The mixture was concentrated to low volume and then partitioned between $CHCl_3$ and water. The organic phase was washed with water, dried ($MgSO_4$), and evaporated to give **62** (900 mg) as a syrup, ^{1}H-NMR: δ_H 6.48 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 5.35–5.40 (m, 2 H, H-3 and 4), 4.40 (q, 1H, $J_{5,6}$ 6.6 Hz, H-5), 3.95 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 2.19 (s, 3 H, OAc), 2.07 (s, 3 H, OAc), and 1.22 (d, 3 H, $J_{5,6}$ 6.6 Hz, H-6), which was used in the glycosylation reaction immediately after preparation.

8-(Methoxycarbonyl)octyl 3,4-di-O-acetyl-2-azido-2-deoxy α-L-fucopyranoside (**63**) *and its β anomer* (**65**).—Condensation of **62** (415 mg, 1.31 mmol) with 8-(methoxycarbonyl)octanol (246 mg, 1.31 mmol) in the presence of $Hg(CN)_2$ (331 mg) and Drierite (800 mg, 1.31 mmol) in benzene (8 mL) as described for the preparation of **27**, and chromatography of the product on a column of silica gel with 6:1 hexane–EtOAc gave **63** (187 mg, 32.3%) and **65** (249 mg, 43%).

Compound **63** had $[\alpha]_D^{23}$ −121.8° (*c* 1); ν_{max}^{film} 2110, 1760, and 1220 cm^{-1}; ^{1}H-NMR: δ_H 5.37 (dd, 1 H, $J_{2,3}$ 11.2, $J_{3,4}$ 3.4 Hz, H-3), 5.30 (m, 1 H, H-4), 4.94 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 3.67 (s, 3 H, OCH_3), 3.58 (dd, 1 H, H-2), 2.31 (t, 2 H, *J* 7.3 Hz, $-CH_2CO-$), 2.17 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 1.75–1.2 (m, 12 H, $-CH_2-$), and 1.14 (d, 3 H, $J_{5,6}$ 6.6 Hz, H-6).

Anal. Calcd for $C_{22}H_{35}N_3O_{10}$: C, 52.68; H, 7.03; N, 8.38. Found: C, 52.69; H, 7.21; N, 8.34.

Compound **65** had $[\alpha]_D^{22}$ −3.1° (*c* 0.9); ν_{max}^{film} 2110, 1760, and 1220 cm^{-1}; ^{1}H-NMR: δ_H 5.18 (m, 1 H, H-4), 4.77 (dd, 1 H, $J_{2,3}$ 11, $J_{3,4}$ 3.4 Hz, H-3), 4.32 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 3.67 (s, 3 H, OCH_3), 3.64 (dd, 1 H, H-2), 2.30 (t, 2 H, *J* 7.3 Hz, $-CH_2CO-$), 2.05 (s, 3 H, OAc), 2.17 (s, 3 H, OAc), 1.75–1.2 (m, 12 H, $-CH_2-$), and 1.15 (d, 3 H, $J_{5,6}$ 7.5 Hz, H-6).

Anal. Calcd for $C_{22}H_{35}N_3O_{10}$: C, 52.68; H, 7.03; N, 8.38. Found: C, 52.86; H, 6.98; N, 8.37.

8-(Methoxycarbonyl)octyl 2-acetamido-2-deoxy-α-L-fucopyranoside (**64**).—To a solution of **63** (180 mg, 0.406 mmol) in EtOH (10 mL) was added $NaBH_4$ (46 mg, 1.22 mmol) and $NiCl_2 \cdot 6H_2O$ (29 mg). The mixture was stirred for 4 h at room temperature. The mixture was evaporated, and the residue was chromatographed on a column of SiO_2 with 50:10:1 $CHCl_3$–MeOH–NH_4OH to give the crude reduction product. The product was dissolved in MeOH (1 mL) and Ac_2O (0.5 mL) was added. The mixture was kept for 16 h at room temperature and then evaporated. Chromatography of the residue on a column of SiO_2 with 20:1 $CHCl_3$–MeOH gave **64** (111 mg, 73%), mp 92°, $[\alpha]_D^{20}$ −158.3° (*c* 0.5, MeOH); ν_{max}^{KBr} 3300, 2930, 1740, 1650, and 1050 cm^{-1}; ^{1}H-NMR: δ_H 4.73 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 4.19 (dd, 1 H, $J_{2,3}$ 11.1 Hz, H-2), 3.75 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3), 3.64 (s, 3 H, OCH_3), 2.31 (t, 2 H, *J* 7.3 Hz, $-CH_2CO-$), 1.97 (s, 3 H, NAc), 1.75–1.2 (m, 12 H, $-CH_2-$), and 1.21 (d, 3 H, $J_{5,6}$ 6.6 Hz, H-6).

Anal. Calcd for $C_{18}H_{33}NO_7 \cdot H_2O$: C, 57.58; H, 8.86; N, 3.73. Found: C, 57.69; H, 9.01; N, 3.89.

8-(Methoxycarbonyl)octyl 2-acetamido-2-deoxy-β-L-fucopyranoside (**66**).—Compound **65** (240 mg, 0.541 mmol) was reduced with $NaBH_4$ (61 mg) in EtOH (20 mL) in the presence of $NiCl_2 \cdot 6H_2O$ (38 mg), followed by *N*-acetylation with Ac_2O (1.3 mL) in MeOH (2 mL), as described for the preparation of **64**, giving **66** (141 mg, 69.9%), $[\alpha]_D^{20}$ +3.9° (*c* 0.5, MeOH); ν_{max}^{KBr} 3300, 2930, 1730, 1650, and 1070 cm^{-1}; ^{1}H-NMR: δ_H 4.31 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1), 3.64 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7.3 Hz, $-CH_2CO-$), 1.96 (s, 3 H, NAc), 1.75–1.2 (m, 12 H, $-CH_2-$), and 1.26 (d, 3 H, $J_{5,6}$ 6.6 Hz, H-6).

Anal. Calcd for $C_{18}H_{33}NO_7$: C, 57.58; H, 8.86; N, 3.73. Found: C, 57.32; H, 8.45; N, 3.62.

8-(Methoxycarbonyl)octyl 2-O-(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (**69**) *and 8-(methoxycarbonyl)octyl 2-O-(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)-3,4,6-tri-O-benzyl-α-D-mannopyranoside* (**72**). —Condensation of **7** (602 mg, 1.08 mmol) with 8-(methoxycarbonyl)octyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside[25] (**68**, 0.6 g, 0.966 mmol) in the presence of silver silicate (1 g) and powdered molecular sieve 4A (2 g) in benzene (20 mL) as described for the preparation of **10** and **21**, and chromatography of the product on a Lobar column with 2:1 hexane–EtOAc gave **69** (484 mg, 42.3%) and **72** (120 mg, 10%).

Compound **69** had $[\alpha]_D^{25}$ −38.5° (*c* 0.9), $\nu_{max}^{CHCl_3}$ 1731, 1498, 1452, 1362, 1100, and 1065 cm^{-1}; ^{1}H-NMR: δ_H 7.6–7.0 (m, 35 H, Ph), 4.90 (d, 1 H, $J_{1,2}$ 1.0 Hz, H-1), 4.41 (d, 1 H, $J_{1',2'}$ 1.6 Hz, H-1'), 3.67 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.7–1.2 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{71}H_{82}O_{13}$: C, 74.58; H, 7.23. Found: C, 74.32; H, 7.30.

Compound **72** had $[\alpha]_D^{25}$ +15° (*c* 0.8), $\nu_{max}^{CHCl_3}$ 1732, 1498, 1455, 1315, 1105, and 1029 cm^{-1}; ^{1}H-NMR: δ_H 7.4–7.1 (m, 35 H, Ph), 5.18 (d, 1 H, $J_{1',2'}$ 1.0 Hz, H-1'), 4.86 (d, 1 H, $J_{1,2}$ 1.0 Hz, H-1), 3.66 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.7–1.15 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{71}H_{82}O_{13}$: C, 74.58; H, 7.23. Found: C, 74.46; H, 7.22.

8-(Methoxycarbonyl)octyl 2-O-(2-O-acetyl-3,4,6-tri-O-benzyl-β-D-mannopyranosyl)-3,4,6-tri-O-benzyl-β-D-mannopyranoside (**70**) *and 8-(methoxycarbonyl)octyl 2-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-3,4,6-tri-O-benzyl-α-D-mannopyranoside* (**73**).—Compound **68** (621 mg, 1 mmol), silver triflate (283 mg), and *N,N,N',N'*-tetramethylurea (0.53 mL) were dissolved in anhydrous benzene (7 mL) and a small amount of the solvent was removed by distillation in an N_2 atmosphere. The solution was cooled to −78° in a dry ice–acetone bath. To this mixture was added dichloroethane (8 mL), followed by a solution of 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl chloride[28] (**67**, 509 mg, 1 mmol) in 1,2-dichloroethane (3 mL), with stirring. The cooling bath was removed and stirring was continued for 20 h at ambient temperature. After filtration through Celite, the filtrate was washed successively with aq $NaHCO_3$ and water, dried ($MgSO_4$), and evaporated. Chromatography of the residue on a Lobar column with 4:1 hexane–EtOAc gave **70** (81 mg, 7.4%) and **73** (607 mg, 55.4%).

Compound **70** had $[\alpha]_D^{25}$ −16.1° (*c* 1.1), $\nu_{max}^{CHCl_3}$ 1740, 1498, 1455, 1365, 1095, and 1075 cm^{-1}; ^{1}H-NMR: δ_H 7.5–7.1 (m, 30 H, Ph), 5.68 (dd, 1 H, $J_{2,3}$ 2.6 Hz, H-2), 4.86 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 4.71 (s, 1 H, H-1'), 3.66 (s, 3 H, OCH_3), 3.40 (m, 1 H, CH_2O), 2.30 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), 2.01 (s, 3 H, OAc), and 1.7–1.2 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{66}H_{78}O_{14}$: C, 72.37; H, 7.18. Found: C, 71.76; H, 7.12.

Compound **73** had $[\alpha]_D^{25}$ +23.3° (*c* 0.9), $\nu_{max}^{CHCl_3}$ 1738, 1498, 1455, 1370, 1085 cm^{-1}; ^{1}H-NMR: δ_H 7.4–7.1 (m, 30 H, Ph), 5.53 (dd, 1 H, $J_{2,3}$ 2.5 Hz, H-2), 5.08 (d,

1 H, $J_{1',2'}$ 1.6 Hz, H-1'), 4.86 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 3.66 (s, 3 H, OCH_3), 3.55 (dt, 1 H, *J* 8 Hz, CH_2O), 3.30 (dt, 1 H, *J* 8 Hz, CH_2O), 2.28 (t, 2 H, *J* 7.5 Hz, -CH_2CO-), 2.00 (s, 3 H, OAc), and 1.7–1.15 (m, 12 H, -CH_2-).

Anal. Calcd for $C_{66}H_{78}O_{14}$: C, 72.37; H, 7.18. Found: C, 72.13; H, 7.12.

8-(Methoxycarbonyl)octyl 2-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (**74**).—Compound **73** (607 mg) was *O*-deacetylated with NaOMe in MeOH as described for the preparation of **34**, and chromatography of the product on a Lobar column with 3:1 hexane–EtOAc gave **74** (514 mg, 88.1%), $[\alpha]_D^{24}$ +31.4° (*c* 0.9), $\nu_{max}^{CHCl_3}$ 3580, 1735, 1498, 1455, 1362, 1105, and 1085 cm^{-1}; ^{1}H-NMR: δ_H 7.4–7.1 (m, 30 H, Ph), 5.14 (d, 1 H, $J_{1',2'}$ 1.2 Hz, H-1'), 4.88 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 3.66 (s, 3 H, OCH_3), 3.55 (dt, 1 H, *J* 8 Hz, CH_2O), 3.30 (dt, 1 H, *J* 8 Hz, CH_2O), 2.30 (t, 2 H, *J* 7.5 Hz, -CH_2CO-), and 1.7–1.15 (m, 12 H, -CH_2-).

Anal. Calcd for $C_{64}H_{76}O_{13}$: C, 72.98; H, 7.27. Found: C, 72.73; H, 7.27.

8-(Methoxycarbonyl)octyl 2-O-(β-D-mannopyranosyl)-α-D-mannopyranoside (**71**). —A solution of **69** (480 mg, 0.42 mmol) in MeOH (28 mL) was hydrogenolyzed over 10% Pd–C (100 mg) as described for the preparation of **16**, giving **71** (181 mg, 84.2%) as an amorphous powder, $[\alpha]_D^{24}$ -4.9° (*c* 0.7, MeOH), ν_{max}^{KBr} 1740 and 1060 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.86 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 4.65 (d, 1 H, $J_{1',2'}$ 0.8 Hz, H-1'), 4.01 (dd, 1 H, $J_{2,3\text{ or }2',3'}$ 2.8 Hz, H-2 or 2'), 3.65 (s, 3 H, OCH_3), 2.31 (t, 2 H, *J* 7.5 Hz, -CH_2CO-), and 1.7–1.2 (m, 12 H, -CH_2-).

Anal. Calcd for $C_{22}H_{40}O_{13} \cdot H_2O$: C, 49.80; H, 7.98. Found: C, 50.10; H, 7.67.

8-(Methoxycarbonyl)octyl 2-O-(α-D-mannopyranosyl)-α-D-mannopyranoside (**75**). —(*A*) *From 72*, a solution of **72** (150 mg) in MeOH (40 mL) was hydrogenolyzed over 10% Pd–C as described for the preparation of **16**, giving **75** (68 mg, 94%) as a hygroscopic powder, $[\alpha]_D^{24}$ +64.2° (*c* 0.6, MeOH), ν_{max}^{KBr} 1740 and 1055 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.86 (d, 1 H, $J_{1,2}$ 0.7 Hz, H-1), 4.65 (d, 1 H, $J_{1',2'}$ 0.8 Hz, H-1'), 3.65 (s, 3 H, OCH_3), 2.31 (t, 2 H, *J* 7.5 Hz, -CH_2CO-), and 1.7–1.2 (m, 12 H, -CH_2-). (Lit.[16a], peracetate $[\alpha]_D^{25}$ +31° ($CHCl_3$)).

Anal. Calcd for $C_{22}H_{40}O_{13} \cdot 0.5H_2O$: C, 50.66; H, 7.92. Found: C, 50.86; H, 7.81.

(B) From 74, a solution of **74** (273 mg) in MeOH (25 mL) was hydrogenolyzed over 10% Pd–C as described for the preparation of **16**, giving **75** (125 mg, 94%), identical with the authentic **75** by comparison of specific rotation, ^{1}H-NMR and TLC.

8-(Methoxycarbonyl)octyl 6-O-(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)-2,3,4-tri-O-benzyl-α-D-mannopyranoside (**77**) *and 8-(methoxycarbonyl)octyl 6-O-(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)-2,3,4-tri-O-benzyl-α-D-mannopyranoside* (**79**). —(*A*) Condensation of **7** (90 mg, 0.161 mmol) with 8-(methoxycarbonyl)octyl 2,3,4-tri-*O*-benzyl-α-D-mannopyranoside [26] (**76**, 100 mg, 0.161 mmol) in the presence of silver silicate (325 mg) and molecular sieve 4A (1.5 g) in 1,2-dichloroethane (2.5 mL) as described for the preparation of **10** and **21**, and chromatography of the product on a column of SiO_2 with 30:1 toluene–EtOAc gave **77** (103 mg, 55.9%) and **79** (44 mg, 23.9%).

Compound **77** had $[\alpha]_D^{24}$ −5.3° (*c* 1), ν_{max}^{KBr} 1740 cm^{-1}; ^{1}H-NMR: δ_H 7.5–7.1 (m, 35 H, Ph), 4.70 (d, 1 H, $J_{1,2}$ 1 Hz, H-1), 4.65 (s, 1 H, H-1′), 3.65 (s, 3 H, OCH_3), 2.28 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.7–1.15 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{71}H_{82}O_{13}$: C, 74.58; H, 7.23. Found: C, 74.32; H, 7.30.

Compound **79** had $[\alpha]_D^{24}$ +56.2° (*c* 1), $\nu_{max}^{CHCl_3}$ 1740 cm^{-1}; ^{1}H-NMR: δ_H 7.5–7.1 (m, 35 H, Ph), 5.15 (s, 1 H, H-1′), 4.75 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 3.65 (s, 3 H, OCH_3), 2.28 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.7–1.2 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{71}H_{82}O_{13}$: C, 74.58; H, 7.23. Found: C, 74.21; H, 7.30.

(*B*) Silver triflate (496 mg, 1.93 mmol) and *N,N,N′,N′*-tetramethylurea (337 mg, 2.90 mmol) were added, with stirring, to a solution of **7** (265 mg, 0.47 mmol) and **76** (300 mg, 0.483 mmol) in 1,2-dichloroethane (5 mL) in an Ar atmosphere. The mixture was stirred for 48 h at room temperature. The mixture was partitioned between $CHCl_3$ and water. The organic phase was washed with aq $NaHCO_3$ and water, successively, dried ($MgSO_4$), and evaporated. Chromatography of the residue on a column of SiO_2 with 30:1 toluene–EtOAc gave **77** (151 mg, 27.3%) and **79** (273 mg, 42.9%).

8-(Methoxycarbonyl)octyl 6-O-(β-D-mannopyranosyl)-α-D-mannopyranoside (**78**). —A solution of **77** (117 mg, 0.102 mmol) in MeOH (20 mL) was hydrogenolyzed over 10% Pd–C (100 mg) as described for the preparation of **16**, and chromatography of the product on a column of SiO_2 with 5:5:1 $CHCl_3$–MeOH–NH_4OH gave **78** (45 mg, 86.3%), $[\alpha]_D^{24}$ +0.1° (*c* 0.9, MeOH), ν_{max}^{KBr} 1740 and 1055 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.70 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 4.59 (s, 1 H, H-1′), 3.65 (s, 3 H, OCH_3), 2.31 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.7–1.2 (m, 12 H, $-CH_2-$); SIMS: *m/z* 535 $[M + Na]^+$.

Anal. Calcd $C_{22}H_{40}O_{13} \cdot H_2O$: C, 49.80; H, 7.98. Found: C, 49.65; H, 7.86.

8-(Methoxycarbonyl)octyl 6-O-(α-D-mannopyranosyl)-α-D-mannopyranoside (**80**). —A solution of **79** (183 mg, 0.16 mmol) in MeOH (20 mL) was hydrogenolyzed over 10% Pd–C (150 mg) as described for the preparation of **16**, and chromatography of the product on a column of SiO_2 with 5:5:1 $CHCl_3$–MeOH–NH_4OH gave **80** (38 mg, 47%), $[\alpha]_D^{24}$ +55.1° (*c* 0.8, MeOH), ν_{max}^{KBr} 1740 and 1055 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.70 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 3.65 (s, 3 H, OCH_3), 2.31 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.7–1.2 (m, 12 H, $-CH_2-$); SIMS: *m/z* 535 $[M + Na]^+$.

Anal. Calcd $C_{22}H_{40}O_{13} \cdot H_2O$: C, 49.80; H, 7.98. Found: C, 49.77; H, 7.96.

8-(Methoxycarbonyl)octyl 2-O-(3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-mannopyranosyl)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (**83**).—Condensation of **47** (505 mg, 1.278 mmol) with **68** (793 mg, 1.278 mmol) in the presence of silver silicate (800 mg) and powdered molecular sieve 4A (800 mg) in toluene (25 mL) as described for the preparation of **10** and **21**, and chromatography of the product on a Lobar column with 3:1 hexane–EtOAc gave **83** (557 mg, 59.7%), $[\alpha]_D^{25}$ +37.4° (*c* 0.9), $\nu_{max}^{CHCl_3}$ 2028, 1745, 1452, 1369, and 1045 cm^{-1}. ^{1}H-NMR: δ_H 7.5–7.1 (m, 15 H, Ph), 5.43 (dd, 1 H, $J_{2',3'}$ 3.7 Hz, $J_{3',4'}$ 9.4 Hz, H-3′), 5.29 (t, 1 H, $J_{3',4'} = J_{4',5'}$ 9.4 Hz, H-4′), 4.98 (d, 1 H, $J_{1',2'}$ 1.8 Hz, H-1′), 4.85 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 3.66 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7 Hz, $-CH_2CO-$), 2.10 (s, 3 H, OAc), 2.09 (s, 3 H, OAc), 1.99 (s, 3 H, OAc), and 1.8–1.2 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{49}H_{63}N_3O_{15}$: C, 62.94; H, 6.79; N, 4.49. Found: C, 62.76; H, 6.83; N, 4.61.

8-(Methoxycarbonyl)octyl 2-O-(2-azido-2-deoxy-α-D-mannopyranosyl)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (**84**).—Compound **83** (557 mg, 0.596 mmol) was *O*-deacetylated with NaOMe in MeOH as described for the preparation of **34**, giving **84** (447 mg, 93%), $[\alpha]_D^{25}$ +46.7° (*c* 0.6), $\nu_{max}^{CHCl_3}$ 2027, 1731, 1498, 1453, and 1065 cm^{-1}; ^{1}H-NMR: δ_H 7.4–7.15 (m, 15 H, Ph), 4.99 (d, 1 H, $J_{1',2'}$ 1.4 Hz, H-1'), 4.93 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 3.62 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7 Hz, $-CH_2CO-$), and 1.7–1.2 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{43}H_{57}N_3O_{12}$: C, 63.92; H, 7.11; N, 5.20. Found: C, 63.17; H, 7.09; N, 5.22.

8-(Methoxycarbonyl)octyl 2-O-(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (**85**).—Condensation of 2,3,4-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl bromide[29] (**81**, 410 mg, 0.66 mmol) with **68** (427 mg, 0.85 mmol) in the presence of silver silicate (400 mg) and powdered molecular sieve 4A (1 g) in CH_2Cl_2 (20 mL) as described for the preparation of **10** and **21**, and chromatography of the product on a column of SiO_2 with 2:1 hexane–EtOAc gave **85** (400 mg, 58.3%), $[\alpha]_D^{24}$ +13.7° (*c* 0.4); ^{1}H-NMR: δ_H 7.9–6.9 (m, 19 H, Ph), 5.82 (t, 1 H, $J_{2',3'} = J_{3',4'}$ 10 Hz, H-3'), 5.51 (d, 1 H, $J_{1',2'}$ 8.5 Hz, H-1'), 5.20 (t, 1 H, $J_{3',4'} = J_{4',5'}$ 10 Hz, H-4'), 4.54 (s, 1 H, H-1), 3.65 (s, 3 H, OCH_3), 2.28 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), 2.04 (s, 6 H, OAc), 1.87 (s, 3 H, OAc), and 1.7–1.0 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{57}H_{67}NO_{17}$: C, 65.94; H, 6.51, N, 1.35. Found: C, 66.23; H, 6.68; N, 1.52.

8-(Methoxycarbonyl)octyl 2-O-(2-deoxy-2-phthalimido-β-D-glucopyranosyl)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (**86**).—Compound **85** (400 mg, 0.385 mmol) was *O*-deacetylated with NaOMe in MeOH as described for the preparation of **16**, giving **86** (290 mg, 82.6%), $[\alpha]_D^{24}$ +13.7° (*c* 0.4); ^{1}H-NMR: δ_H 7.8–7.1 (m, 19 H, Ph), 5.30 (d, 1 H, $J_{1',2'}$ 7.5 Hz, H-1'), 4.49 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 3.65 (s, 3 H, OCH_3), 2.28 (t, 2 H, *J* 7.5 Hz, $-CH_2CO-$), and 1.7–1.1 (m, 12 H, $-CH_2-$).

Anal. Calc for $C_{51}H_{61}NO_{14} \cdot 0.5H_2O$: C, 66.50; H, 6.68; N, 1.52. Found: C, 66.33; H, 6.78; N, 1.82.

8-(Methoxycarbonyl)octyl 2-O-(2-acetamido-2-deoxy-α-D-mannopyranosyl)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (**87**).—Compound **84** (310 mg, 0.384 mmol) was reduced with $NaBH_4$ (44 mg, 1.15 mmol) in EtOH (8 mL) containing 0.16 mM $NiCl_2 \cdot 6H_2O$ in EtOH (0.07 mL), followed by *N*-acetylation with Ac_2O (0.2 mL), as described for the preparation of **54**, and chromatography of the product with 10:1 $CHCl_3$–MeOH gave **87** (184 mg, 58.2%), $[\alpha]_D^{24}$ +42.3° (*c* 0.5, MeOH), ^{1}H-NMR: δ_H 7.4–7.1 (m, 15 H, Ph), 4.95 (d, 1 H, $J_{1',2' \text{ or } 1,2}$ 1.8 Hz, H-1' or 1), 4.93 (d, 1 H, $J_{1,2 \text{ or } 1',2'}$ 1.6 Hz, H-1 or 1'), 3.62 (s, 3 H, OCH_3), 2.28 (t, 2 H, *J* 7 Hz, $-CH_2CO-$), 2.01 (s, 3 H, NAc) and 1.7–1.2 (m, 12 H, $-CH_2-$).

Anal. Calcd for $C_{45}H_{61}NO_{13}$: C, 65.59; H, 7.46; N, 1.70. Found: C, 65.23; H, 7.33; N, 1.95.

8-(Methoxycarbonyl)octyl 2-O-(2-acetamido-2-deoxy-α-D-mannopyranosyl)-α-D-mannopyranoside (**88**).—A solution of **87** (170 mg, 0.206 mmol) in MeOH (15 mL) was hydrogenolyzed over 10% Pd–C (50 mg) as described for the preparation of **16**, giving **88** (86 mg, 75.4%), $[\alpha]_D^{24}$ +49.3° (*c* 0.7, MeOH), ν_{max}^{KBr} 1740, 1650, 1545, 1125, 1060, and 1020 cm^{-1}; ^{1}H-NMR: δ_H 5.01 (s, 1 H, H-1′), 4.90 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 4.44 (dd, 1 H, $J_{2',3'}$ 4.6 Hz, H-2′), 3.65 (s, 3 H, OCH_3), 2.31 (t, 2 H, *J* 7 Hz, –CH_2CO–), 2.00 (s, 3 H, NAc) and 1.7–1.2 (m, 12 H, –CH_2–).

Anal. Calcd for $C_{24}H_{43}NO_{13} \cdot H_2O$: C, 50.43; H, 7.94; N, 2.45. Found: C, 50.52; H, 7.76; N, 2.62.

8-(Methoxycarbonyl)octyl 2-O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (**89**).—A mixture of **86** (230 mg, 0.252 mmol) and hydrazine acetate (1.53 g, 16.6 mmol) in abs MeOH (50 mL) was heated under reflux for 5 h in an N_2 atomosphere. After being cooled to room temperature, the mixture was evaporated. The residue was partitioned between EtOAc and water. The organic phase was washed with water, dried ($MgSO_4$), and evaporated. The residue was dissolved in abs MeOH (20 mL) and Ac_2O (2 mL) was added. After being kept for 16 h at room temperature, the mixture was evaporated. Chromatography of the residue on a column of SiO_2 with 10:1 $CHCl_3$–MeOH gave **89** (154 mg, 74.4%), $[\alpha]_D^{25}$ –6.1° (*c* 0.7, MeOH); ^{1}H-NMR (CD_3OD): δ_H 7.5–7.1 (m, 15 H, Ph), 4.80 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 4.51 (d, 1 H, $J_{1',2'}$ 8 Hz, H-1′), 3.62 (s, 3 H, OCH_3), 2.27 (t, 2 H, *J* 7.5 Hz, –CH_2CO–), 1.94 (s, 3 H, NAc), and 1.7–1.1 (m, 12 H, –CH_2–).

Anal. Calcd for $C_{45}H_{61}NO_{13}$: C, 65.99; H, 7.46; N, 1.70. Found: C, 65.67; H, 7.35; N, 1.81.

8-(Methoxycarbonyl)octyl 2-O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-α-D-mannopyranoside (**90**).—A solution of **89** (144 mg, 0.174 mmol) in MeOH (10 mL) was hydrogenolyzed over 10% Pd–C (40 mg) as described for the preparation of **16**, giving **90** (84 mg, 87.5%), $[\alpha]_D^{24}$ +4.7° (*c* 0.8, MeOH); ν_{max}^{KBr} 1740, 1645, 1560, and 1065 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.77 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 4.45 (d, 1 H, $J_{1',2'}$ 8.1 Hz, H-1′), 3.65 (s, 3 H, OCH_3), 2.32 (t, 2 H, *J* 7.5 Hz, –CH_2CO–), 1.99 (s, 3 H, NAc), and 1.7–1.1 (m, 12 H, –CH_2–).

Anal. Calcd for $C_{24}H_{43}NO_{13} \cdot 2H_2O$: C, 46.71; H, 8.38; N, 2.48. Found: C, 46.90; H, 8.35; N, 2.01.

8-(Methoxycarbonyl)octyl 6-O-(3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-mannopyranosyl)-2,4-di-O-benzyl-α-D-mannopyranoside (**91**).—A solution of **47** (1.01 g, 2.678 mmol) in CH_2Cl_2 (5 mL) was added, with stirring, to a cooled (–78°) mixture of 8-(methoxycarbonyl)octyl 2,4-di-*O*-benzyl-α-D-mannopyranoside[26] (**82**, 710 mg, 1.339 mmol), silver triflate (757 mg, 2.94 mmol), and *N,N,N′,N′*-tetramethylurea (1.4 mL, 11.78 mmol) in CH_2Cl_2 (15 mL) in an N_2 atmosphere. The cooling bath was removed and the temperature was raised gently to room temperature. The stirring was continued for 18 h at ambient temperature. The mixture was filtered through Celite. The filtrate was washed successively with aq $NaHCO_3$ and water, dried ($MgSO_4$), and evaporated. Chromatography of the residue on a Lobar

column with 1:1 hexane–EtOAc gave **91** (486 mg, 43%), $[\alpha]_D^{25}$ +62.3° (*c* 0.9), $\nu_{max}^{CHCl_3}$ 3560, 2110, 1745, 1455, 1370, and 1060 cm^{-1}; ^{1}H-NMR: δ_H 7.5–7.25 (m, 10 H, Ph), 5.35 (dd, 1 H, $J_{2',3'}$ 2.8, $J_{3',4'}$ 8.9 Hz, H-3'), 5.31 (t, 1 H, $J_{3',4'} = J_{4',5'}$ 8.9 Hz, H-4'), 5.04 (d, 1 H, $J_{1',2'}$ 1.6 Hz, H-1'), 4.81 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 3.66 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7.5 Hz, –CH_2CO–), 2.08 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 2.03 (s, 3 H, OAc), and 1.7–1.2 (m, 12 H, –CH_2–).

Anal. Calcd for $C_{42}H_{57}N_3O_{15} \cdot 0.5H_2O$: C, 59.14; H, 6.85; N, 4.93. Found: C, 59.07; H, 6.77; N, 5.07.

8-(Methoxycarbonyl)octyl 6-O-(2-azido-2-deoxy-α-D-mannopyranosyl)-2,4-di-O-benzyl-α-D-mannopyranoside (**92**).—Compound **91** (470 mg, 0.557 mmol) was *O*-deacetylated with NaOMe in MeOH as described for the preparation of **34**, giving **92** (333 mg, 83.2%), $[\alpha]_D^{25}$ +69.1° (*c* 0.7), $\nu_{max}^{CHCl_3}$ 3560, 2120, 1731, and 1075 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 7.5–7.2 (m, 10 H, Ph), 4.95 (d, 1 H, $J_{1',2'}$ 1.3 Hz, H-1'), 4.73 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 3.64 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7.5 Hz, –CH_2CO–), and 1.7–1.2 (m, 12 H, –CH_2–).

Anal. Calcd for $C_{36}H_{51}N_3O_{12} \cdot 0.6H_2O$: C, 59.34; H, 7.22; N, 5.77. Found: C, 59.04; H, 7.02; N, 5.80.

8-(Methoxycarbonyl)octyl 6-O-(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-2,4-di-O-benzyl-α-D-mannopyranoside (**93**) *and 8-(methoxycarbonyl)octyl 3,6-di-O-(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-2,4-di-O-benzyl-α-D-mannopyranoside* (**99**).—Condensation of **81** (564 mg, 1.06 mmol) with **82** (1.05 g, 2.12 mmol) in the presence of silver silicate (2 g) and powdered molecular sieve 4A (1 g) in benzene (20 mL) as described for the preparation of **16** and **21**, and chromatography of the product on a Lobar column with 1:1 hexane–EtOAc gave **93** (184 mg, 18.9%) and **99** (693 mg, 48.9%).

Compound **93** had $[\alpha]_D^{24}$ +22.3° (*c* 0.8, MeOH); ^{1}H-NMR: δ_H 7.7–7.15 (m, 14 H, Ph), 5.82 (dd, 1 H, $J_{2',3'}$ 9, $J_{3',4'}$ 10 Hz, H-3'), 5.45 (d, 1 H, $J_{1',2'}$ 8.6 Hz, H-1'), 5.19 (t, 1 H, $J_{3',4'} = J_{4',5'}$ 10 Hz, H-4'), 4.40 (s, 1 H, H-1), 3.60 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7.5 Hz, –CH_2CO–), 2.09 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), 1.87 (s, 3 H, OAc), and 1.7–1.1 (m, 12 H, –CH_2–).

Anal. Calcd for $C_{50}H_{61}NO_{17} \cdot H_2O$: C, 62.11; H, 6.57; N, 1.45. Found: C, 61.87; H, 6.27; N, 1.50.

Compound **99** had $[\alpha]_D^{25}$ +16° (*c* 0.7); ^{1}H-NMR: δ_H 7.5–7.1 (m, 14 H, Ph), 5.78 (dd, 1 H, $J_{2',3' \text{ or } 2'',3''}$ 9.2, $J_{3'4' \text{ or } 3'',4''}$ 11 Hz, H-3' or 3''), 5.76 (dd, 1 H, $J_{2'',3'' \text{ or } 2',3'}$ 9.2, $J_{3'',4'' \text{ or } 3',4'}$ 11 Hz, H-3'' or 3'), 5.47 (d, 1 H, $J_{1',2' \text{ or } 1'',2''}$ 8 Hz, H-1' or 1''), 5.35 (d, 1 H, $J_{1'',2'' \text{ or } 1',2'}$ 8.4 Hz, H-1'' or 1'), 5.14 (t, 1 H, $J_{4',5' \text{ or } 4'',5''}$ 9.4 Hz, H-4' or 4''), 5.13 (t, 1 H, $J_{4'',5'' \text{ or } 4',5'}$ 9.6 Hz, H-4'' or 4'), 3.68 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7.5 Hz, –CH_2CO–), 2.05 (s, 3 H, OAc), 2.01 (s, 6 H, OAc), 1.99 (s, 3 H, OAc), 1.84 (s, 3 H, OAc), 1.82 (s, 3 H, OAc), and 1.7–1.1 (m, 12 H, –CH_2–).

Anal. Calcd for $C_{70}H_{80}NO_{26} \cdot H_2O$: C, 60.77; H, 5.97; N, 2.03. Found: C, 60.63; H, 5.85; N, 1.96.

8-(Methoxycarbonyl)octyl 6-O-(2-deoxy-2-phthalimido-β-D-glucopyranosyl)-2,4-di-O-benzyl-α-D-mannopyranoside (**94**).—Compound **93** (161 mg) was *O*-deacetylated

with NaOMe in MeOH as described for the preparation of **34**, giving **94** (111 mg, 80%), $[\alpha]_D^{24}$ +5.5° (*c* 0.7, MeOH); ^{1}H-NMR: δ_H 7.72–7.15 (m, 14 H, Ph), 5.31 (d, 1 H, $J_{1',2'}$ 8.1 Hz, H-1'), 4.59 (s, 1 H, H-1), 3.65 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7.5 Hz, –CH_2CO–), and 1.7–1.1 (m, 12 H, –CH_2–).

Anal. Calcd for $C_{44}H_{55}NO_{14} \cdot 2H_2O$: C, 61.60; H, 6.93; N, 1.63. Found: C, 61.67; H, 6.70; N, 1.82.

*8-(Methoxycarbonyl)octyl 6-O-(2-acetamido-2-deoxy-α-*D*-mannopyranosyl)-2,4-di-O-benzyl-α-*D*-mannopyranoside* (**95**).—Compound **92** (320 mg, 0.446 mmol) was reduced with $NaBH_4$ (67 mg) in EtOH (8 mL) containing 0.16 mM $NiCl_2 \cdot 6H_2O$ in EtOH (0.08 mL), followed by *N*-acetylation with Ac_2O (0.2 mL), as described for the preparation of **54**, and chromatography on a column of SiO_2 with 10:1 $CHCl_3$–MeOH, gave **95** (234 mg, 71.5%), $[\alpha]_D^{25}$ +54.7° (*c* 0.6), $\nu_{max}^{CHCl_3}$ 1730, 1660, 1455, and 1075 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 7.5–7.25 (m, 10 H, Ph), 4.78 (d, 1 H, $J_{1',2'}$ 1.4 Hz, H-1'), 4.71 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 4.41 (dd, 1 H, $J_{2',3'}$ 5 Hz, H-2'), 3.64 (s, 3 H, OCH_3), 2.31 (t, 2 H, *J* 7.5 Hz, –CH_2CO–), 2.00 (s, 3 H, NAc), and 1.7–1.25 (m, 12 H, –CH_2–).

Anal. Calcd for $C_{38}H_{55}NO_{13} \cdot H_2O$: C, 60.70; H, 7.64; N, 1.86. Found: C, 60.84; H, 7.56; N, 2.02.

*8-(Methoxycarbonyl)octyl 6-O-(2-acetamido-2-deoxy-α-*D*-mannopyranosyl-α-*D*-mannopyranoside* (**96**).—A solution of **95** (230 mg, 0.313 mmol) in MeOH (20 mL) was hydrogenolyzed over 10% Pd–C (80 mg) as described for the preparation of **16**, giving **96** (118 mg, 68.3%), $[\alpha]_D^{25}$ +56.6° (*c* 0.8), ν_{max}^{KBr} 1740, 1650, and 1545 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 4.74 (d, 1 H, $J_{1',2'}$ 1.2 Hz, H-1'), 4.71 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1), 4.36 (dd, 1 H, $J_{2',3'}$ 5 Hz, H-2'), 3.95 (dd, 1 H, $J_{3',4'}$ 9.3 Hz, H-3'), 3.65 (s, 3 H, OCH_3), 2.32 (t, 2 H, *J* 7.5 Hz, –CH_2CO–), 2.01 (s, 3 H, NAc), and 1.7–1.25 (m, 12 H, –CH_2–).

Anal. Calcd for $C_{24}H_{43}NO_{13} \cdot H_2O$: C, 50.43; H, 7.94; N, 2.45. Found: C, 50.55; H, 7.76; N, 2.58.

*8-(Methoxycarbonyl)octyl 6-O-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-2,4-di-O-benzyl-α-*D*-mannopyranoside* (**97**).—Compound **94** (104 mg, 0.132 mmol) was dephthaloyled with hydrazine acetate (762 mg, 8.27 mmol) in MeOH (30 mL), followed by *N*-acetylation with Ac_2O (1 mL) in MeOH (10 mL), as described for the preparation of **89**, giving **97** (66 mg, 71.1%), $[\alpha]_D^{25}$ +12.3° (*c* 0.7, MeOH); ν_{max}^{KBr} 1740, 1652, and 1555 cm^{-1}; ^{1}H-NMR (CD_3OD): δ_H 7.48–7.25 (m, 10 H, Ph), 4.69 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 4.47 (d, 1 H, $J_{1',2'}$ 8.2 Hz, H-1'), 3.63 (s, 3 H, OCH_3), 2.30 (t, 2 H, *J* 7.5 Hz, –CH_2CO–), 1.98 and 1.86 (s, total 3 H, NAc), and 1.7–1.1 (m, 12 H, –CH_2–); SIMS (glycerol): *m/z* 734 $[M + H]^+$.

Anal. Calcd for $C_{38}H_{55}NO_{13} \cdot H_2O$: C, 60.70; H, 7.37; N, 1.86. Found: C, 60.50; H, 7.57; N, 2.01.

*8-(Methoxycarbonyl)octyl 6-O-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-α-*D*-mannopyranoside* (**98**).—A solution of **97** (54 mg, 0.082 mmol) in MeOH (11 mL) was hydrogenolyzed over 10% Pd–C (20 mg) as described for the preparation of **16**, giving **98** (36 mg, 78%) as a hygroscopic powder, $[\alpha]_D^{25}$ –12.4° (*c* 0.7, MeOH);

^{1}H-NMR (CD_3OD): δ_H 4.68 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1), 4.44 (d, 1 H, $J_{1',2'}$ 8.4 Hz, H-1′), 3.63 (s, 3 H, OCH_3), 2.23 (t, 2 H, J 7.5 Hz, $-CH_2CO-$), 1.98 (s, 3 H, NAc), and 1.7–1.25 (m, 12 H, $-CH_2-$); SIMS (glycerol): m/z 576 $[M + Na]^+$ and m/z 592 $[M + K]^+$.

Anal. Calcd for $C_{24}H_{43}NO_{13} \cdot 2H_2O$: C, 46.71; H, 8.38; N, 2.48. Found: C, 46.89; H, 8.45; N, 2.31.

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