Carbohydrate Research, 137 (1985) 79–88
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SYNTHESIS OF A MODEL, LINEAR D-MANNOPENTAOSE FOR THE NONREDUCING-END SEQUENCE OF THE CELL-SURFACE D-MANNAN OF *Escherichia coli, Candida albicans,* AND *Saccharomyces cerevisiae**

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(Received May 24th, 1984; accepted for publication, August 22nd, 1984)

ABSTRACT

Synthesis, in a regio- and stereocontrolled way, of a linear D-*manno*-oligosaccharide, namely, *O*-α-Man-(1→3)-*O*-α-Man-(1→2)-*O*-α-Man-(1→2)-*O*-α-Man-(1→2)-α-Man, which corresponds to a part of the structure of the cell-surface D-mannan of *Escherichia coli, Candida albicans,* and *Saccharomyces cerevisiae,* is described.

INTRODUCTION

Linear D-*manno*-oligosyl structures containing both α-D-(1→2) and α-D-(1→3) interglycosidic linkages have been proposed for partial structures of the microbial, cell-surface glycans. For example, in 1976, Prehm *et al.* proposed[2] structure **1** for the O9 antigenic polysaccharide found in the outer membrane of *E. coli.* Similar nonreducing-end D-mannosyl sequences were found in the D-mannan structures **2** and **3**, which were proposed for the cell-surface glycans of *Candida albicans*[3] and *Saccharomyces cerevisiae*[4], respectively. As part of a project on the synthesis of microbial glycans, we had reported[5] a synthesis of the linear D-mannohexaose **4** having an α-(1→2) interglycosidic linkage. We now describe a synthesis of the model, linear D-mannopentaose **5**, which corresponds to the nonreducing-end D-mannosyl sequence of **1, 2,** and **3**, and which was also isolated from the cell wall of *Hansenula wingei* NRRL Y-2340 (ref. 6) and characterized by its ^{1}H-N.m.r. data[7].

RESULTS AND DISCUSSION

Based on a retrosynthetic analysis of **5**, the D-mannotriosyl glycosyl acceptor **6** and two D-mannosyl donors (**7** and **8**) were designed as the key synthetic inter-

*Part 30 in the series, "Synthetic Studies on Cell-surface Glycans". For part 29, see ref. 1.
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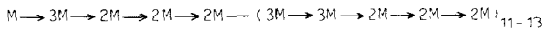

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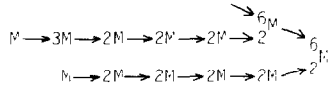

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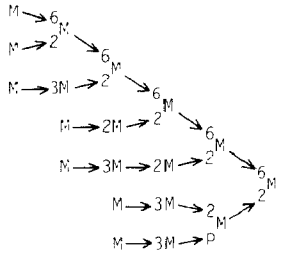

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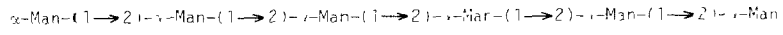

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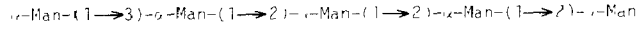

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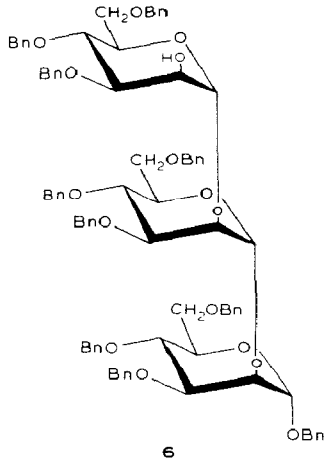

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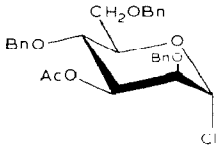

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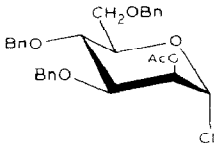

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mediates. As **6** (ref. 5) and **8** (ref. 8) were already available, a synthetic route to **7** was first developed.

Allyl α-D-mannopyranoside (**9**) was tritylated, to give **10**, which was stannylated[9] with $(Bu_3Sn)_2O$, and the product alkylated with allyl bromide in the presence[10] of Bu_4NBr, to give a 66% yield of a mixture of the 3-*O*-allyl (**11**) and 2-*O*-allyl (**12**) derivatives in the ratio of 6:1. Regioselective allylation *via* the inter-

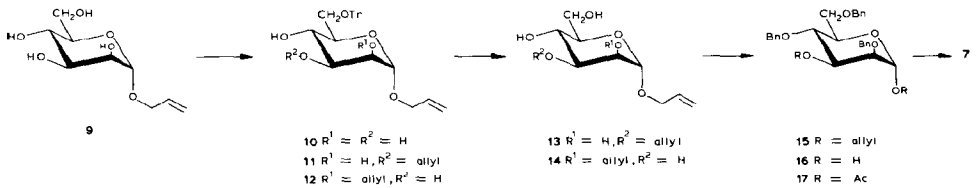
TABLE I

^{13}C-N M.R -CHEMICAL SHIFTS OF D-MANNOSE DERIVATIVES[a]

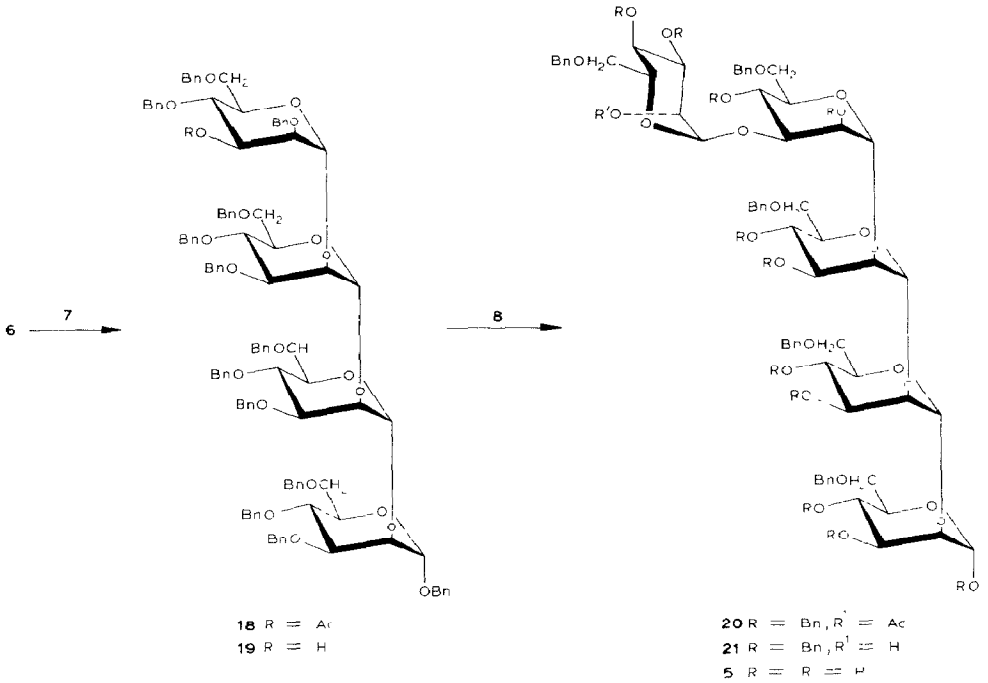
Structure	*Chemical shift (p.p.m.) for each carbon atom*								
	1	2	3	4	5	6	$-CPh_3$	$-CH_2-CH=$	$-CH_2Ph$
Tr-6M-OA (**10**)	98.65 (170.0)	71.73	70.68	69.40	70.39	64.54	87.06	67.87	
A-3M-OA (**13**)	98.76 (168.5)	67.99	78.99	64.66	72.44	60.80		67.76(1-O) 70.86(3-O)	
A-2M-OA (**14**)	96.77 (168.5)	77.53	70.86	67.17	72.26	61.26		67.52(1-O) 72.26(2-O)	
$(Bn)_3$-2,4,6M-OH (**16**)	91.44 (168.5)	76.82	70.44	78.75	71.26	69.56			72.72(2-O) 73.25(6-O) 74.59(4-O)

[a]The values of δ_c are recorded for solutions in $CDCl_3$ at 20°, and are expressed in p.p.m. downward from tetramethylsilane. Values in parentheses correspond to $^1J_{CH}$ in Hz. M = α-D-mannopyranosyl, A = allyl, and Bn = benzyl.

mediacy of the stannylene[11] derivative of **10** resulted in a lower yield of the 3-*O*-allyl derivative **11**. The regiochemistry of **11** and **12** was assigned by converting them into diallyl ethers **13** and **14**, respectively, and by recording their ^{13}C-n.m.r. spectra. Thus, the ^{13}C-n.m.r. spectrum of **13** contains a deshielded signal at δ 78.99 for C-3, and that of **14** contains a deshielded signal at δ 77.53 for C-2 and a shielded signal for C-1 at δ 96.77 (see Table I). Benzylation of **13** to give **15**, and deallylation of **15** with $PdCl_2$–NaOAc in aq. AcOH[12] afforded the tri-*O*-benzyl-D-mannopyranose **16** in 55% overall yield from **13**. Acetylation of **16** to give **17**, and treatment of **17** with HCl afforded the desired chloride **7**. It may be noted that chloride **7** and the bromide corresponding to **7** have recently been prepared by Kong and Schuerch[13] and by Matta and his coworkers[14], respectively, *via* different routes.



Having prepared the D-mannosyl donor **7**, glycosylation of the acceptor **6** with **7** was performed in the presence of $AgOSO_2CF_3$ and powdered molecular sieves 4A, to give an 80% yield of the protected D-mannotetraoside **18**. The presence, in the ^{1}H-n.m.r. spectrum of **18**, of a singlet at δ 1.96 for the acetyl methyl group indicated the stereochemical homogeneity of **18**, even though the configuration at the newly introduced anomeric carbon atom remained to be assigned later (at the pentasaccharide stage).



O-Deacetylation of **18** afforded the D-mannotetraosyl glycosyl acceptor **19**, which was, in turn, glycosylated with the D-mannosyl donor **8**, again by use of $AgOSO_2CF_3$ and powdered molecular sieves 4A, to give a 58% yield of the protected D-mannopentaoside **20**. *O*-Deacetylation of **20**, to give **21**, and hydrogenolysis of **21** in the presence of 10% Pd–C in AcOH gave the target molecule **5**. The regiochemistry of the free D-mannopentaose **5** was evident from the synthetic sequence, and the stereochemistry was firmly assigned according to the ^{1}H- and ^{13}C-n.m.r. data (see Figs. 1 and 2). Thus, in the ^{13}C-n.m.r. spectrum, three signals were observed, at δ 102.98, 101.37, and 93.28, having $^1J_{CH}$ values of ~170 Hz for C-1d and C-1e, C-1b and C-1c, and C-1a, respectively, in accordance with the α-D-configurations of the five anomeric carbon atoms[15]. The chemical shifts for each anomeric carbon atom were assigned based on the data for both α-D-mannopyranose[16] and the related model D-manno-oligosides[5,17]. The ^{13}C-n.m.r. data for synthetic **5** were found to be in good agreement with those reported by Gorin[18] for a natural sample. ^{1}H-N.m.r. data for **5** were assignable, as shown in Fig. 1, based on our previous observation for the synthetic D-manno-oligosides[5,17] and found to be identical with the data for the natural D-mannopentaose reported by Ballou and co-workers[7].

In conclusion, D-mannopentaose **5**, corresponding to a part of the proposed structure for the lipopolysaccharide of *E. coli* and yeast cell-wall D-mannan, was synthesized unambiguously. The ^{1}H- and ^{13}C-n.m.r. data for the synthetic **5** were

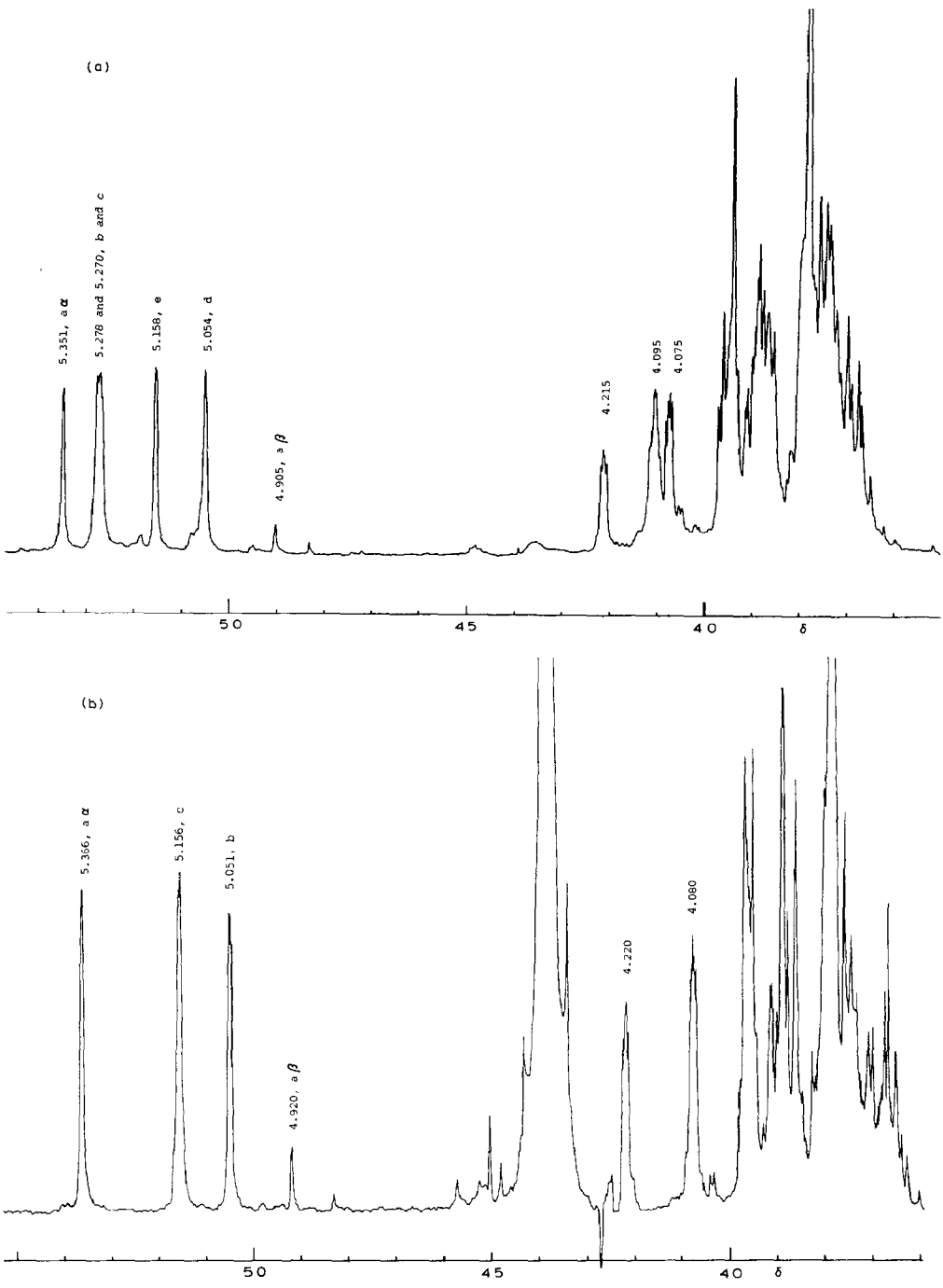


Fig. 1. 400-MHz, ^{1}H-n.m.r. spectra (in D_2O at 63°) of (a) M_e-3M_d-2M_c-2M_b-2M_a (**5**) and (b) M_c-3M_b-2M_a. This mannotriose was prepared in a synthetic sequence similar to that in the case of **5**. The values of δ_H are expressed in p.p.m. downward from the internal standard, sodium 2,2,3,3-tetradeuterio-4,4-dimethyl-4-silapentanoate.

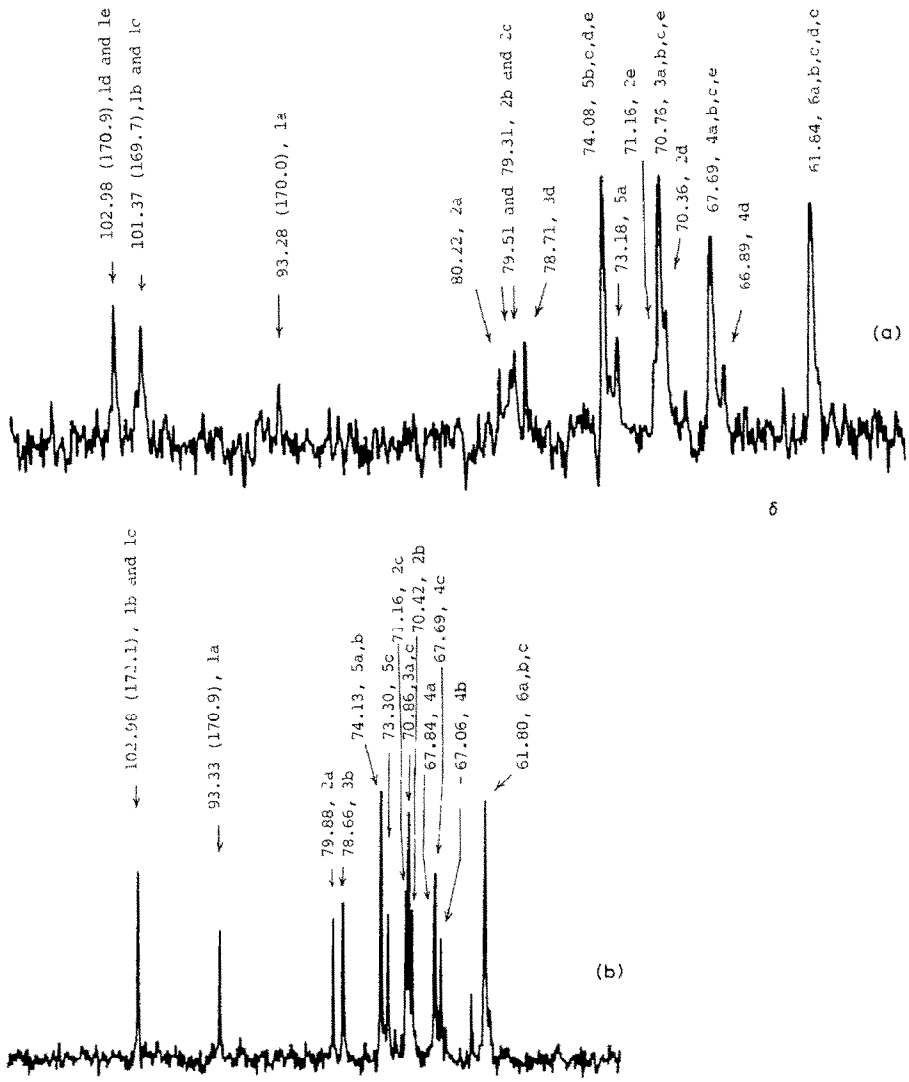


Fig. 2. ^{13}C-N.m.r. spectra (in D_2O at 20°) of (a) M_e-3M_d-2M_c-2M_b-2M_a (**5**) and (b) M_c-3M_b-2M_a. [The values of δ_c are expressed in p.p.m. downward from tetramethylsilane, referenced indirectly with an internal standard of 1,4-dioxane (δ 67.40). Values in parentheses correspond to $^1J_{CH}$ in Hz.]

found to be identical with those for a natural sample, thus providing synthetic support for the structure proposed.

EXPERIMENTAL

General. — Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Optical rotations were determined with a

Perkin–Elmer Model 241 MC polarimeter, for solutions in $CHCl_3$ at 25°, unless noted otherwise. Column chromatography was performed on columns of Silica Gel Merck (70–230 mesh; E. Merck, Darmstadt, Germany). Flash chromatography was performed on columns of Wako gel C-300 (200–300 mesh; Wako Pure Chemicals, Osaka, Japan). Thin-layer chromatography (t.l.c.) was performed on plates (layer thickness, 0.25 mm) precoated with Silica Gel 60 F_{254} (E. Merck, Darmstadt, Germany). "High performance" thin-layer chromatography (h.p.t.l.c.) was performed on plates (layer thickness, 0.20 mm) precoated with Silica Gel 60 F_{254} (E. Merck, Darmstadt, Germany). I.r. spectra were recorded with an EPI-G2 Hitachi spectrophotometer, using KBr pellets for the crystalline samples, and neat films for the liquid samples. ^{1}H-N.m.r. spectra were recorded with either a JNM-GX400 or a JNM-FX90Q n.m.r. spectrometer, using tetramethylsilane as the internal standard. ^{13}C-N.m.r. spectra were recorded with a JNM-FX 100FT n.m.r. spectrometer operated at 25.05 MHz. The values of δ_c and δ_H are expressed in p.p.m. downwards from the internal standard, for solutions in $CDCl_3$, unless noted otherwise.

Allyl 6-O-trityl-α-D-mannopyranoside (**10**). — A mixture of allyl alcohol (500 mL) and acetyl chloride (25 mL) was stirred for 1 h at 25°. To this solution was added D-mannose (100 g, 0.55 mol) with ice cooling, and the mixture was stirred for 9 days at 25°, when t.l.c. showed the disappearance of D-mannose (at R_F 0.15) and appearance of allyl α-D-mannopyranoside (**9**) at R_F 0.57 (in 2:1 $CHCl_3$–MeOH). Neutralization with Et_3N (100 mL) and evaporation *in vacuo* afforded crude **9** (172 g). To a solution of **9** (172 g) in pyridine (500 mL) was added trityl chloride (180 g, 0.65 mol), and the mixture was stirred for 16 h at 25°. Evaporation of the solvent *in vacuo*, and flash chromatography through silica gel C-300 (500 g) in toluene, and then in 2:1 toluene–EtOAc, afforded crude **10** (302 g, 95%). An analytical sample of **10** was obtained by rechromatography; $[\alpha]_D$ +2.1° (*c* 0.72); R_F 0.35 in 2:1 toluene–EtOAc; δ_H 6.1–5.7 (m, 1 H, -C*H*=CH_2), 5.36–5.10 (m, 2 H, -CH=CH_2), and 4.98 (d, 1 H, *J* 2 Hz, H-1).

Anal. Calc. for $C_{28}H_{30}O_6$: C, 72.73; H, 6.49. Found: C, 73.11; H, 6.65.

Allyl 3-O-allyl-6-O-trityl-α-D-mannopyranoside (**11**) *and allyl 2-O-allyl-6-O-trityl-α-D-mannopyranoside* (**12**). — *Method A.* A mixture of **10** (1.14 g, 2 mmol) and $(Bu_3Sn)_2O$ (900 mg, 1.5 mmol) in toluene (50 mL) was stirred under reflux, with azeotropic removal of water, during 14 h, and 30 mL of toluene was distilled off. To the remaining solution were added allyl bromide (10 mL) and Bu_4NBr (0.1 g) at 80°, and the mixture was stirred thereat for 16 h. Solvent was evaporated *in vacuo*, and the residue, in EtOAc (30 mL), was stirred with saturated aq. KF solution (20 mL) for 3 h at 25°. The precipitated Bu_3SnF was filtered off (Celite), and the organic layer was successively washed with water and satd. saline, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed through silica gel C-300 (20 g) in 2:1 toluene-EtOAc, to give **11** (596 mg, 56%) and **12** (104 mg, 9.8%).

Compound **11**: $[\alpha]_D$ +9.7° (*c* 0.60); R_F 0.50 in 2:1 toluene–EtOAc; δ_H 6.2–5.76 (m, 2 H, -C*H*=CH_2), 5.4–5.1 (m, 4 H, -CH=CH_2), and 4.92 (d, 1 H, *J* 2 Hz, H-1).

Anal. Calc. for $C_{31}H_{34}O_6$: C, 74.08; H, 6.82. Found: C, 74.01; H, 6.87.

Compound **12**: R_F 0.36 in 2:1 toluene–EtOAc; δ_H 6.2–5.76 (m, 2 H, -C*H*=CH_2), 5.4–5.1 (m, 4 H, -CH=CH_2), and 4.52 (s, 1 H, H-1), used for the next step without further characterization.

Method B. A mixture of **10** (1.14 g, 2 mmol) and Bu_2SnO (863 mg) in MeOH (20 mL) was stirred under reflux for 16 h. MeOH was evaporated *in vacuo*, and a solution of the residue and allyl bromide (1 mL) in $HCONMe_2$ (20 mL) was stirred for 16 h at 80°. Processing, and chromatography over silica gel C-300 (20 g) in 2:1 toluene–EtOAc, afforded **11** (405 mg, 33%).

Allyl 3-O-allyl-α-D-mannopyranoside (**13**). — A solution of **11** (350 mg) in AcOH (20 mL)–H_2O (4 mL) was stirred for 15 min at 80°. Processing, and chromatography over SiO_2–C-300 (20 g) in $CHCl_3$ and then in 5:1 $CHCl_3$–MeOH, afforded **13** (150 mg, quant. yield); $[\alpha]_D$ +22.5° (*c* 0.5, MeOH); R_F 0.55 in 1:1 toluene–EtOAc; δ_c 134.39 (-*C*H=CH_2), 133.57 (-*C*H=CH_2), 117.78 (-CH=*C*H_2), and 117.07 (-CH=*C*H_2).

Allyl 2-O-allyl-α-D-mannopyranoside (**14**). — A solution of **12** (100 mg) in AcOH (10 mL)–H_2O (4 mL) was stirred for 15 min at 80°. Processing, and chromatography over silica gel C-300 (5 g) in $CHCl_3$ and then in 5:1 CHCl–MeOH, afforded **14** (40 mg, 93%); R_F 0.56 in 1:1 toluene–EtOAc; δ_c 134.27 (-*C*H=CH_2), 133.40 (-*C*H=CH_2), 117.72 (-CH=*C*H_2), and 116.96 (-CH=*C*H_2).

Allyl 3-O-allyl-2,4,6-tri-O-benzyl-α-D-mannopyranoside (**15**). — A solution of **13** (520 mg, 2 mmol) in $HCONMe_2$ (20 mL) was benzylated with NaH (50%; 316 mg, 6.6 mmol) and benzyl bromide (0.9 mL). Processing, and chromatography over silica gel C-300 (50 g) in 40:1 toluene–EtOAc, gave **15** (930 mg, 87%); $[\alpha]_D$ +26.3° (*c* 0.20); R_F 0.66 in 10:1 toluene–EtOAc; δ_H 7.5–7.1 (m, 15 H, aromatic), 6.1–5.6 (m, 2 H, -C*H*=CH_2), and 5.4–5.0 (m, 4 H, -CH=CH_2).

Anal. Calc. for $C_{33}H_{38}O_6$: C, 74.69; H, 7.22. Found: C, 74.29; H, 7.16.

2,4,6-Tri-O-benzyl-α-D-mannopyranose (**16**). — A mixture of **15** (126 mg, 0.24 mmol), $PdCl_2$ (50 mg), NaOAc (50 mg), and H_2O (0.1 mL) in AcOH (2 mL) was stirred for 2 days at 25°. Solvent was evaporated *in vacuo*, and a solution of the residue in EtOAc (10 mL) was successively washed with H_2O and satd. saline and dried ($MgSO_4$). Evaporation of the solvent, and chromatography of the residue over silica gel C-300 (5 g) in 2:1 toluene–EtOAc gave **16** (86 mg, 63%); crystals from *i*-PrOH; m.p. 75–76°, R_F 0.13 in 5:1 toluene–EtOAc; δ_H 7.4–7.1 (m, 15 H, aromatic), 5.27 (bs, 1 H, H-1), and 4.9–4.4 (m, 6 H, 3 CH_2Ph).

Anal. Calc. for $C_{27}H_{30}O_6$: C, 71.98; H, 6.71. Found: C, 72.15; H, 6.63.

3-O-Acetyl-2,4,6-tri-O-benzyl-α-D-mannopyranosyl acetate (**17**). — A mixture of **16** (1.0 g) and Ac_2O (10 mL) in pyridine (20 mL) was stirred for 16 h at 25°. Processing, and chromatography over silica gel C-300 (50 g) in 7:1 toluene–EtOAc, gave **17** (1.1 g, 93%); $[\alpha]_D$ 0° (*c* 0.25); R_F 0.63 in 3:1 toluene–EtOAc; δ_H 7.4–7.1 (m, 15 H, aromatic), 6.20 (d, 1 H, *J* 2 Hz, H-1), 5.18 (q, 1 H, *J* 4, 9 Hz, H-3), 4.13 (t, 1 H, *J* 9 Hz, H-4), 2.08 (s, 3 H, Ac), and 1.96 (s, 3 H, Ac).

Anal. Calc. for $C_{31}H_{34}O_8$: C, 69.65; H, 6.41. Found: C, 69.99; H, 6.66.

3-O-Acetyl-2,4,6-tri-O-benzyl-α-D-mannopyranosyl chloride (**7**). — A solution of **17** (100 mg) in CH_2Cl_2 (10 mL) was saturated with dry HCl at −5°. After standing for 1 h at 25°, solvent was coevaporated with toluene (3 times), to give **7** quantitatively; this was used for the next step without further purification; R_F 0.78 in 5:1 toluene–EtOAc.

Benzyl O-(3-O-acetyl-2,4,6-tri-O-benzyl-α-D-mannopyranosyl)-[(1→2)-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)]$_2$-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (**18**). — A mixture of molecular sieves 4A (2 g) and $AgOSO_2CF_3$ (200 mg) in toluene (10 mL) was evaporated *in vacuo* at 50°. To the residue were added a solution of **6** (290 mg, 208 μmol) in $Cl(CH_2)_2Cl$ (15 mL), and a solution of **7** (110 mg, 215 μmol) in $Cl(CH_2)_2Cl$ (5 mL) dropwise, at −15°. The mixture was stirred for 3 h at 20–25°, and a solution of **7** (20 mg, 67 μmol) in $Cl(CH_2)_2Cl$ (2 mL) was added at −15°. The mixture was stirred for 16 h at 20–25°, diluted with $Cl(CH_2)_2Cl$ (20 mL), and filtered through Celite. The filtrate was washed with aq. $NaHCO_3$, H_2O, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed through silica gel C-300 (20 g), to give **18** (310 mg, 80%); $[\alpha]_D$ +20.0° (*c* 0.39); R_F 0.64 in 10:1 toluene–EtOAc; δ_H 1.96 (s, 3 H, Ac) and 7.4–6.9 (m, 65 H, aromatic).

Anal. Calc. for $C_{117}H_{122}O_{22}$: C, 74.74; H, 6.54. Found: C, 74.23; H, 6.50.

Benzyl O-(2,4,6-tri-O-benzyl-α-D-mannopyranosyl)-[(1→2)-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)]$_2$-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (**19**). — A solution of **18** (260 mg) in oxolane (20 mL) and 0.01M NaOMe–MeOH (30 mL) was stirred for 16 h at 20–25°. Neutralization with Amberlist A-15, and chromatography of the product through silica gel C-300 (5 g) in 10:1 toluene–EtOAc, gave **19** (210 mg, 83%); $[\alpha]_D$ +12.8° (*c* 0.60); R_F 0.74 in 5:1 toluene–EtOAc.

Anal. Calc. for $C_{115}H_{120}O_{21} \cdot 0.5\ CH_3CO_2C_2H_5$: C, 74.66; H, 6.64. Found: C, 74.49; H, 6.61.

Benzyl O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→3)-O-(2,4,6-tri-O-benzyl-α-D-mannopyranosyl)-[(1→2)-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)]$_2$-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (**20**). — To a mixture of molecular sieves 4A (1 g) and $AgOSO_2CF_3$ (150 mg) were added a solution of **19** (105 mg, 58 μmol) in $Cl(CH_2)_2Cl$ (10 mL), and a solution of **8** (100 mg, 189 μmol) in $Cl(CH_2)_2Cl$ (1 mL) dropwise at −15°, under Ar. The mixture was stirred for 16 h at 20–25°, and diluted with Cl_2CH_2 (30 mL). Processing, and chromatography through silica gel C-300 (10 g) in 10:1 toluene–EtOAc, gave **20** (77 mg, 58%); R_F 0.49 in 10:1 toluene–EtOAc; δ_H 2.08 (s, 3 H, Ac).

Benzyl O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-O-(2,4,6-tri-O-benzyl-α-D-mannopyranosyl)-[(1→2)-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)]$_2$-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (**21**). — A solution of **20** (77 mg) in oxolane (5 mL) and 0.01M NaOMe–MeOH (5 mL) was stirred for 8 h at 20–25°. Processing, and chromatography over silica gel C-300 (15 g) in 5:1 toluene–EtOAc, gave **21** (60 mg, 79.4%); $[\alpha]_D$ +34.5° (*c* 0.17); R_F 0.59 in 5:1 toluene–EtOAc.

Anal. Calc. for $C_{142}H_{145}O_{26}$: C, 75.11; H, 6.57. Found: C, 75.11; H, 6.55.

O-α-D-*Mannopyranosyl-(1→3)*-O-α-D-*mannopyranosyl*-[*(1→2)*-O-α-D-*mannopyranosyl*]$_2$-*(1→2)*-α-D-*mannopyranose* (**5**). — A mixture of **21** (55 mg) and 10% Pd–C (30 mg) in AcOH (10 mL) was stirred under H_2 for 6 h at 50°, diluted with water, and filtered through Celite. The filtrate was evaporated *in vacuo*, and the residue was purified with Sephadex G 25 (20 g in H_2O), to give **5** (17 mg, 85.0%); $[\alpha]_D$ +27.2° (*c* 0.4, H_2O); R_F 0.16 in 2:1:1 BuOH–AcOH–H_2O.

ACKNOWLEDGMENTS

We thank Dr. J. Uzawa and Mrs. T. Chijimatsu for recording and measuring the n.m.r. spectra, and Dr. H. Homma and his staff for the elemental analyses. We also thank Mrs. A. Takahashi for her technical assistance.

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