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SYNTHESIS OF A MODEL OF AN INNER CHAIN OF CELL-WALL PROTEO-HETEROGLYCAN ISOLATED FROM *Piricularia oryzae*: BRANCHED D-MANNOPENTAOSIDES*

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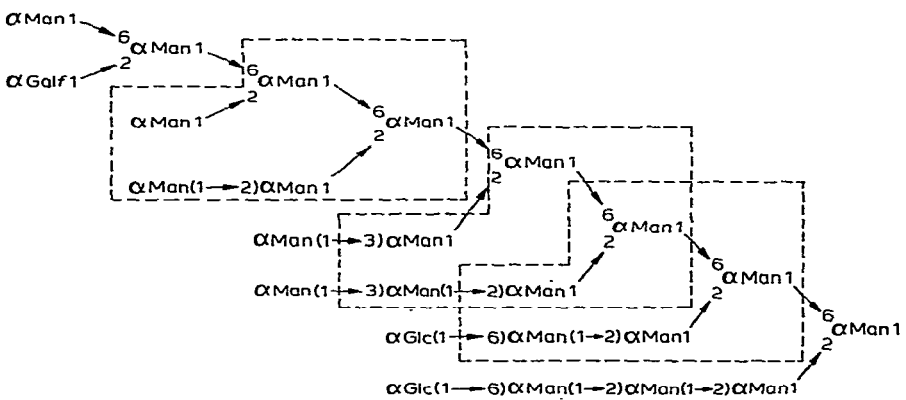
ABSTRACT

Efficient syntheses are described of the branched D-mannopentaosides methyl 2,6-di-*O*-(2-*O*-α-D-mannopyranosyl-α-D-mannopyranosyl)-α-D-mannopyranoside and methyl 2,4-di-*O*-(2-*O*-α-D-mannopyranosyl-α-D-mannopyranosyl)-α-D-mannopyranoside, starting from the glycosyl acceptors methyl 3,4-di-*O*-benzyl-α-D-mannopyranoside and methyl 3,6-di-*O*-benzyl-α-D-mannopyranoside, and employing the protected D-mannotriosides methyl 3,4-di-*O*-benzyl-2,6-di-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside, and methyl 3,6-di-*O*-benzyl-2,4-di-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside as key intermediates.

INTRODUCTION

In 1977, Nakajima *et al.*[2] reported the isolation and characterization of the



1

*Synthetic Studies on Cell-surface Glycans, Part 6. For Part 5, see ref. 1.
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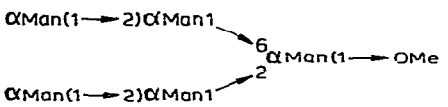
cell-wall proteoheteroglycan from *Piricularia oryzae*, and proposed that the structure of the glycan unit is **1**.

Availability of such precise, synthetic glycan-chains as **1** should facilitate the uncovering of the molecular mechanism of recognition[3] between higher plants and microbes, whereby, in certain plants, invading microbes eventually induce defending responses[3] within the plant tissue.

RESULTS AND DISCUSSION

As simple, model structures, we chose the branched D-mannopentaoside **2**, which corresponds to the inner chain of **1**, and its regio-isomer **3** for the synthetic targets. We describe their synthesis, starting from the three monosaccharide synthons **4**, **6** (ref. 4), and **8** (ref. 5).



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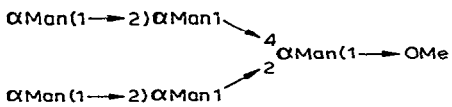

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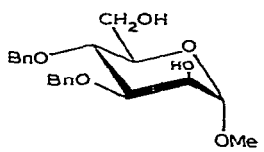
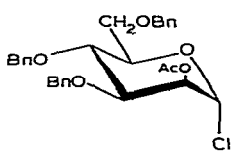


4

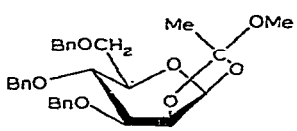
5 β anomer of 4

Bn = $PhCH_2$



6

Ac = CH_3CO



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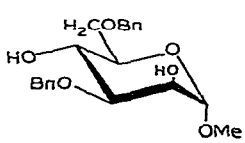
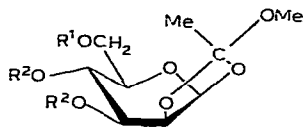


8

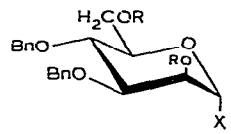
Synthesis of protected mannotriosides **22** *and* **25**, *the key intermediates*

The glycosyl acceptor **4** was prepared *via* triacetate **13** which was readily obtained by selective acetolysis of **7** according to Ponpipom[6] (with some modifications). Treatment[7] of **7** in 25:25:1 Ac_2O–AcOH–H_2SO_4 for 2 h at 0–5° led to the formation of triacetate **13** in 72.9% yield. Similar susceptibility of the 6-*O*-benzyl group on a D-mannopyranosyl residue toward acetolysis was observed in the case of diacetate **18** which, on acetolysis in 20:20:1 Ac_2O–AcOH–H_2SO_4 for 20 h at 20°, afforded tetraacetate **19** in 74.8% yield. The structure of **13** was confirmed by an alternative, synthetic sequence. Tritylation of the orthoester[7] **9** with trityl chloride in pyridine surprisingly gave none of the desired product **10**. However, initial

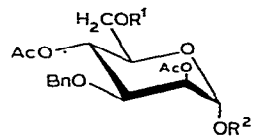
stannylation[8] of **9** with $(Bu_3Sn)_2O$ and treatment with trityl chloride afforded trityl orthoester **10** in 85.2% yield. Benzylation of **10** with NaH and benzyl bromide in $HCONMe_2$ (DMF) to dibenzyl ether **11**, and acetolysis of **11** in 50:50:1 Ac_2O–AcOH–H_2SO_4 for 1.5 h at 0°, gave a 60% yield of the triacetate, identical with **13** prepared from **7**. The anomeric configurations of the acetolysis products **13** and **19** were assigned according to the ^{13}C-n.m.r. data, which showed the anomeric carbon atom at δ 91.0 with $^1J_{CH}$ 176.5 Hz for both **13** and **19**, in agreement with observations of Bock and Pedersen[9].



9 $R^1 = R^2 = H$
10 $R^1 = Tr$, $R^2 = H$
11 $R^1 = Tr$, $R^2 = Bn$
12 $R^1 = Ac$, $R^2 = Bn$
Tr = Ph_3C



13 R = X = Ac
14 R = Ac, X = Cl
15 R = Ac, X = OMe
16 β anomer of **15**
17 R = H, X = OH



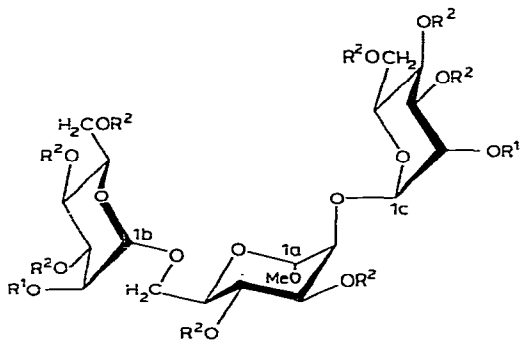
18 $R^1 = Bn$, $R^2 = Me$
19 $R^1 = R^2 = Ac$

Triacetate **13** was transformed into diol **4** in two ways, with similar efficiency. Compound **13** was treated with HCl in CH_2Cl_2, to give the substituted α-D-mannopyranosyl chloride (**14**), and treatment of **14** with MeOH–Et_3N in $Cl(CH_2)_2Cl$ gave the orthoester **12** in 77.5% yield from **13**. Compound **12** was directly heated[10] with $HgBr_2$ for 1 h at 150° *in vacuo*, to give methyl glycosides **15** and **16** in 56.9 and 12.1% yield, respectively. The anomeric configurations of **15** and **16** were assigned as α and β, respectively, from the ^{13}C-n.m.r. data.

Treatment of **14** with MeOH under the Hanessian–Banoub conditions[11], and deacetylation of the products, gave **4** and **5** in 58.9 and 21.5% yield, respectively. The ^{13}C-n.m.r. spectra showed a signal for the anomeric carbon atom at δ 100.2 ($^1J_{CH}$ 169.0 Hz) for **4** and at δ 101.0 ($^1J_{CH}$ 157.4 Hz) for **5**, indicating the α and β configuration, respectively. Diol **4** was also obtainable by deacetylation of diacetate **15**.

Having prepared the glycosyl acceptor **4** in ~40% overall yield from **7** in 4 steps, glycosylation of **4** with glycosyl donor **6** was next examined, using the Hanessian–Banoub procedure[11].

Glycosylation of diol **4** with 2.9 molar equivalents of the substituted D-mannopyranosyl chloride **6** led to the formation of protected mannotrioside **20** in 75.2% yield; δ_C: 97.4 ($^1J_{CH}$ 170.6 Hz, C-1b), 99.5 ($^1J_{CH}$ 172.1 Hz, C-1a, 1c). Zemplén deacetylation of **20** gave a 94.3% yield of properly protected D-mannotrioside **21**, a key intermediate for the synthesis of **2**. Catalytic hydrogenolysis of **21** gave the free D-mannotrioside **22**, the structure of which was confirmed as follows. The ^1H-n.m.r. spectrum showed three doublets, J 2 Hz, for three anomeric protons, at δ 4.94 (H-1b), 4.96 (H-1a), and 5.04 (H-1c), and the ^{13}C-n.m.r. spectrum contained two



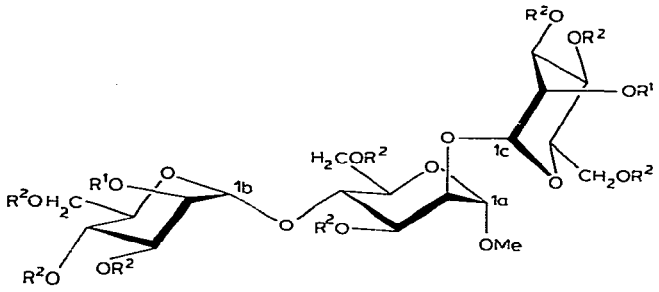
20 R^1 = Ac, R^2 = Bn
21 R^1 = H, R^2 = Bn
22 R^1 = R^2 = H

signals, with $^1J_{CH}$ ~170 Hz, for three anomeric carbon atoms having the α-D configuration[9], at δ 99.8 (C-1a, C-1b) and 102.6 (C-1c). The 2,6-branching pattern of **22** was also supported by the ^{13}C-n.m.r. data, which showed two deshielded signals, due to a glycosylation shift[12], at δ 65.4 for C-6a and 79.0 for C-2a. This assignment for 2,6-branching was further confirmed by the ^{1}H-n.m.r. data for **22**, which showed a low-field shift of 0.23 p.p.m. for H-1a [compared with the normal value for H-1 (δ 4.73) of methyl α-D-mannopyranoside] which was found to be characteristic of the chemical shift of an anomeric proton of an α-D-mannopyranoside carrying an α-D-mannopyranosyl group* at O-2.

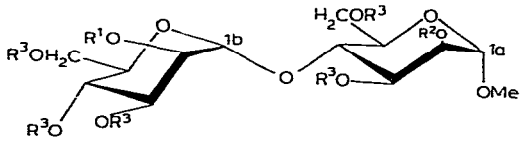
Another key intermediate, compound **24**, was prepared by attaching two α-D-mannopyranosyl groups to the known glycosyl acceptor[5] **8**. Glycosylation of **8** with 4.2 molar equivalents of the glycosyl donor **6** led to the formation, in 70% yield, of **23**, the structure of which was supported as follows. The ^{1}H-n.m.r. spectrum showed a singlet at 2.07 for two acetyl groups, and the ^{13}C-n.m.r. spectrum showed two signals, with $^1J_{CH}$ ~170 Hz, at δ 99.5 for C-1a and C-1b, and at δ 99.8 for C-1c. Zemplén deacetylation of **23** afforded an 88.5% yield of the partially benzylated D-mannotrioside **24**, the key intermediate for the synthesis of **3**. Catalytic hydrogenolysis of **24** gave the free D-mannotrioside **25**, whose ^{1}H-n.m.r. spectrum showed three broad singlets, with w_{hh} ~2 Hz, at δ 4.96 (H-1a), 5.02 (H-1c), and 5.21 (H-1b), and ^{13}C-n.m.r. spectrum showed three signals, with $^1J_{CH}$ ~170 Hz, at δ 99.4 (C-1a), 101.8 (C-1b), and 102.6 (C-1c), and two deshielded signals at δ 74.9 (C-4a) and 79.6 (C-2a), supporting the 2,4-branching pattern in **25**.

It may be noted that, by employing 1.8 molar equivalents of glycosyl donor **6**, diol **8** was selectively glycosylated at O-4, to afford a 58.4% yield of protected D-mannobioside **26**, together with a 21.5% yield of protected D-mannotrioside **23**. The structure of **26** was determined in the following way. The ^{1}H-n.m.r. spectrum of **26**

*Similarly, the signal[4b] for H-1a in α-D-Man-(1b→2)-α-D-Man-(1a→OMe was deshielded, and appeared at δ 4.94.



23 R^1 = Ac, R^2 = Bn
24 R^1 = H, R^2 = Bn
25 R^1 = R^2 = H



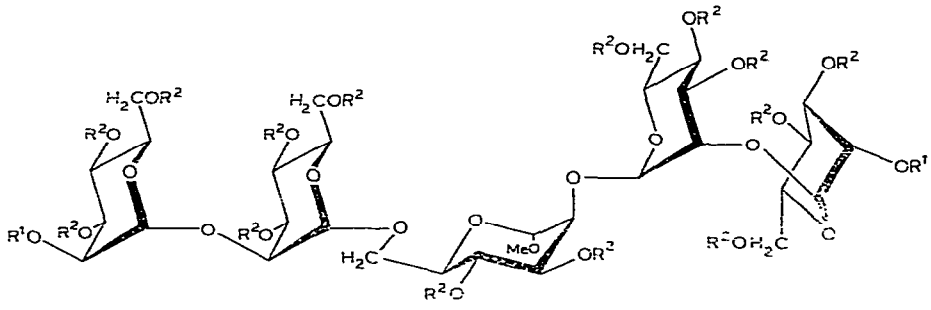
26 R^1 = Ac, R^2 = H, R^3 = Bn
27 R^1 = R^2 = Ac, R^3 = Bn
28 R^1 = R^2 = H, R^3 = Bn
29 R^1 = R^2 = R^3 = H

showed a singlet for one acetyl group at δ 2.05, and a deshielded triplet, with J 2 Hz, at δ 5.46 for H-2b, and the ^{13}C-n.m.r. spectrum contained two signals, $^1J_{CH}$ ~170 Hz, for two anomeric carbon atoms having the α-D configuration, at δ 99.2 for C-1b, and 100.0 for C-1a. Diacetate **27**, obtained from **26** in the usual way, showed, in its ^{1}H-n.m.r. spectrum, two deshielded triplets, J 2 Hz, at δ 5.32 for H-2a, and 5.47 for H-2b, confirming the presence of a free OH on C-2a, and of a (1→4)-interglycosidic linkage in **26**. Zemplén deacetylation of **26** to diol **28**, and hydrogenolysis of **28** in the presence of 10% Pd–C, gave the free D-mannobioside **29**. The ^{1}H-n.m.r. spectrum of **29** showed two doublets, with J 2 Hz, at δ 4.73 (H-1a) and 5.21 (H-1b), and the ^{13}C-n.m.r. spectrum showed two signals, with $^1J_{CH}$ ~170 Hz, for two anomeric carbon atoms having the α-D configuration, at δ 101.0 for C-1b and 101.8 for C-1a, and a deshielded signal for C-4a at δ 74.5. These n.m.r. data are not identical with those for methyl 2-*O*-α-D-mannopyranosyl-α-D-mannopyranoside, previously prepared by an unambiguous route[4], confirming the structure of **29** beyond doubt.

As two key intermediates, **21** and **24**, for the synthesis of the target compounds **2** and **3** had now been prepared unequivocally, further elongation of the carbohydrate chain therein was next studied.

Synthesis of the branched D-*mannopentaosides* **2** *and* **3**

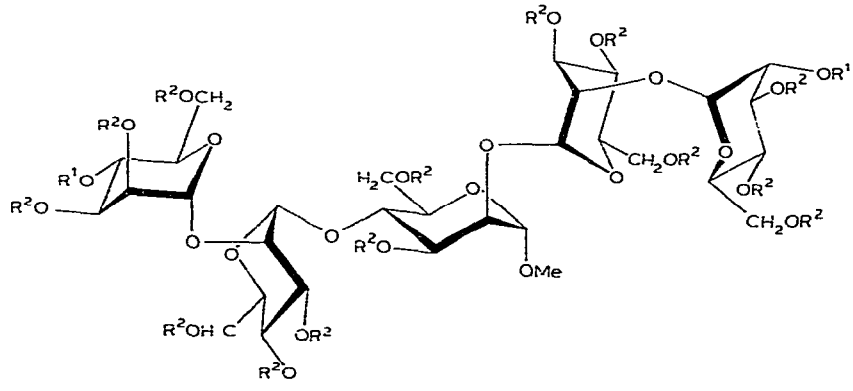
Glycosylation of diol **21** with 4 molar equivalents of the D-mannosyl donor **6** led to the formation of protected mannopentaoside **30** in 56.7% yield. The ^{1}H-n.m.r. spectrum of **30** showed a singlet at δ 2.10 for two acetyl groups, and the ^{13}C-n.m.r.



30 R^1 = Ac, R^2 = Bn
31 R^1 = H, R^2 = Bn
2 R^1 = R^2 = H

spectrum showed three signals, with $^1J_{CH}$ ~170 Hz, for five anomeric carbon atoms having the α-D configuration, at δ 98.2 (C-1b), 99.5 (C-1a, 1d, 1e), and 100.6 (C-1c). Zemplén deacetylation of **30** to **31**, and catalytic hydrogenolysis of **31** in the usual way, gave the target molecule **2**, the structure assigned to which was confirmed as follows. The ^{1}H-n.m.r. spectrum showed four doublets, with J 2 Hz, at δ 4.89 (H-1a), 5.00 (H-1d, 1e), 5.05 (H-1b), and 5.22 (H-1c). The ^{13}C-n.m.r. spectrum contained four signals, with $^1J_{CH}$ ~170 Hz, for five anomeric carbon atoms having the α-D configuration, at δ 98.3 (C-1b), 99.7 (C-1a), 100.9 (C-1c), and 102.6 (C-1d, 1e), as well as a deshielded signal for C-2a, C-2b, and C-2c at δ 78.9.

Simultaneous introduction of two D-mannosyl groups onto diol **24** was similarly achieved. Glycosylation of **24** with 4 molar equivalents of the glycosyl donor **6** led to the isolation of the protected D-mannopentaoside **32** in 87.8% yield. Zemplén



32 R^1 = Ac, R^2 = Bn
33 R^1 = H, R^2 = Bn
3 R^1 = R^2 = H

deacetylation of **32** to **33**, and hydrogenolysis of **33**, afforded the other target molecule (**3**). The ^{1}H-n.m.r. spectrum of **3** showed four doublets, with J 2 Hz, at δ 4.94 (H-1a),

5.04 (H-1d, 1e), 5.22 (H-1c), and 5.42 (H-1b), and the ^{13}C-n.m.r. spectrum showed four signals, with $^{1}J_{CH}$ ~170 Hz, at δ 99.4 (C-1a), 100.2 (C-1b), 101.0 (C-1c), and 102.6 (C-1d, 1e), as well as four deshielded signals at δ 75.2 (C-4a), and 78.9, 79.3 and 80.0 for either C-2a, C-2b, or C-2c, confirming the assigned structure **3**.

In conclusion, efficient and unambiguous synthetic routes to branched D-mannopentaosides **2** and **3**, model structures for the proteoheteroglycan present in the cell wall of *Piricularia oryzae*, have been developed by employing properly protected D-mannotriosides **21** and **24** as key intermediates.

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 141 polarimeter for solutions in $CHCl_3$ at 25°, unless otherwise noted. I.r. spectra were recorded with an EPI-G2 Hitachi Spectrophotometer, using KBr discs for the crystalline samples, and neat films for the liquid samples. ^{1}H-N.m.r. spectra were recorded with a Varian HA-100 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 otherwise noted. Column chromatography was performed on columns of Silica Gel Merck (70–230 mesh; E. Merck, Darmstadt, Germany). Thin-layer chromatography was performed on precoated plates (layer thickness, 0.25mm) of Silica Gel 60 F_{254} (E. Merck, Darmstadt, Germany).

1,2,6-Tri-O-acetyl-3,4-di-O-benzyl-α-D-mannopyranose (**13**). — To a solution of **7** (2.5 g, 5.0 mmol) in 1:1 Ac_2O–AcOH (30 mL) was added H_2SO_4 (0.6 mL) at −5 to −10°, and the mixture was stirred for 2 h at 0–5°. The H_2SO_4 was neutralized by adding NaOAc (4.0 g), and the Ac_2O and AcOH were then evaporated *in vacuo*, and the residue dissolved in EtOAc. The solution was successively washed with H_2O, aq. $NaHCO_3$, and H_2O, dried ($MgSO_4$), and evaporated *in vacuo*, to give an oily product (3.37 g) which was chromatographed on SiO_2 (300 g) with 6:1 toluene–EtOAc, to give[6] **13** (1.749 g, 72.9%), m.p. 78–80° (iPr_2O–hexane), $[\alpha]_D$ +32.4° (*c* 0.54); R_F 0.49 in 3:1 toluene-EtOAc; δ_H: 2.04, 2.08, 2.15 (s, 3 H, 3 Ac), and 6.04 (d, 1 H, *J* 2 Hz, H-1); δ_C: 20.8 (Ac), 62.9 (C-6), 67.2 (C-2), 71.7 (C-5 and O-3–CH_2Ph). 73.4 (C-4), 75.3 (O-4-CH_2Ph), 77.6 (C-3), and 91.0 ($^{1}J_{CH}$ 176.5 Hz, C-1).

Anal. Calc. for $C_{26}H_{30}O_9$: C, 64.18; H, 6.22. Found: C, 64.08; H, 6.21.

Methyl 2,4-di-O-acetyl-3,6-di-O-benzyl-α-D-mannopyranoside (**18**). — Compound **8** (3.85 g) was acetylated in the usual way (Ac_2O–pyridine) for 1 day at 20°. Purification by chromatography on SiO_2 (300 g) with 10:1 toluene–EtOAc gave **18** (3.63 g, 76.9%), $[\alpha]_D$ +7.3° (*c* 0.66); R_F 0.55 in 3:1 toluene–EtOAc; δ_H: 1.98 and 2.10 (two s, 3 H, each 2 OAc), 3.36 (s, 3 H, OMe), 4.62 (d, 1 H, *J* 2 Hz, H-1), 5.21 (t, 1 H, *J* 10 Hz, H-4), and 5.33 (t, 1 H, *J* 2 Hz, H-2); δ_C: 20.8 (Ac), 21.0 (Ac),

55.1 (OMe), 68.2 (C-2,4), 69.5 (C-6), 69.8 (C-5), 71.3 (O-3-CH_2Ph), 73.5 (O-6-CH_2Ph), 74.6 (C-3), and 98.7 ($^1J_{CH}$ 170.6 Hz, C-1).

Anal. Calc. for $C_{25}H_{30}O_8$: C, 65.49; H, 6.60. Found: C, 65.43; H, 6.45.

1,2,4,6-Tetra-O-acetyl-3-O-benzyl-α-D-mannopyranose (**19**). — To a solution of compound **18** (230 mg) in 1:1 Ac_2O–AcOH (3 mL) was added H_2SO_4 (0.05 mL) at −5 to 0°, and the mixture was stirred for 7 h at 20°. After neutralization with NaOAc (0.5 g), the Ac_2O and AcOH were evaporated *in vacuo*. The residue was processed in the usual way, to give an oil (303 mg) which was chromatographed on SiO_2 (30 g) with 5:1 toluene–EtOAc, to give **19** (163.8 mg, 74.8%), $[\alpha]_D$ +1.8° (*c* 1.03); R_F 0.32 in 3:1 toluene–EtOAc; δ_H: 2.01, 2.06, 2.10, and 2.14 (4 s, 12 H, 4 OAc), 5.28 (t, 1 H, *J* 10 Hz, H-4), 5.34 (dd, 1 H, $J_{2,3}$ 3 Hz, H-2), and 6.08 (d, 1 H, $J_{1,2}$ 2 Hz, H-1); δ_C: 20.8 (Ac), 62.4 (C-6), 66.9 (C-5), 67.0 (C-2), 70.8 (C-4), 71.5 (O-3-CH_2Ph), 74.2 (C-3), and 91.0 ($^1J_{CH}$ 176.5 Hz, C-1).

Anal. Calc. for $C_{21}H_{26}O_{10}$: C, 57.53; H, 5.98. Found: C, 57.43; H, 6.03.

1,2-O-(1-Methoxyethylidene)-6-O-trityl-β-D-mannopyranose (**10**). — A mixture of **9** (814 mg) and $(Bn_3Sn)_2O$ (2.91 g, 4.88 mmol) in toluene (25 mL) was stirred under reflux for 2 h with continuous, azeotropic removal of H_2O. The solution was concentrated to 10 mL, and TrCl (1.09 g, 3.9 mmol) was added at 20°. The mixture was stirred for 16 h at 20°, and then evaporated *in vacuo*, to give a residue (4.71 g) which was chromatographed on SiO_2 (180 g) with 250:50:3 $CHCl_3$–Me_2CO–Et_3N, to afford **10** (1.346 g, 85.2%) as a foam, $[\alpha]_D$ +9.7° (*c* 0.445); R_F 0.50 in 2:1 $CHCl_3$–Me_2CO and 0.42 in 10:1 $CHCl_3$–MeOH; δ_H: 1.74 (C-Me), 3.30 (s, 3 H, OMe), 3.94 (t, 1 H, *J* 9 Hz, H-4), 3.68 (dd, H, $J_{2,3}$ 3, $J_{3,4}$ 10 Hz, H-3), 4.49 (dd, 1 H, $J_{1,2}$ 2.5, $J_{2,3}$ 4 Hz, H-2), 5.43 (d, *J* 2.5 Hz, H-1), and 7.2–7.5 (m, 15 H, trityl).

Anal. Calc. for $C_{28}H_{30}O_7$: C, 70.28; H, 6.32. Found: C, 69.91; H, 6.34.

3,4-Di-O-benzyl-1,2-O-(1-methoxyethylidene)-6-O-trityl-β-D-mannopyranose (**11**). — Sodium hydride (60%; 210 mg, ~5.2 mmol) was washed with petroleum ether, and then suspended in dry DMF (10 mL). To this suspension was added a solution of **10** (1.0 g, 2.09 mmol) in DMF (5 mL) at −5°, and the mixture was stirred for 20 min at 20°. To this mixture was added benzyl bromide (0.63 mL, 5.3 mmol), and the mixture was stirred for 16 h at 20°. The excess of NaH was decomposed with MeOH (1 mL), and the mixture was evaporated *in vacuo*, to give a residue which was partitioned between EtOAc and aq. $NaHCO_3$. The organic layer was dried ($MgSO_4$), and evaporated, to give crude **11** (1.32 g, 96.0%), which was pure enough for the next step, R_F 0.65 in 5:1 toluene–EtOAc; δ_H: 3.31 (s, 3 H, OMe), and 5.35 (d, 1 H, *J* 3 Hz, H-1).

1,2,6-Tri-O-acetyl-3,4-di-O-benzyl-α-D-mannopyranose (**13**). — To a solution of crude **11** (997 mg, 1.5 mmol) in 1:1 Ac_2O–AcOH (15 mL) was added H_2SO_4 (0.15 mL) at −5 to 0°, and the mixture was stirred for 1.5 h at 0°. After neutralization with NaOAc (1 g), the mixture was processed as already described, to afford crude **13** (1.76 g) which was chromatographed on SiO_2 (80 g) with 5:1 toluene–EtOAc, to give **13** (441 mg, 60.0%), identical with the sample prepared from **7**; $[\alpha]_D$ +33.0° (*c* 0.86); R_F 0.53 in 3:1 toluene–EtOAc.

2,6-Di-O-acetyl-3,4-di-O-benzyl-α-D-mannopyranosyl chloride (**14**). — A solution of **13** (195 mg, 0.4 mmol) in CH_2Cl_2 (10 mL) was saturated with HCl at −5 to 0°. The mixture was kept for 2 days at 20°, and then evaporated *in vacuo*, to give **14** (183 mg, 98.9%) which was used directly for the next step; R_F 0.57 in 3:1 toluene–EtOAc; δ_H: 2.05 and 2.16 (2 s, 6 H, 2 OAc), and 5.98 (d, 1 H, *J* 2 Hz, H-1).

Methyl 2,6-di-O-acetyl-3,4-di-O-benzyl-α(and β)-D-mannopyranoside (**15**) (*and* **16**). — A mixture of **14** (463 mg, 1 mmol), MeOH (82 μL, 2 mmol), Et_3N (0.22 mL, 1.5 mmol), and Bu_4NBr (323 mg, 1 mmol) in $Cl(CH_2)_2Cl$ (3.5 mL) was stirred for 2 days at 45–55° under argon. The mixture was filtered through Celite, and the filtrate was evaporated to give a residue which was chromatographed on SiO_2 (50 g) with 250:50:3 toluene–EtOAc–Et_3N, to afford **12** (338 mg, 77.5% from **13**); R_F 0.35 in 3:1 toluene–EtOAc; δ_H: 1.71 (s, 3 H, C-Me), 2.00 (s, 3 H, Ac), 3.27 (s, 3 H, OMe), and 5.33 (d, 1 H, *J* 3 Hz, H-1). This oil was used directly for the next step.

A mixture of **12** (319 mg, 0.70 mmol), and $HgBr_2$ (80 mg) was stirred for 1 h at 150° (bath) *in vacuo* (1 mmHg). After being cooled to 20°, the mixture was directly subjected to chromatography on SiO_2 (30 g) with 40:1 CH_2Cl_2–Me_2CO, to give **15** (185 mg, 56.9%), $[\alpha]_D$ +22.2° (*c* 0.185); R_F 0.67 in 20:1 CH_2Cl_2–Me_2CO; δ_H: 2.05 and 2.14 (2 s, 6 H, 2 OAc), 3.34 (s, 3 H, OMe), 4.65 (d, 1 H, *J* 2 Hz, H-1), and 5.35 (dd, 1 H, $J_{1,2}$ 2, $J_{2,3}$ 4 Hz, H-2); δ_C: 20.8 (Ac), 21.0 (Ac), 54.9 (OMe), 63.3 (C-6), 68.4 (C-2), 69.5 (C-5), 71.7 (O-3-CH_2Ph), 74.0 (C-4), 75.1 (O-4-CH_2Ph), 78.0 (C-3), and 98.7 ($^1J_{CH}$ 170.6 Hz, C-1).

Anal. Calc. for $C_{25}H_{30}O_8$: C, 65.20; H, 7.00. Found: C, 64.69; H, 6.57.

Further elution with the same solvent afforded **16** (40.7 mg, 12.1%); R_F 0.55 in 20:1 CH_2Cl_2–Me_2CO; δ_H: 2.03 and 2.19 (2 s, 6 H, 2 OAc), 3.49 (s, 3 H, OMe), 4.33 (d, 1 H, *J* 2 Hz, H-1), and 5.62 (bt, 1 H, *J* ~2 Hz, H-2); δ_C: 21.0 (Ac), 20.9 (Ac), 57.2 (OMe), 63.4 (C-6), 67.6 (C-2), 71.5 (O-3-CH_2Ph), 73.3 (C-4), 74.0 (C-5), 75.2 (O-4-CH_2Ph), 80.2 (C-3), and 100.0 ($^1J_{CH}$ 155.9 Hz, C-1).

Methyl 3,4-di-O-benzyl-α(and β)-D-mannopyranoside (**4**) (*and* **5**). — To a mixture of $AgSO_3CF_3$ (1.39 g, 5.4 mmol), MeOH (0.5 mL, 12 mmol), $Me_2NCONMe_2$ (0.9 mL, 7.5 mmol) in CH_2Cl_2 (6 mL) was added a solution of **14** (1.693 g, prepared from 3.6 mmol of **13**) in CH_2Cl_2 (6 mL) during 10 min at −10° under argon. The mixture was stirred for 16 h at 20°, diluted with CH_2Cl_2 (30 mL), and filtered through Celite. The filtrate was washed with aq. $NaHCO_3$, dried ($MgSO_4$), and evaporated, to give an oily product (2.048 g), t.l.c. of which showed the presence of partially deacetylated products. This oily product was used without purification.

A solution of the oil (2.048 g) in MeOH (30 mL) and 2M NaOMe–MeOH (1 mL) was stirred for 16 h at 20°, made neutral with Amberlist 15 (H^+) resin, filtered, and the filtrate evaporated, to afford a syrup (1.754 g) which was chromatographed on SiO_2 (150 g) with 2:1 CCl_4–Me_2CO, to give **4** (804 mg, 58.9% from **13**), $[\alpha]_D$ +50.0° (*c* 0.22); R_F 0.55 in 1:1 CCl_4–Me_2CO; δ_H: 2.81 and 2.36 (bs, two 1 H, disappeared on addition of D_2O, 2 OH), 3.33 (s, 3 H, OMe), and 4.75 (d, 1 H, 2 Hz, H-1); δ_C: 54.8 (OMe), 61.8 (C-6), 68.3 (C-2), 71.4 (C-5), 72.0 (O-3-CH_2Ph), 73.9 (C-4), 75.1 (O-4-CH_2Ph), 79.9 (C-3), and 100.2 ($^1J_{CH}$ 169 Hz, C-1).

Anal. Calc. for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found: C, 67.53; H, 6.70.

Further elution with the solvent afforded **5** (293 mg, 21.5% from **13**), $[\alpha]_D$ −33.8° (*c* 0.56); R_F 0.40 in 1:1 CCl_4–Me_2CO; δ_H: 2.61 (bs, 2 H, 2 OH, disappeared on addition of D_2O), 3.52 (s, 3 H, OMe), and 4.34 (s, 1 H, H-1); δ_C: 57.7 (OMe), 61.9 (C-6), 68.2 (C-2), 71.5 (O-3-CH_2-Ph), 73.9 (C-4), 75.3 (O-4-CH_2Ph), 75.4 (C-5), 81.3 (C-3), and 101.0 ($^1J_{CH}$ 157.4 Hz, C-1).

Anal. Calc. for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found: C, 66.87; H, 7.08.

Further elution with the same solvent afforded **17** (242.5 mg, 18.7% from **13**); R_F 0.24 in 1:1 CCl_4–Me_2CO. Compound **17** could be reconverted into **13** by acetylation with Ac_2O–pyridine.

*Methyl 2,6-di-*O-[*2-*O-*acetyl-3,4,6-tri-*O-*benzyl-*α-D-*mannopyranosyl*]-*3,4-di-*O-*benzyl-*α-D-*mannopyranoside* (**20**). — To a stirred mixture of **4** (306 mg, 0.82 mmol) and $AgSO_3CF_3$ (925 mg, 3.6 mmol), dried *in vacuo* for 5 h, were successively added CH_2Cl_2 (5 mL), $Me_2NCONMe_2$ (0.6 mL, 5.0 mmol), and then half of a solution of **6** [1.317 g, prepared from **7** (1.22 g, 2.4 mmol) by refluxing it with chlorotrimethylsilane (0.7 mL) in CH_2Cl_2 (25 mL) for 1.5 h] in CH_2Cl_2 (5 mL) at −10 to −15° under argon. The mixture was stirred for 3 h at 20°, the rest of the solution of **6** in CH_2Cl_2 was added at −10 to −15°, and the mixture was stirred for a further 20 h at 20°, diluted with CH_2Cl_2 (50 mL), and filtered through Celite. The filtrate was washed with aq. $NaHCO_3$, dried ($MgSO_4$), and evaporated *in vacuo*, to give an oily product which was chromatographed on SiO_2 (150 g) with 6:1 toluene–EtOAc, to afford **20** (815.2 mg, 75.2%), $[\alpha]_D$ +30.7° (*c* 0.41); R_F 0.57 in 3:1 toluene–EtOAc; δ_H: 2.08 (s, 6 H, 2 OAc), 3.16 (s, 3 H, OMe), 5.05 (d, 1 H, *J* 2 Hz, anomeric H), and 5.54 (bt, 2 H, *J* 2 Hz, H-2a, 2c); δ_C: 21.1 (2 OAc, 54.8 (OMe), 66.5 (C-6a), 97.4 ($^1J_{CH}$ 170.6 Hz, C-1b), and 99.5 ($^1J_{CH}$ 172.1 Hz, C-1a, 1c).

Anal. Calc. for $C_{79}H_{86}O_{18}$: C, 71.69; H, 6.55. Found: C, 71.28; H, 6.52.

*Methyl 3,4-di-*O-*benzyl-2,6-di-*O-(*3,4,6-tri-*O-*benzyl-*α-D-*mannopyranosyl*)-α-D-*mannopyranoside* (**21**). — A solution of **20** (582.6 mg, 0.44 mmol) in MeOH (20 mL)–THF (3 mL) and 2M NaOMe–MeOH (0.2 mL) was stirred for 16 h at 20°, made neutral with Amberlist 15 resin, and processed as usual to afford the product as a foam (585 mg) which was chromatographed on SiO_2 (90 g) with 11:1 CH_2Cl_2–Me_2CO, to give **21** (517.6 mg, 94.3%), $[\alpha]_D$ +46.8° (*c* 0.47); R_F 0.55 in 10:1 CH_2Cl_2–Me_2CO; δ_H: 2.45 and 2.63 (bs, two 1 H, 2 OH); disappeared on addition of D_2O), 3.14 (s, 3 H, OMe), 5.07 (bd, 2 H, *J* ~2 Hz, H-1b, 1c); δ_C: 54.6 (OMe), 65.4 (C-6a), 71.2 (3 O-3-CH_2Ph), 73.3 (2 O-6-CH_2Ph), 75.1 (3 O-4-CH_2Ph), 74.9 (C-2a), 99.5 ($^1J_{CH}$ 170.6 Hz, C-1a, 1b), and 101.3 ($^1J_{CH}$ 169.1 Hz, C-1c).

Anal. Calc. for $C_{75}H_{82}O_{16}$: C, 72.68; H, 6.67. Found: C, 72.22; H, 6.64.

*Methyl 2,6-di-*O-α-D-*mannopyranosyl-*α-D-*mannopyranoside* (**22**). — A mixture of **21** (308.8 mg, 0.25 mmol) and 10% Pd–C (250 mg) in EtOH (40 mL) and H_2O (4 mL) was stirred under H_2 for 5 h at 50°. The usual processing gave amorphous **22** (137.8 mg, quantitative), $[\alpha]_D$ +66.7° (*c* 0.33, H_2O); R_F 0.23 in 2:1:1 1-BuOH–EtOH–H_2O; δ_H (D_2O, 60°): 3.40 (s, 3 H, OMe), 4.94 (d, 1 H, *J* 2 Hz, H-1b), 4.96 (d, 1 H, *J* 2 Hz, H-1a), and 5.04 (d, 1 H, *J* 2 Hz, H-1c); δ_C (D_2O): 65.4 (C-6a),

79.0 (C-2a), 99.8 ($^1J_{CH}$ 171.9 Hz, C-1a, 1b), and 102.6 ($^1J_{CH}$ 169.9 Hz, C-1c).

Anal. Calc. for $C_{19}H_{34}O_{16} \cdot 1.5\ H_2O$: C, 41.83; H, 6.84. Found: C, 41.81; H, 6.54.

Methyl 2,6-di-O-[2-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl]-3,4-di-O-benzyl-α-D-mannopyranoside (**30**).— To a mixture of **21** (975.7 mg, 0.79 mmol) and $AgSO_3CF_3$ (1.22 g, 4.75 mmol), dried *in vacuo* for 3 h, were added $Me_2NCONMe_2$ (0.8 ml, 6.68 mmol), CH_2Cl_2 (15 mL) and half of a solution of **6** [1.63 g; prepared from **7** (1.6 g; 3.16 mmol)] in CH_2Cl_2 (15 mL) at −10 to −15°, with efficient stirring, during 5 min under argon. After the mixture had been stirred for 5 h at 20°, the rest of the solution of **6** in CH_2Cl_2 was added at −10 to −15°, and the mixture was stirred for a further 16 h at 20°. The usual processing gave an oily product (3.0 g) which was chromatographed on SiO_2 (300 g) with 8:1 toluene–EtOAc, to afford **30** (887 mg, 56.7%), $[\alpha]_D$ +33.9° (*c* 0.375); R_F 0.50 in 10:1 toluene–THF; δ_H: 2.1 (s, 6 H, 2 OAc), and 3.17 (s, 3 H, OMe); δ_C: 21.1 (2 OAc), 54.7 (OMe), 98.2 ($^1J_{CH}$ 167.7 Hz, C-1b), 99.5 ($^1J_{CH}$ 172.1 Hz, C-1a, 1d, 1e), and 100.6 ($^1J_{CH}$ 170.6 Hz, C-1c).

Anal. Calc. for $C_{133}H_{142}O_{28}$: C, 72.99; H, 6.54. Found: C, 72.96; H, 6.55.

Methyl 3,4-di-O-benzyl-2,6-di-O-[3,4,6-tri-O-benzyl-2-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranosyl]-α-D-mannopyranoside (**31**). — A solution of **30** (964 mg, 0.44 mmol) in MeOH (80 mL)–THF (20 mL) and 2M NaOMe–MeOH (0.7 mL) was stirred for 16 h at 20°. The usual processing gave an amorphous material (926 mg) which was chromatographed on SiO_2 (150 g) with 20:1 CH_2Cl_2–Me_2CO, to give **31** (832.7 mg, 89.2%), $[\alpha]_D$ +43.8° (*c* 0.56); R_F 0.20 in 40:1 CH_2Cl_2–Me_2CO; δ_H: 3.13 (s, 3 H, OMe), and 4.84, 4.94, 5.09 and 5.20 (anomeric H); δ_C: 54.4 (OMe), 98.3 ($^1J_{CH}$ 170.9 Hz, C-1b), 99.4 ($^1J_{CH}$ 168.9 Hz, C-1a), 100.9 ($^1J_{CH}$ 170.9 Hz, C-1c, 1d), and 101.1 ($^1J_{CH}$ 170.9 Hz, C-1e).

Anal. Calc. for $C_{129}H_{138}O_{26}$: C, 73.62; H, 6.61. Found: C, 73.13; H, 6.57.

Methyl 2,6-di-O-(2-O-α-D-mannopyranosyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**2**). — A mixture of **31** (575.5 mg, 0.27 mmol) and 10% Pd–C (400 mg) in EtOH (60 mL)–H_2O (8 mL) was stirred under H_2 for 5.5 h at 50°. The usual processing gave amorphous, powdery **2** (222.2 mg, 95.4%), $[\alpha]_D$ +71.9° (*c* 0.325, H_2O); R_F 0.19 in 2:1:1 1-BuOH–EtOH–H_2O; δ_H (D_2O), 60°): 4.89 (bd, 1 H, *J* 2 Hz, H-1a), 5.00 (bd, 2 H, *J* 2 Hz, H-1d, 1e), 5.05 (bd, 1 H, *J* 2 Hz, H-1b), and 5.22 (bd, 1 H, *J* 2 Hz, H-1c); δ_C (D_2O): 55.3 (OMe), 78.9 (C-2a, 2b, 2c), 98.3 ($^1J_{CH}$ 173.8 Hz, C-1b), 99.7 ($^1J_{CH}$ 170.9 Hz, C-1a), 100.9 ($^1J_{CH}$ 172.9 Hz, C-1c), and 102.6 ($^1J_{CH}$ 170.9 Hz, C-1d, 1e).

Anal. Calc. for $C_{31}H_{54}O_{26} \cdot H_2O$: C, 43.25; H, 6.56. Found: C, 43.26; H, 6.46.

Methyl 2,4-di-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-3,6-di-O-benzyl-α-D-mannopyranoside (**23**) *and methyl 4-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-3,6-di-O-benzyl-α-D-mannopyranoside* (**26**). — (*A*) To a mixture of **8** (750 mg, 2.0 mmol) and $AgSO_3CF_3$ (1.42 g, 5.5 mmol), dried *in vacuo* for 1.5 h, were added CH_2Cl_2 (7 mL), $Me_2NCONMe_2$ (1.5 mL, 12.5 mmol), and half of a solution of **6** [1.9 g, prepared **7** from (1.80 g, 3.55 mmol)] in CH_2Cl_2 (7 mL) at

−10 to −15°, with stirring, under argon. Then, the mixture was stirred for 16 h at 20°, at which time, t.l.c. examination showed the presence of a major product (**26**) at R_F 0.25 in 3:1 toluene–EtOAc, and traces of both **23** at R_F 0.70 and **8** at R_F 0.14. To this mixture was now added the rest of the solution of **6** in CH_2Cl_2 at −10 to −15°, and the mixture was stirred for a further 24 h at 20° under argon. The usual processing gave an oily product (3.0 g) which was chromatographed on SiO_2 (250 g) with 4:1 toluene–EtOAc, to give **23** (570 mg, 21.5%), $[\alpha]_D$ +23.5° (*c* 0.52); R_F 0.70 in 3:1 toluene–EtOAc; δ_H: 1.97 and 2.07 (2 s, 6 H, 2 OAc), 3.23 (s, 3 H, OMe), and 5.44 (bt, 2 H, H-2b, 2c); δ_C: 21.0 (OAc), 54.9 (OMe), 71.5 (O-3-CH_2Ph), 71.8 (2 O-3-CH_2Ph), 73.3 (3 O-6-CH_2Ph), 75.1 (2 O-4-CH_2Ph), 99.5 ($^1J_{CH}$ 173.5 Hz, C-1a, 1b), and 99.8 ($^1J_{CH}$ 164.5 Hz, C-1c).

Anal. Calc. for $C_{79}H_{86}O_{18}$: C, 71.69; H, 6.55. Found: C, 71.62; H, 6.60.

Further elution by the same solvent afforded **26** (991.6 mg, 58.4%), $[\alpha]_D$ +42.4° (*c* 0.695); R_F 0.25 in 3:1 toluene–EtOAc; δ_H: 2.05 (s, 3 H, OAc), 2.24 (bs, 1 H, OH), 3.36 (s, 3 H, OMe), 5.36 (d, 1 H, *J* 2 Hz, H-1b), and 5.46 (t, 1 H, *J* 2 Hz, H-2b); δ_C: 21.0 (OAc), 55.0 (OMe), 71.5 (O-3-CH_2Ph), 71.7 (O-3-CH_2Ph), 72.4 (C-4a), 73.3 (2 O-6-CH_2Ph), 75.0 (O-4-CH_2Ph), 99.2 ($^1J_{CH}$ 173.5 Hz, C-1b), and 100.0 ($^1J_{CH}$ 169.1 Hz, C-1a).

Anal. Calc. for $C_{50}H_{56}O_{12}$: C, 70.73; H, 6.65. Found: C, 70.66; H, 6.62.

(*B*) To a mixture of **8** (810 mg, 2.16 mmol) and $AgSO_3CF_3$ (3.5 g, 13.6 mmol), dried *in vacuo* for 3 h, were added CH_2Cl_2 (15 mL), $Me_2NCONMe_2$ (2.2 mL, 18.9 mmol), and half of a solution of **6** [4.846 g, prepared from **7** (4.56 g, 9.0 mmol)] in CH_2Cl_2 (10 mL) at −10 to −15°, with stirring under argon. After stirring for 11 h at 20°, the rest of the solution of **6** was added at −10 to −15°, and the mixture was stirred for a further 24 h at 20° under argon. The usual processing and chromatography on SiO_2 (500 g) with 5:1 toluene–EtOAc, gave crude **23** (3.02 g) which was rechromatographed on SiO_2 (300 g) with 9:1 toluene–EtOAc, to afford **23** (1.992 g, 69.7%).

*Methyl 2-*O*-acetyl-4-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl)-3,6-di-*O*-benzyl-α-*D*-mannopyranoside* (**27**). — A solution of **26** (188 mg, 0.22 mmol) in pyridine (2 mL) and Ac_2O (1 mL) was kept for 16 h at 20°, and the usual processing gave an oily product (207 mg) which was chromatographed on SiO_2 (25 g) with 15:1 toluene–THF, to give **27** (119 mg, 61.7%); R_F 0.45 in 10:1 toluene–THF; δ_H: 2.02 and 2.07 (2 s, 6 H, 2 OAc), 3.37 (s, 3 H, OMe), 5.32 (bt, 1 H, *J* 2 Hz, H-2a), 5.38 (d, 1 H, *J* 2 Hz, H-1b), and 5.47 (bt, 1 H, *J* 2 Hz, H-2b).

Anal. Calc. for $C_{52}H_{58}O_{13}$: C, 70.09, H, 6.56. Found: C, 69.84; H, 6.63.

*Methyl 3,6-di-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranoside* (**28**). — A solution of **26** (350 mg, 0.4 mmol) in MeOH (10 mL) and 2M NaOMe–MeOH (0.1 mL) was stirred for 16 h at 20°. The usual processing gave an amorphous material (312 mg) which was chromatographed on SiO_2 (60 g) with 20:1 CH_2Cl_2–Me_2CO, to give **28** (261.1 mg, 76.8%), $[\alpha]_D$ +49.5° (*c* 0.75); R_F 0.19 in 20:1 CH_2Cl_2–Me_2CO; δ_H: 3.35 (s, 3 H, OMe) and 5.31 (d, 1 H, *J* 2 Hz, H-1b); δ_C: 55.0 (OMe), 71.2 (O-3-CH_2Ph), 71.9 (O-3-CH_2Ph), 73.3 (2 O-6-CH_2Ph

and C-4a), 75.0 (O-4-CH_2Ph), 100.0 ($^1J_{CH}$ 168.5 Hz, C-1a), and 101.1 ($^1J_{CH}$ 173.5 Hz, C-1b).

Anal. Calc. for $C_{48}H_{54}O_{11}$: C, 71.14; H, 6.75. Found: C, 71.07; H, 6.73.

*Methyl 4-*O*-α-*D*-mannopyranosyl-α-*D*-mannopyranoside* (**29**). — A mixture of **28** (124.7 mg, 0.15 mmol) and 10% Pd–C (50 mg) in EtOH (10 mL)–H_2O (1 mL) was stirred under H_2 for 16 h at 20° and then for 4 h at 45°. The usual processing gave amorphous **29** (55.4 mg, 98.9%), $[\alpha]_D$ +101.0° (*c* 0.10, H_2O); R_F 0.56 in 2:1:1 1-BuOH–EtOH–H_2O; δ_H (D_2O, 60°): 3.40 (s, 3 H, OMe), 4.73 (bd, 1 H, *J* 2 Hz, H-1a), and 5.21 (d, 1 H, *J* 2 Hz, H-1b); δ_C: 74.5 (C-4a), 101.0 ($^1J_{CH}$ 170.9 Hz, C-1b), and 101.8 ($^1J_{CH}$ 171.9 Hz, C-1a).

Anal. Calc. for $C_{13}H_{24}O_{11} \cdot H_2O$: C, 41.71; H, 7.00. Found: C, 41.93; H, 6.68.

*Methyl 3,6-di-*O*-benzyl-2,4-di-*O*-(3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranoside* (**24**). — A solution of **23** (1.759 g, 1.33 mmol) in MeOH (60 mL)–THF (8 mL) and 2M NaOMe–MeOH (0.5 mL) was stirred for 20 h at 20°. The usual processing afforded an amorphous material (1.562 g) which was chromatographed on SiO_2 (80 g) with 10:1 CH_2Cl_2–Me_2CO, to give **24** (1.459 g, 88.5%), $[\alpha]_D$ +39.0° (*c* 0.52); R_F 0.43 in 10:1 CH_2Cl_2–Me_2CO; δ_H: 3.24 (s, 3 H, OMe), 2.33 (bs, 3 H, 2 OH), 4.94 (bd, 1 H, H-1c), and 5.32 (bd, 1 H, H-1b); δ_C: 54.8 (OMe), 71.5 (2 O-3-CH_2Ph), 71.8 (O-3-CH_2Ph), 72.0 (C-2a), 73.2 (O-6-CH_2Ph), 73.3 (2 O-6-CH_2Ph), 73.8 (C-4a), 74.9 (2 O-4-CH_2Ph), 99.4 ($^1J_{CH}$ 170.6 Hz, C-1a), and 101.1 ($^1J_{CH}$ 172.1 Hz, C-1b, C-1c).

Anal. Calc. for $C_{75}H_{82}O_{16}$: C, 72.68; H, 6.67. Found: C, 72.62; H, 6.79.

*Methyl 2,4-di-*O*-α-*D*-mannopyranosyl-α-*D*-mannopyranoside* (**25**). — A mixture of **24** (248 mg, 0.20 mmol) and 10% Pd–C (200 mg) in EtOH (40 mL) and H_2O (4 mL) was stirred under H_2 for 3.5 h at 45–50°. The usual processing afforded amorphous **25** (113 mg, 98.7%), $[\alpha]_D$ +38.5° (*c* 0.385, H_2O); R_F 0.35 in 2:1:1 1-BuOH–EtOH–H_2O; δ_H (D_2O, 60°): 3.39 (s, 3 H, OMe), 4.96 (bs, 1 H, H-1a), 5.02 (bs, 1 H, H-1c), and 5.21 (bs, 1 H, H-1b); δ_C (D_2O): 74.9 (C-4a), 79.6 (C-2a), 99.4 ($^1J_{CH}$ 172.9 Hz, C-1a), 101.8 ($^1J_{CH}$ 170.9 Hz, C-1b), and 102.6 ($^1J_{CH}$ 169.9 Hz, C-1c).

Anal. Calc. for $C_{19}H_{34}O_{16} \cdot 3\ H_2O$: C, 39.38; H, 7.04. Found: C, 39.33: H, 6.44.

*Methyl 2,4-di-*O*-[2-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl)-3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl]-3,6-di-*O*-benzyl-α-*D*-mannopyranoside* (**32**).— To a mixture of **24** (767 mg, 0.62 mmol) and $AgSO_3CF_3$ (600 mg, 2.33 mmol), dried *in vacuo* for 5 h, were added CH_2Cl_2 (5 mL), $Me_2NCONMe_2$ (0.6 mL, 5.0 mmol) and half of a solution of **6** [1.355 g, prepared from **7** (1.25 g, 2.4 mmol)] in CH_2Cl_2 (5 mL) at −10 to −15° with stirring under argon. After stirring for 12 h at 20°, t.l.c. showed the presence of two mannotetraoside intermediates, at R_F 0.22 and 0.29 as major products, and only a trace of **32** at R_F 0.59 in 10:1 toluene–THF. The rest of the solution of **6** in CH_2Cl_2 was added at −10 to −15°, and the mixture was stirred for a further 24 h. The usual processing gave an oily product (2.36 g) which was chromatographed on SiO_2 (300 g) with 20:1 toluene–THF, to give **32** (1.19 g, 87.8%).

An analytical sample was obtained by re-chromatography on SiO_2 with 40:1 toluene–THF; $[\alpha]_D$ +19.2° (*c* 0.26); R_F 0.59 in 10:1 toluene–THF; δ_H: 2.08 (s, 6 H, 2 OAc), and 3.18 (s, 3 H, OMe); δ_C: 21.1 (2 OAc), 54.8 (OMe), 98.6 ($^1J_{CH}$ 170 Hz), 99.2 ($^1J_{CH}$ 170 Hz), 99.6 ($^1J_{CH}$ 170 Hz), 100.0 ($^1J_{CH}$ 173 Hz), and 101.3 ($^1J_{CH}$ 170.6 Hz) for five anomeric carbon atoms.

Anal. Calc. for $C_{133}H_{142}O_{28}$: C, 72.99; H, 6.54. Found: C, 72.87; H, 6.41.

Methyl 3,6-di-O-benzyl-2,4-di-O-[3,4,6-tri-O-benzyl-2-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranosyl]-α-D-mannopyranoside (33). — A solution of 32 (764 mg, 0.35 mmol) in MeOH (25 mL)–THF (5 mL) and 2M NaOMe–MeOH (0.2 mL) was stirred for 24 h at 20°. The usual processing afforded an amorphous powder (711 mg) which was chromatographed on SiO_2 (80 g) with 30:1 CH_2Cl_2–Me_2CO, to give 33 (574 mg, 78.1%), $[\alpha]_D$ +36.9° (*c* 0.255); R_F 0.41 in 20:1 CH_2Cl_2–Me_2CO; δ_H: 3.18 (s, 3 H, OMe); δ_C: 54.8 (OMe), 99.2 ($^1J_{CH}$ 167 Hz, C-1), 100.1 ($^1J_{CH}$ 170.6 Hz, 2 C-1), and 101.2 ($^1J_{CH}$ 169.1 Hz, 2 C-1).

Anal. Calc. for $C_{129}H_{138}O_{26}$: C, 73.62; H, 6.61. Found: C, 73.74; H, 6.64.

Methyl 2,4-di-O-(2-O-α-D-mannopyranosyl-α-D-mannopyranosyl)-α-D-mannopyranoside (3). — A mixture of 33 (292 mg, 0.14 mmol) and 10% Pd–C (200 mg) in EtOH (30 mL) and H_2O (4 mL) was stirred under H_2 for 4 h at 45–50°. The usual processing afforded 3 (122 mg, quantitative), $[\alpha]_D$ +85.2° (*c* 0.31, H_2O); R_F 0.20 in 2:1:1 1-BuOH–EtOH–H_2O; δ_H (D_2O, 60°): 3.39 (s, 3 H, OMe), 4.94 (d, 1 H, *J* 2 Hz, H-1a), 5.04 (d, 2 H, *J* 2 Hz, H-1d, 1e), 5.22 (d, 1 H, *J* 2 Hz, H-1c), and 5.42 (d, 1 H, *J* 2 Hz, H-1b); δ_C (D_2O): 55.2 (OMe), 75.2 (C-4a), 78.9, 79.3, and 80.0 (C-2a, 2b, 2c), 99.4 ($^1J_{CH}$ 170.9 Hz, C-1a), 100.2 ($^1J_{CH}$ 172.3 Hz, C-1b), 101.0 ($^1J_{CH}$ 173.8 Hz, C-1c), and 102.6 ($^1J_{CH}$ 170.9 Hz, C-1d, 1e).

Anal. Calc. for $C_{31}H_{54}O_{26} \cdot H_2O$: C, 43.25; H, 6.56. Found: C, 43.17; H, 6.60.

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