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SYNTHESIS OF A BRANCHED D-MANNOPENTAOSIDE AND A BRANCHED D-MANNOHEXAOSIDE: MODELS OF THE OUTER CHAIN OF THE GLYCAN OF SOYBEAN AGGLUTININ*

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ABSTRACT

Synthetic routes are described to the D-mannopentaoside methyl 3-*O*-(3,6-di-*O*-α-D-mannopyranosyl-α-D-mannopyranosyl)-6-*O*-α-D-mannopyranosyl-α-D-mannopyranoside, and the D-mannohexaoside methyl 3-*O*-(3,6-di-*O*-α-D-mannopyranosyl-α-D-mannopyranosyl)-6-*O*-(2-*O*-α-D-mannopyranosyl-α-D-mannopyranosyl)-α-D-mannopyranoside, formed in a regio- and stereo-controlled way by employing the properly protected D-mannobioside methyl 2,4-di-*O*-benzyl-3-*O*-(2,4-di-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside and D-mannotrioside methyl 2,4-di-*O*-benzyl-3-*O*-(2,4-di-*O*-benzyl-α-D-mannopyranosyl)-6-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside as key intermediates.

INTRODUCTION

In 1964, Lis *et al.*[2] reported the isolation of a glycopeptide from soybean agglutinin as the first example of the presence of glycoprotein in higher plants, and in 1978, Lis and Sharon[3] proposed, from chemical and enzymic results, that the structure of the carbohydrate unit of this glycopeptide is **1**. Two structural features of **1** are to be noted; first, **1** shares the common, inner-core pentasaccharide structure having the high-D-mannose type of glycan chain **2**, isolated from such glycopeptides as calf-thyroglobulin glycopeptide[4], Chinese-hamster ovary-cell glycopeptide[5], and human IgM myeloma glycopeptide[6], and second, the outer chain of **1** shows an isomeric branching pattern comparable to that of **2**.

In order to develop a versatile and practical, synthetic route to the glycan chain **1**, the model structures **3** and **4** were chosen as the primary targets for our synthetic studies, and we now describe their synthesis, employing three known monosaccharide synthons **5** (refs. 7,8), **6** (ref. 1), and **7** (ref. 8).

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*Synthetic Studies on Cell-surface Glycans, Part 5. For Part 4, see ref. 1.
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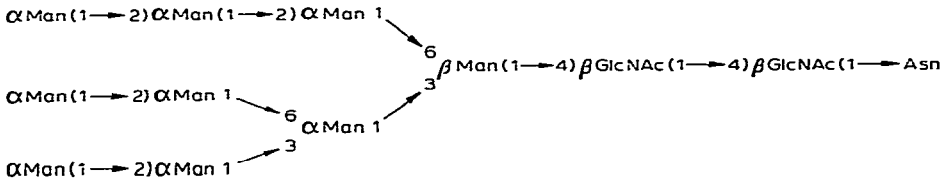

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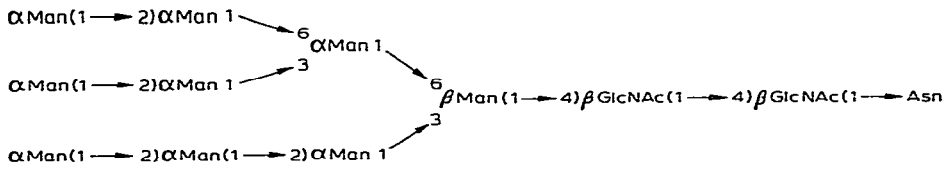

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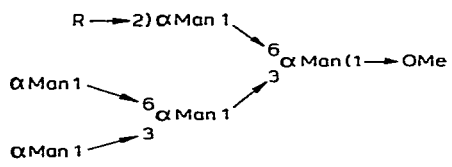
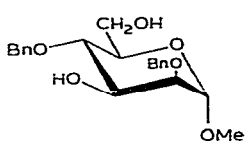


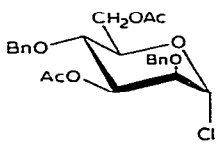
3 R = H

4 R = αMan(1



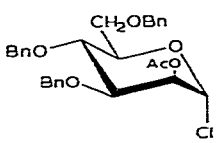
5

Bn = $PhCH_2$



6

Ac = CH_3CO



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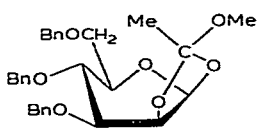


8

RESULTS AND DISCUSSION

Synthesis of protected D-*mannobioside* **20** *and* D-*mannotrioside* **25** *as key intermediates*

We first describe the synthetic sequence which led from the starting diol **5** to

compound **20**. In order to introduce a D-mannopyranosyl group at O-3, diol **5** was first converted into the 6-trityl ether (**9**), the 6-*tert*BuMe$_2$Si ether (**10**) and the 6-benzoate (**11**) in the usual way, and each of these compounds was submitted to glycosylation with the D-mannosyl donor **6** according to the Hanessian–Banoub procedure[9].

On glycosylation of trityl ether **9** with 2.6 molar equivalents of **6**, the protected D-mannobiosides **16** and **17** and the protected D-mannotrioside **23** were isolated, in 16.2, 25.0, and 43.6% yield, respectively. Glycosylation of the 6-*tert*-butyldimethylsilyl ether **10** with 1.9 molar equivalents of **6** led to the isolation of the protected D-mannobiosides **18** and **17** and the protected D-mannotrioside **23** in 3.4, 39.8, and 40.9% yield, respectively. Accordingly, both the trityl and the *tert*-butyldimethylsilyl group are labile under these glycosylation conditions, giving rise to a large proportion of the (undesired) D-mannotrioside derivative **23**.

However, the benzoate group in **11** proved to be stable. Glycosylation of benzoate **11** with 1.7 molar equivalents of **6**, and chromatography of the products, afforded protected D-mannobioside **19** in 67.7% yield. The ^{1}H-n.m.r. spectrum of **19** showed two singlets, for the two newly introduced, acetyl groups, at δ 1.94 and 2.01, and the ^{13}C-n.m.r. spectrum of **19** showed signals for two anomeric carbon atoms, at δ 98.4 (C-1a) and 99.6 (C-1b), with $^1J_{CH} \sim 170$ Hz, in agreement with the empirical rule of Bock *et al.*[10] for the α-D-anomeric configuration. Compound **19** was deacylated to triol **20**, and hydrogenolysis of **20** gave the free D-mannobioside **21**, whose ^{1}H- and ^{13}C-n.m.r. data were in good agreement with the assigned structure. Two doublets, with J 2 Hz, for anomeric protons were observed in the ^{1}H-n.m.r. spectrum of **21** (in D_2O at 60°) at δ 4.74 (H-1a) and 5.12 (H-1b), and two signals for anomeric carbon atoms were detected in the ^{13}C-n.m.r. spectrum (D_2O) at δ 101.0 ($^1J_{CH}$ 170.9 Hz, C-1a) and 102.6 ($^1J_{CH}$ 171.9 Hz, C-1b). The (1→3) nature of the interglycosidic linkage in **21** was also supported by the presence of the deshielded signal due to the glycosidation shift[11] for C-3a, at δ 78.5 in the ^{13}C-n.m.r. spectrum. Synthesis of **21** by a different route was reported by Lee and Wood[12].

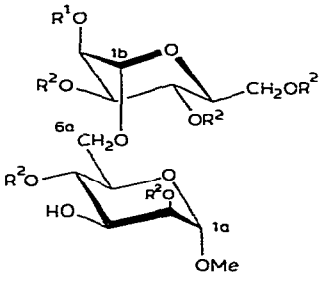
Thus, a practical synthesis of the key intermediate **20** (for the synthesis of D-mannopentaoside **3**) could be achieved in 47% overall yield from the dibenzyl ether **5**, and its structure was unequivocally determined by the synthetic sequence and the n.m.r. data.

We now describe a synthetic sequence for another key intermediate, namely, **25**, by the sequential introduction, by use of the glycosyl donors **7** and **6**, of glycosyl groups at O-6 and O-3 of the glycosyl acceptor **5**.

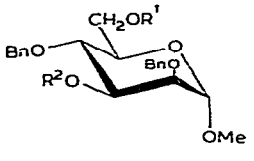
Selective glycosylation at O-6 of **5** was achieved by employing 1.1 molar equivalents of **7**, to give a 55.1% yield of protected D-mannobioside **13** and a 4.5% yield of D-mannotrioside derivative **22**, along with a 14.8% recovery of **5**. The assignment of structure **13** was supported by the ^{1}H-n.m.r. data, which showed the presence of a singlet for one acetyl group at δ 2.13, indicating the introduction of only one mannosyl group (derived from **7**) into **5**, and also by the ^{13}C-n.m.r. data, which disclosed two signals for two anomeric carbon atoms having the α-D configuration,

at δ 97.6 ($^1J_{CH}$ 172 Hz, C-1a) and 97.9 ($^1J_{CH}$ 173.5 Hz, C-1b), as well as a deshielded signal, due to a glycosidation shift for C-6a, at δ 66.5. Compound **13** was deacetylated to diol **14**, which was hydrogenolyzed over 10% Pd–C to give free mannobioside **15**, identical with an authentic sample[1].

The suitably protected mannobioside **13** was glycosylated with two molar equivalents of the glycosyl donor **6**, and the usual processing and chromatographic purification afforded an 83.6% yield of **24**. The structure of **24** was confirmed by its

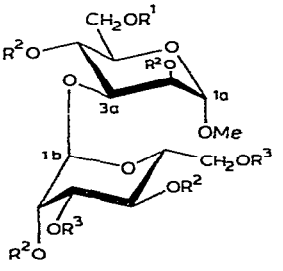


13 R^1 = Ac, R^2 = Bn
14 R^1 = H, R^2 = Bn
15 R^1 = R^2 = H

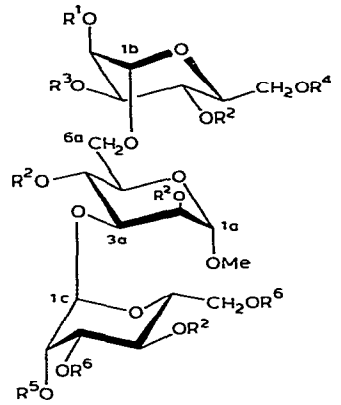


9 R^1 = Tr, R^2 = H
10 R^1 = $(Me_3C)Me_2Si$, R^2 = H
11 R^1 = Bz, R^2 = H
12 R^1 = R^2 = Bz

Bz = PhCO
Tr = Ph_3C



16 R^1 = Tr, R^2 = Bn, R^3 = Ac
17 R^1 = H, R^2 = Bn, R^3 = Ac
18 R^1 = $(Me_3C)Me_2Si$, R^2 = Bn, R^3 = Ac
19 R^1 = Bz, R^2 = Bn, R^3 = Ac
20 R^1 = R^3 = H, R^2 = Bn
21 R^1 = R^2 = R^3 = H



22 $R^1 = R^5 = Ac, R^2 = R^3 = R^4 = R^6 = Bn$
23 $R^1 = R^2 = R^5 = Bn, R^3 = R^4 = R^6 = Ac$
24 $R^1 = R^6 = Ac, R^2 = R^3 = R^4 = R^5 = Bn$
25 $R^1 = R^6 = H, R^2 = R^3 = R^4 = R^5 = Bn$
26 $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = H$

^{1}H-n.m.r. spectrum, which showed singlets for three acetyl groups, at δ 1.92, 1.97, and 2.11. The ^{13}C-n.m.r. spectrum also supported the structure, as it revealed three signals, with $^1J_{CH} \sim 170$ Hz, for anomeric carbon atoms having the α-D configuration, at δ 98.2 (C-1a), 98.3 (C-1b), and 99.5 (C-1c). Zemplén deacetylation of **24** gave the desired, key intermediate **25** (for the synthesis of the target molecule **4**) in 40% overall yield from **5**. Hydrogenolysis of **25** gave rise to the free mannotrioside **26**, identical with an authentic sample[8].

Having unambiguously synthesized two key intermediates, further elongation of the glycan chain on the glycosyl acceptors **20** and **25** was next studied.

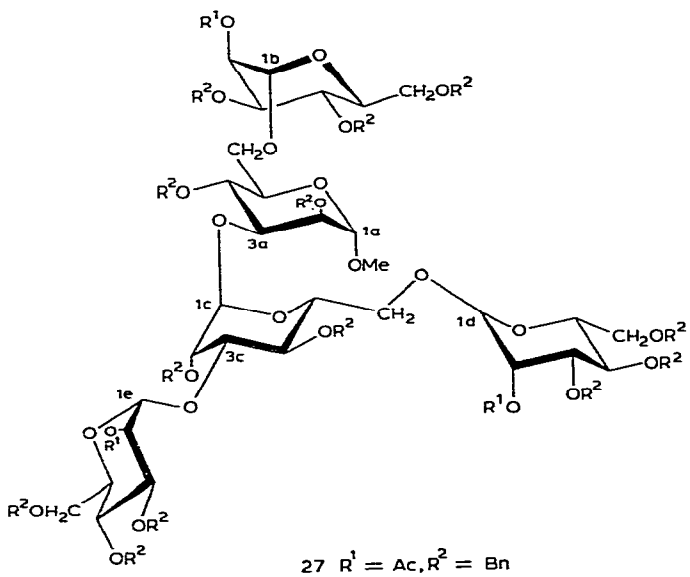
Synthesis of branched D-*mannopentaoside* **3** *and* D-*mannohexaoside* **4**

Simultaneous introduction of three D-mannosyl groups onto the glycosyl acceptor **20** was successfully achieved by employing 5.0 molar equivalents of glycosyl donor **7** under Hanessian–Banoub conditions. A 76.1% yield of the protected D-mannopentaoside **27** was isolated after chromatography on a column of silica gel. The ^{1}H-n.m.r. spectrum of **27** revealed the presence of three acetyl groups as two singlets, at δ 2.04 (3 H) and 2.12 (6 H), that originated from three molecules of glycosyl donor **7**. The ^{13}C-n.m.r. spectrum of **27** showed four signals, with $^1J_{CH} \sim 170$ Hz, at δ 97.9 (C-1a and C-1b), 98.2 (C-1d), 99.0 (C-1c), and 99.6 (C-1e), confirming the α-D configuration at all of the anomeric centers. Zemplén deacetylation of **27**, to **28**, and hydrogenolysis of **28** over 10% Pd–C in aq. EtOH, afforded the target D-mannopentaoside (**3**) as an amorphous powder. The structure of **3** was deduced from the synthetic sequence, and was supported by the following ^{1}H- and ^{13}C-n.m.r. data: five doublets, with J 2 Hz, for five anomeric protons, at δ 4.70 (H-1a), 4.85 (H-1b), 4.89 (H-1d), 5.03 (H-1e), and 5.10 (H-1c); four signals, with

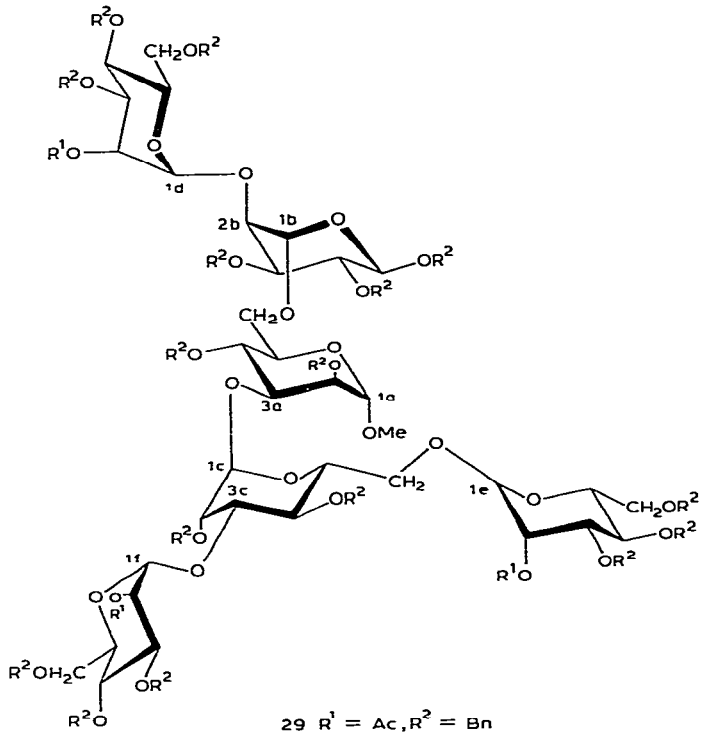
$^1J_{CH}$ ~170 Hz, for five anomeric carbon atoms having the α-D configuration, at δ 99.9 (C-1b), 100.1 (C-1d), 101.3 (C-1a), and 102.8 (C-1c and C-1e); and two deshielded signals due to the glycosidation shift, for C-3a and C-3c, at δ 78.5 and 79.0.

Synthesis of the other target molecule, **4**, could be achieved similarly. Glycosylation of the key intermediate **25** with five molar equivalents of the glycosyl donor **7** afforded a 60.0% yield of the protected D-mannohexaoside **29**. The ^{13}C-n.m.r. spectrum of **29** showed the presence of four signals, with $^1J_{CH}$ ~170 Hz, for six anomeric carbon atoms having the α-D configuration, at δ 98.0 (C-1a), 98.2 (C-1e), 99.0 (C-1b and C-1c), and 99.5 (C-1d and C-1f). Zemplén deacetylation of **29** to **30**, and hydrogenolysis of **30**, gave the target D-mannohexaoside **4** as an amorphous material. The structure of **4** was assignable from the synthetic sequence, and was confirmed by its ^{1}H- and ^{13}C-n.m.r. data: the ^{1}H-n.m.r. spectrum (D_2O at 60°) showed 5 doublets, with J ~2 Hz, for six anomeric protons, at δ 4.70 (H-1a), 4.86 (H-1e), 5.00 (H-1d), 5.04 (H-1f), and 5.09 (H-1b and H-1c); the ^{13}C-n.m.r. spectrum (D_2O) showed 4 signals, with $^1J_{CH}$ ~170 Hz, for 6 anomeric carbon atoms having the α-D configuration, at δ 98.2 (C-1b), 99.9 (C-1e), 101.3 (C-1a), and 102.7 (C-1c, C-1d, and C-1f), and three deshielded signals, due to the glycosidation shift, for C-3a, C-3c, and C-2b at δ 78.6, 78.9, and 79.1.

In conclusion, regio- and stereo-controlled, synthetic sequences to the branched D-mannopentaoside **3** and D-mannohexaoside **4**, which are models of the outer chain of the glycan unit of soybean agglutinin, were developed by employing regioselectively protected D-mannobioside **20** and D-mannobioside **25** as key intermediates.



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



29 R^1 = Ac, R^2 = Bn
30 R^1 = H, R^2 = Bn
4 R^1 = R^2 = H

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, for 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 NMR spectrometer operated at 25.05 MHz. The values of δ_C and δ_H are expressed in p.p.m. downward 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 plates pre-coated with a layer (thickness, 0.25 mm) of Silica Gel 60 F_{254} (E. Merck, Darmstadt, Germany).

Methyl 2,4-di-O-benzyl-6-O-trityl-α-D-mannopyranoside (**9**). — To a solution of **5** (759 mg, 2 mmol) in pyridine (5 mL) was added chlorotriphenylmethane (777 mg). The mixture was stirred for 2 days at 20°, and diluted with CH_2Cl_2. The usual processing, and chromatography on SiO_2 (120 g) with 100:10:1 toluene–EtOAc–

Et_3N gave **9** as a foam (1.068 g, 85.3%); R_F 0.64 in 3:1 toluene–EtOAc; δ_H 3.40 (s, 3 H, OMe). Compound **9** was unstable at 20°, and was slowly converted into **5**. When a solution of **9** in $CDCl_3$ was kept for 4 h at 20° in a n.m.r. tube, 30% of **9** was converted back into **5**. Accordingly, freshly prepared **9** was used directly for the next step.

*Methyl 2,4-di-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-α-*D*-mannopyranoside* (**10**). — A mixture of **5** (751 mg, 2 mmol), imidazole (340 mg, 5 mmol), and *tert*$BuMe_2SiCl$ (365 mg, 2.4 mmol) in $HCONMe_2$ (3 mL) was stirred for 2 h at 0–5°, and then kept for 2 days at 4°. The solvent was evaporated off *in vacuo*, and the residue was chromatographed on SiO_2 (100 g) with 3:1 toluene–EtOAc, to give **10** as a syrup (745 mg, 76.3%); $[\alpha]_D$ +20.0° (*c* 0.525); R_F 0.65 in 3:1 toluene–EtOAc; δ_H: 0.89 (s, 9 H, *t*Bu), 2.12 (bs, 1 H, OH), 3.31 (s, 3 H, OMe), and 4.73 (d, 1 H, *J* 2 Hz, H-1); δ_C: 18.3 (CMe_3), 26.0 (C-Me_3), 54.5 (OMe), 62.6 (C-6), 71.7 (C-3), 72.2 (C-5), 72.7 (O-2-CH_2Ph), 74.7 (O-4-CH_2Ph), 76.5 (C-4), 78.6 (C-2), and 97.7 ($^1J_{CH}$ 167.7 Hz, C-1).

Anal. Calc. for $C_{27}H_{40}O_6Si$: C, 66.36; H, 8.25. Found: C, 66.21; H, 8.25.

*Methyl 6-*O*-benzoyl-2,4-di-*O*-benzyl-α-*D*-mannopyranoside* (**11**). — To a solution of **5** (5.62 g, 15 mmol) in pyridine (150 mL) was added BzCl (3.2 g, 22.8 mmol) at 0°. After the mixture had been stirred for 16 h at 20°, t.l.c. examination showed the presence of a monobenzoate as the major product, as well as a small proportion of starting material (**5**) and a trace of a dibenzoate. More BzCl (1 g, 7.2 mmol) was added, and the mixture was stirred for 16 h at 20°. The excess of BzCl was decomposed by adding H_2O (1 mL), and evaporation *in vacuo* gave a residue which was partitioned between EtOAc and cold water. The organic layer was successively washed with water, aq. $NaHCO_3$, and saturated saline, dried ($MgSO_4$), and evaporated *in vacuo*, to afford an oily product which was chromatographed on SiO_2 (300 g) with 11:1 toluene–EtOAc, affording **11** (6.33 g, 87.5%); $[\alpha]_D$ +30.9° (*c* 0.615); R_F 0.52 in 3:1 toluene–EtOAc; δ_H: 3.36 (s, 3 H, OMe), 4.06 (dd, 1 H, $J_{2,3}$ 3, $J_{3,4}$ 9 Hz, H-3), and 4.82 (d, 1 H, $J_{1,2}$ 2 Hz, H-1); δ_C: 54.9 (OMe), 63.8 (C-6), 69.3 (C-5), 71.9 (C-3), 72.8 (O-2-CH_2Ph), 74.9 (O-4-CH_2Ph), 76.2 (C-4), 78.4 (C-2), and 97.7 ($^1J_{CH}$ 169.1 Hz, C-1).

Anal. Calc. for $C_{28}H_{30}O_7$: C, 70.28; H, 6.32. Found: C, 70.44; H, 6.29.

From the less polar fraction, dibenzoate **12** (0.960 g, 11.0%), R_F 0.78 in 3:1 toluene–EtOAc, was isolated, and identified with an authentic sample[8].

*Methyl 6-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl)-2,4-di-*O*-benzyl-α-*D*-mannopyranoside* (**13**). — To a mixture of **5** (1.845 g, 4.93 mmol) and $AgSO_3CF_3$ (2.06 g, 8 mmol), dried *in vacuo* for 4 h, were added, with stirring, $Me_2NCONMe_2$ (2.5 mL, 20 mmol), CH_2Cl_2 (8 mL), and half of a solution of **7** [prepared from **8** (2.80 g, 5.5 mmol) in CH_2Cl_2 (5 ml)] under argon at −10 to −15°. After stirring for 6.5 h at 20°, the rest of the solution of **7** was added at −10 to −15°; the mixture was stirred for a further 16 h at 20°, diluted with CH_2Cl_2 (50 mL), and filtered through a bed of Celite. The filtrate was washed with aq. $NaHCO_3$, dried ($MgSO_4$), and evaporated, to give an oil (6.55 g) which was chromatographed on

SiO_2 (500 g) with 5:1 toluene–EtOAc, affording methyl 3,6-di-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-2,4-di-*O*-benzyl-α-D-mannopyranoside (**22**) (296.8 mg, 4.5%), $[\alpha]_D$ +46.1° (*c* 0.49); R_F 0.58 in 3:1 toluene–EtOAc.

Anal. Calc. for $C_{79}H_{86}O_{18}$: C, 71.69; H, 6.55. Found: C, 71.59; H, 6.54.

Compound **22** was identified with an authentic sample[8] by comparing ^{13}C- and ^1H-n.m.r. data. Further elution with 3:1 toluene-EtOAc afforded **13** (2.307 g, 55.1%), $[\alpha]_D$ +48.3° (*c* 0.90), R_F 0.49 in 3:1 toluene–EtOAc; δ_H: 2.13 (s, 3 H, Ac), 3.26 (s, 3 H, OMe), and 5.44 (bt, 1 H, *J* ~2 Hz, H-2b); δ_C: 21.1 ($COCH_3$), 54.7 (OMe), 66.5 (C-6a), 97.6 ($^1J_{CH}$ 172 Hz, C-1a), and 97.9 ($^1J_{CH}$ 173.5 Hz, C-1b).

Anal. Calc. for $C_{50}H_{56}O_{12}$: C, 70.73; H, 6.65. Found: C, 70.25; H, 6.61.

Further elution with the same solvent afforded *2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranose* (618.6 mg, 22.8% from **8**), a hydrolysis product of 7, $[\alpha]_D$ +16.7° (*c* 0.825); R_F 0.34 in 3:1 toluene–EtOAc; δ_H 2.14 (s, 3 H, Ac); δ_C 21.2 (OCO*Me*), 69.2 (C-2), 69.3 (C-6), 71.0 (C-5), 71.7 (O-3-*C*H_2Ph), 73.4 (O-6-*C*H_2Ph), 74.6 (C-4), 75.0 (O-4-*C*H_2Ph), 77.0 (C-3), and 92.3 ($^1J_{CH}$ 170.5 Hz, C-1).

Anal Calc. for $C_{29}H_{32}O_7$: C, 70.71; H, 6.55. Found: C, 70.78; H, 6.62.

The same compound was also obtained, in 85% yield, by treating **8** with aq. AcOH. Finally, a product (272 mg, 14.8%) of R_F 0.23 in 3:1 toluene–EtOAc was eluted, and was identified as the starting alcohol **5**.

Methyl 2,4-di-O-benzyl-6-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**14**). — Compound **13** (210 mg, 0.25 mmol) was deacetylated in the usual way with NaOMe–MeOH–THF. Purification of the product by chromatography on SiO_2 (20 g) with 15:1 CH_2Cl_2–Me_2CO afforded **14** (161.6 mg, 80.0%), $[\alpha]_D$ +68.9° (*c* 0.19); R_F 0.50 in 10:1 CH_2Cl_2–Me_2CO; δ_H: 3.27 (s, 3 H, OMe) and 5.03 (d, 1 H, *J* 2 Hz, H-1b); δ_C: 54.8 (OMe), 66.2 (C-6a), 97.6 ($^1J_{CH}$ 166.2 Hz, C-1a), and 99.5 ($^1J_{CH}$ 170.6 Hz, C-1b).

Anal. Calc. for $C_{48}H_{54}O_{11}$: C, 75.56; H, 7.13. Found: C, 75.53; H, 6.74.

Methyl 6-O-α-D-mannopyranosyl-α-D-mannopyranoside (**15**). — Compound **14** (58.6 mg) was hydrogenolyzed in EtOH–THF over 10% Pd–C in the usual way, to afford **15** (30.1 mg), R_F 0.42 in 2:1:1 BuOH–EtOH–H_2O, which was identified with an authentic sample[1] by comparing the ^1H-n.m.r. data.

Methyl 2,4-di-O-benzyl-3-O-(3,6-di-O-acetyl-2,4-di-O-benzyl-α-D-mannopyranosyl)-6-O-trityl-α-D-mannopyranoside (**16**). — To a mixture of **9** (217 mg, 0.35 mmol) and $AgSO_3CF_3$ (355 mg, 1.38 mmol), dried *in vacuo* for 10 h, were added $Me_2NCONMe_2$ (0.22 mL, 1.8 mmol), CH_2Cl_2 (3 mL), and half of a solution of **6** (425 mg, 0.91 mmol) in CH_2Cl_2 (3 mL), successively at −5 to −10° under argon with stirring. Then, the mixture was stirred for 4 h at 20°, the remaining 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, and chromatography on SiO_2 (150 g) afforded the following products. (*a*) A fraction eluted by 120:2:1 $CHCl_3$–Me_2CO–Et_3N, R_F 0.88 in 40:1 CH_2Cl_2–Me_2CO, was re-chromatographed on SiO_2 (80 g) with 100:10:1 toluene–EtOAc–Et_3N, to give **16** (59 mg, 16.2%), R_F 0.32 in 10:1 toluene–EtOAc; δ_H 1.94: (s, 3 H, OAc), 2.05 (s, 3 H, OAc), 3.38 (s, 3 H, OMe), and 6.85–7.55 (m, 35 H,

aromatic H). (*b*) A fraction containing more-polar products, R_F 0.59 and 0.26 in 40:1 CH_2Cl_2–Me_2CO, was then eluted by 120:2:1 $CHCl_3$–Me_2CO–Et_3N. (*c*) An oily mixture (328 mg) obtained from this fraction was rechromatographed over SiO_2 (80 g) with 3:1 toluene–EtOAc, to give **23** (187.4 mg, 43.6%), R_F 0.59, and **17** (69.9 mg, 25.0%), R_F 0.26. Compounds **23** and **17** were identified by comparison of ^{13}C- and ^1H-n.m.r. data with those of authentic samples[1].

Methyl 2,4-di-O-benzyl-6-O-(tert-*butyldimethylsilyl*)*-3-O-(3,6-di-O-acetyl-2,4-di-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside* (**18**). — To a mixture of **10** (255 mg, 0.52 mmol) and $AgSO_3CF_3$ (396 mg, 1.54 mmol), dried *in vacuo* for 16 h, were added, under argon, $Me_2NCONMe_2$ (0.25 mL, 2 mmol), CH_2Cl_2 (3 mL), and half of a solution of **6** (460 mg, 0.99 mmol), successively, at — 10 to —15°. Then, the mixture was stirred for 3 h at 20°, the remaining solution of **6** in CH_2Cl_2 was added at —10 to —15°, and the mixture was stirred for a further 4 days at 20°. The usual processing afforded an oily product (904 mg) which was chromatographed on SiO_2 (200 g) with 40:2:1 toluene–THF–Et_3N, to give the following products. Compound **18** (16.3 mg, 3.4%), R_F 0.42 in 10:1 toluene–THF, δ_H: 0.94 (s, 9 H, CMe_3), 1.94 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), and 3.27 (s, 3 H, OMe); compound **23** (261 mg, 40.9%), R_F 0.27; and compound **17** (165.6 mg, 39.8%), R_F 0.13. **23** and **17** were identified with authentic samples[1] by comparison of ^1H- and ^{13}C-n.m.r. data.

Methyl 6-O-benzoyl-2,4-di-O-benzyl-3-O-(3,6-di-O-acetyl-2,4-di-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**19**). — To a mixture of **11** (957 mg, 2.0 mmol) and $AgSO_3CF_3$ (1.35 g, 5 mmol), dried *in vacuo* for 3 h at 20°, were successively added $Me_2NCONMe_2$ (1.2 mL, 10 mmol), CH_2Cl_2 (8 mL), and two-thirds of a solution of **6** (1.537 g, 3.38 mmol) in CH_2Cl_2 (6 mL) at —10 to —15°, with stirring, under argon. Then, the mixture was stirred for 6 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, and chromatography on SiO_2 (300 g), with 25:1 toluene–THF, afforded **19** (1.226 g, 67.7%), $[\alpha]_D$ +29.1° (*c* 0.615); R_F 0.14 in 20:1 toluene–THF; δ_H: 1.94 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 3.34 (s, 3 H, OMe), 5.19 (d, 1 H, *J* 2 Hz, H-1b), and 7.94–8.07 (m, 2 H, benzoyl); δ_C: 54.8 (OMe), 77.4 (C-3a), 98.4 ($^1J_{CH}$ 172 Hz, C-1a), and 99.6 ($^1J_{CH}$ 172.1 Hz, C-1b).

Anal. Calc. for $C_{52}H_{56}O_{14}$: C, 69.01; H, 6.24. Found: C, 68.68; H, 6.28.

Methyl 2,4-di-O-benzyl-3-O-(2,4-di-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**20**). — A solution of **19** (560 mg, 619 μmol) in MeOH (20 mL) and 2M NaOMe–MeOH (0.2 mL) was stirred for 16 h at 20°. Neutralization of the base with Amberlist 15 (H^+) resin, and the usual processing, gave crude **20** (499 mg) which was chromatographed on SiO_2 (30 g) with 8:1 CH_2Cl_2–Me_2CO, to afford **20** (351.3 mg, 79.1%), $[\alpha]_D$ +30.8° (*c* 0.315); R_F 0.22 in 10:1 CH_2Cl_2–Me_2CO; δ_H: 3.28 (s, 3 H, OMe), 5.22 (bd, 1 H, H-1b); δ_C: 54.8 (OMe), 72.4 (2 O-2-CH_2Ph), 74.6 and 74.7 (2 O-4-CH_2Ph), 77.6 (C-3a), 98.9 ($^1J_{CH}$ 170.6 Hz, C-1a), and 99.2 ($^1J_{CH}$ 170.6 Hz, C-1b).

Anal. Calc. for $C_{41}H_{48}O_{11}$: C, 68.10; H, 6.75. Found: C, 67.79; H, 6.72.

Methyl 3-O-α-D-mannopyranosyl-α-D-mannopyranoside (**21**). — A mixture of

20 (50 mg, 69 μmol) and 10% Pd–C (40 mg) in EtOH (5 mL) was stirred under H_2 for 3 h at 45° and then for 16 h at 25°. The usual processing gave **21** (21.8 mg, 87.2%) as an amorphous powder, $[\alpha]_D$ +94.8° (*c* 0.31, H_2O); R_F 0.50 in 2:1:1 1-BuOH–EtOH–H_2O); δ_H (D_2O, 60°): 3.42 (s, 3 H, OMe), 4.74 (d, 1 H, 2 Hz, H-1a), 5.12 (d, 1 H, *J* 2 Hz, H-1b); δ_C (D_2O, 60°): 78.5 (C-3a), 101.0 ($^1J_{CH}$ 170.9 Hz, C-1a), 102.6 ($^1J_{CH}$ 171.9 Hz, C-1b).

Anal. Calc. for $C_{13}H_{24}O_{11} \cdot 0.5\ H_2O$: C, 42.74; H, 6.90. Found: C, 42.70; H, 6.81.

Methyl 6-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-2,4-di-O-benzyl-3-O-(3,6-di-O-acetyl-2,4-di-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**24**). — To a mixture of **13** (850 mg, 1.00 mmol) and $AgSO_3CF_3$ (780 mg, 3.0 mmol), dried *in vacuo* for 24 h at 20°, were successively added CH_2Cl_2 (5 mL), $Me_2NCONMe_2$ (0.85 mL, 7.1 mmol), and half of a solution of **6** (950 mg, ~2.0 mmol) in CH_2Cl_2 (5 mL) at −10 to −15°, with stirring, under argon. After stirring for 4 h at 20°, the remaining solution of **6** in CH_2Cl_2 was added at −10 to −15°, and the mixture was stirred for a further 5 h at 20° under argon. The usual processing gave a crude oil (2.32 g) which was chromatographed on SiO_2 (360 g) with 11:1 toluene–THF, to give **24** (1.066 g, 83.6%), $[\alpha]_D$ +41.3° (*c* 0.56); R_F 0.64 in 10:1 toluene–THF and 0.21 in 3:1 toluene–EtOAc; δ_H: 1.92 (s, 3 H, Ac), 1.97 (s, 3 H, Ac), 2.11 (s, 3 H, Ac), 3.24 (s, 3 H, OMe), 4.91 (d, 1 H, *J* 2 Hz) and 5.16 (d, 1 H, *J* 2 Hz, two anomeric protons), 5.30 (dd, 1 H, H-3c), and 5.43 (bt, 1 H, H-2b); δ_C: 98.2 and 98.3 ($^1J_{CH}$ ~170 Hz, C-1a and C-1b), 99.5 ($^1J_{CH}$ 172.1 Hz, C-1c), and 54.6 (OMe).

Methyl 2,4-di-O-benzyl-3-O-(2,4-di-O-benzyl-α-D-mannopyranosyl)-6-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**25**). — A solution of **24** (950 mg, 745 μmol) in MeOH (25 mL), THF (10 mL), and 2M NaOMe in MeOH (0.5 mL) was stirred for 16 h at 20°. The usual processing afforded crude **25** (835 mg), which was chromatographed on SiO_2 (50 g) with 15:1 CH_2Cl_2–Me_2CO, to give **25** (736.8 mg, 86.1%); $[\alpha]_D$ +49.8° (*c* 0.255); R_F 0.13 in 20:1 CH_2Cl_2–Me_2CO; δ_H: 3.27 (s, 3 H, OMe), 5.05 (bd, 1 H, H-1b), and 5.20 (bd, 1 H, H-1c); δ_C: 54.8 (OMe), 98.2 ($^1J_{CH}$ 167.7 Hz, C-1a), 99.3 ($^1J_{CH}$ 169.1 Hz, C-1c), and 99.7 ($^1J_{CH}$ 170.6 Hz, C-1b).

Anal. Calc. for $C_{68}H_{76}O_{16}$: C, 71.06; H, 6.67. Found: C, 70.93; H, 6.68.

Methyl 3,6-di-O-α-D-mannopyranosyl-α-D-mannopyranoside (**26**). — A mixture of **25** (55.5 mg) and 10% Pd–C (30 mg) in EtOH (10 mL) and H_2O (1 mL) was stirred under H_2 for 3 h at 50° and then for 16 h at 25°. The usual processing gave **26** as an amorphous powder (16.4 mg, 65.9%), $[\alpha]_D$ +93.6° (*c* 0.14, H_2O); R_F 0.37 in 2:1:1 1-BuOH–EtOH–H_2O; δ_H: 3.42 (s, 3 H, OMe), 4.73 (d, 1 H, *J* 2 Hz, H-1a), 4.92 (d, 1 H, *J* 2 Hz, H-1b), and 5.12 (d, 1 H, *J* 2 Hz, H-1c). Compound **26** was identified with an authentic sample[8] (prepared by a different route) through comparison of their ^{1}H-n.m.r. data.

Methyl 6-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-2,4-di-O-benzyl-3-O-[3,6-di-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-2,4-di-O-benzyl-α-D-mannopyranosyl]-α-D-mannopyranoside (**27**). — A mixture of **20** (435 mg,

607 μmol) and $AgSO_3CF_3$ (1.18 g, 4.59 mmol), dried *in vacuo* for 5 h at 20°, was dissolved by adding CH_2Cl_2 (4 mL) and $Me_2NCONMe_2$ (0.75 mL, 5.08 mmol) under argon. To this solution was added half of a solution of **7** [prepared[8] from **8** (1.55 g, 3.06 mmol) in CH_2Cl_2 (5 ml)] at −10 to −15° with stirring, under argon. Then, the mixture was stirred for 3 h at 20°, the rest of the solution of **7** 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 afforded an oily product (2.417 g) which was chromatographed on SiO_2 (200 g) with 11:1 toluene–THF, to give crude **27** (1.315 g). The crude **27** was rechromatographed on SiO_2 (150 g) with 40:1 CH_2Cl_2–Me_2CO, to give pure **27** (988.8 mg, 76.1%), $[\alpha]_D$ +57.1° (*c* 0.385); R_F 0.26 in 10:1 toluene–THF; δ_H: 2.04 (s, 3 H, Ac), 2.12 (s, 6 H, 2 Ac), 3.17 (s, 3 H, OMe), 5.20 (bs, 2 H, 2 anomeric H), and 5.37–5.50 (bm, 3 H, H-2b,2d,2e); δ_C: 54.5 (OMe), 97.9 ($^1J_{CH}$ 170.6 Hz, C-1a,1b), 98.2 ($^1J_{CH}$ ~170 Hz, C-1d), 99.0 ($^1J_{CH}$ 169.7 Hz, C-1c), and 99.6 ($^1J_{CH}$ 169.1 Hz, C-1e).

Anal. Calc. for $C_{128}H_{138}O_{29}$: C, 71.82; H, 6.50. Found: C, 71.88; H, 6.34.

Methyl 2,4-di-O-benzyl-3-O-[2,4-di-O-benzyl-3,6-di-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranosyl]-6-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**28**). — A solution of **27** (855.8 mg, 0.40 mmol) in MeOH (25 mL)–THF (10 mL)–2M NaOMe in MeOH (0.1 mL) was stirred for 16 h at room temperature. The usual processing afforded an oily product (797 mg) which was chromatographed on SiO_2 (80 g) with 20:1 CH_2Cl_2–Me_2CO, to give pure **28** (684.5 mg, 84.2%), $[\alpha]_D$ +61.9° (*c* 0.27); R_F 0.29 in 20:1 CH_2Cl_2–Me_2CO; δ_H: 3.20 (s, 3 H, OMe), 5.00 (bs, 1 H, anomeric H), and 5.20 (bs, 1 H, anomeric H); δ_C: 54.6 (OMe), 98.0 ($^1J_{CH}$ 166.0 Hz, C-1a), 99.2 ($^1J_{CH}$ ~169.9 Hz, C-1c), 99.6 ($^1J_{CH}$ 169.9 Hz, C-1b), 99.8 ($^1J_{CH}$ 169.9 Hz, C-1d), and 101.4 ($^1J_{CH}$ 168.9 Hz, C-1e).

Anal. Calc. for $C_{122}H_{132}O_{26}$: C, 72.10; H, 6.65. Found: C, 72.09; H, 6.60.

Methyl 3-O-(3,6-di-O-α-D-mannopyranosyl-α-D-mannopyranosyl)-6-O-α-D-mannopyranosyl-α-D-mannopyranoside (**3**). — A mixture of **28** (309 mg, 0.15 mmol) and 10% Pd–C (200 mg) in EtOH (30 mL)–H_2O (4 mL) was stirred under H_2 for 6.5 h at 50°. The usual processing afforded **3** as an amorphous material (114.5 mg, 87.7%), $[\alpha]_D$ +98.3° (*c* 0.40, H_2O); R_F 0.13 in 2:1:1 1-BuOH–EtOH–H_2O; δ_H (D_2O, 60°): 4.70 (d, 1 H, *J* 1.7 Hz, H-1a), 4.85 (bs, 1 H, H-1b), 4.89 (bs, 1 H, H-1d), 5.03 (d, 1 H, *J* 1.7 Hz, H-1e), and 5.10 (d, 1 H, *J* 1.7 Hz, H-1e); δ_C (D_2O): 55.3 (OMe), 78.5 and 79.0 (C-3a,3c), 99.9 ($^1J_{CH}$ 168.9 Hz, C-1b), 100.1 ($^1J_{CH}$ 168.9 Hz, C-1d), 101.3 ($^1J_{CH}$ 169.9 Hz, C-1a), and 102.8 ($^1J_{CH}$ 171.9 Hz, C-1c,1e).

Anal. Calc. for $C_{31}H_{54}O_{26} \cdot 1.5\ H_2O$: C, 42.81; H, 6.61. Found: C, 42.91; H, 6.63.

Methyl 6-O-[2-O-2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl]-2,4-di-O-benzyl-3-O-[3,6-di-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-2,4-di-O-benzyl-α-D-mannopyranosyl]-α-D-mannopyranoside (**29**). — A mixture of **25** (574 mg, 0.50 mmol) and $AgSO_3CF_3$ (970 mg, 3.77 mmol), dried *in vacuo* for 5 h at 20°, was dissolved by adding CH_2Cl_2 (6 mL) and $Me_2NCONMe_2$ (1.0 mL, 8.35 mmol) under argon. To this solution was added half of a solution of **7** [prepared from **8** (1.27 g, 2.5 mmol) in CH_2Cl_2 (6 mL)] at −10 to

−15° with stirring, under argon. Then, the mixture was stirred for 3 h at 20°, the rest of the solution of **7** in CH_2Cl_2 was added at −10 to −15°, and the mixture was stirred for a further 2 days. The usual processing gave an oily product (2.657 g) which was chromatographed on SiO_2 (220 g) with 10:1 toluene–THF, to afford **29** (771.3 mg, 60.0%), $[\alpha]_D$ +31.0° (*c* 0.49); R_F 0.27 in 10:1 toluene–THF; δ_H: 3.20 (s, 3 H, OMe); δ_C: 54.4 (OMe), 98.0 ($^1J_{CH}$ 170.6 Hz, C-1a), 98.2 ($^1J_{CH}$ 170.6 Hz, C-1e), 99.0 ($^1J_{CH}$ 173.5 Hz, C-1b,1c), and 99.5 ($^1J_{CH}$ 170.6 Hz, C-1d,1f).

Anal. Calc. for $C_{155}H_{166}O_{34}$: C, 72.35; H, 6.50. Found: C, 71.95; H, 6.64.

*Methyl 2,4-di-*O*-benzyl-3-*O*-[2,4-di-*O*-benzyl-3,6-di-*O*-(3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranosyl]-6-*O*-[3,4,6-tri-*O*-benzyl-2-*O*-(3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranosyl]-α-*D*-mannopyranoside* (**30**). — A solution of **29** (560.8 mg, 0.22 mmol) in MeOH (25 mL)–THF (10 mL)–2M NaOMe in MeOH (0.1 mL) was stirred for 16 h at 20°. The usual processing afforded an oily product (526 mg) which was chromatographed on SiO_2 (60 g) with 30:1 CH_2Cl_2–THF, to give **30** (441 mg, 82.1%), $[\alpha]_D$ +59.6° (*c* 0.28); R_F 0.31 in 30:1 CH_2Cl_2–THF; δ_H: 3.17 (s, 3 H, OMe), 4.99 5.11, 5.19, and 5.24 (bs, 1 H, anomeric protons); δ_C: 55.5 (OMe), 98.0 ($^1J_{CH}$ 164.7 Hz, C-1a), 99.1 ($^1J_{CH}$ 169.1 Hz, C-1b,1c), 99.8 ($^1J_{CH}$ 170.6 Hz, C-1e), 101.1 ($^1J_{CH}$ 172.1 Hz, C-1d), and 101.3 ($^1J_{CH}$ 172.1 Hz, C-1f).

Anal. Calc. for $C_{149}H_{160}O_{31}$: C, 73.14; H, 6.59. Found: C, 72.45; H, 6.67.

*Methyl 3-*O*-(3,6-di-*O*-α-*D*-mannopyranosyl-α-*D*-mannopyranosyl)-6-*O*-(2-*O*-α-*D*-mannopyranosyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranoside* (**4**). — A mixture of **30** (341 mg, 138 μmol) and 10% Pd–C (400 mg) in EtOH (30 mL)–H_2O (6 mL) was stirred under H_2 for 16 h at 20° and then for 3 h at 50°. The usual processing gave **4** as an amorphous material (136 mg, 95.8%), $[\alpha]_D$ +102.1° (*c* 0.28, H_2O); R_F 0.13 in 2:1:1 1-BuOH–EtOH–H_2O; δ_H (D_2O, 60°): 4.70 (d, 1 H, *J* 2 Hz, H-1a), 4.86 (d, 1 H, *J* 2 Hz, H-1e), 5.00 (d, 1 H, *J* 2 Hz, H-1d), 5.04 (d, 1 H, *J* 2 Hz, H-1f), and 5.09 (bs, 2 H, H-1b,1c); δ_C (D_2O): 55.3 (OMe), 78.6, 78.9, and 79.1 (C-3a,3c,2b), 98.2 ($^1J_{CH}$ 171.9 Hz, C-1b), 99.9 ($^1J_{CH}$ 170.9 Hz, C-1e), 101.3 ($^1J_{CH}$ 169.9 Hz, C-1a), and 102.7 ($^1J_{CH}$ 169.9 Hz, C-1c,1d,1f).

Anal. Calc. for $C_{37}H_{64}O_{31} \cdot 1.5\ H_2O$: C, 43.06; H, 6.55. Found: C, 43.02; H, 6.56.

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REFERENCES

1 T. Ogawa and K. Sasajima, *Tetrahedron*, in press.
2 H. Lis, N. Sharon, and E. Katchalski, *Biochim. Biophys. Acta*, 83 (1964) 376–378.
3 H. Lis and N. Sharon, *J. Biol. Chem.*, 253 (1978) 3468–3476; N. Sharon and H. Lis, *Biochem. Rev.*, 7 (1979) 783–799.

4 S. ITO, K. YAMASHITA, R. G. SPIRO, AND A. KOBATA, *J. Biochem. (Tokyo)*, 81 (1977) 1621–1631.
5 E. LI AND S. KORNFELD, *J. Biol. Chem.*, 254 (1979) 1600–1605.
6 A. CHAPMAN AND R. KORNFELD, *J. Biol. Chem.*, 254 (1979) 816–828.
7 T. OGAWA AND M. MATSUI, *Carbohydr. Res.*, 62 (1978) c1–c4.
8 T. OGAWA, K. KATANO, K. SASAJIMA, AND M. MATSUI, *Tetrahedron*, in press; T. OGAWA, K. KATANO, AND M. MATSUI, *Carbohydr. Res.*, 64 (1978) c3–c9.
9 S. HANESSIAN AND J. BANOUB, *Carbohydr. Res.*, 53 (1977) c13–c16; *ACS Symp. Ser.*, 39 (1976) 36–63.
10 K. BOCK, I. LUNDT, AND C. PEDERSEN, *Tetrahedron Lett.*, (1973) 1037–1040; K. BOCK AND C. PEDERSEN, *J. Chem. Soc., Perkin Trans. 2*, (1974) 293–297; *Acta Chem. Scand. Ser. B*, 29 (1975) 258–264.
11 L. RADICS, M. KAJTAR-PEREDY, S. CORSANO, AND L. STANDOLI, *Tetrahedron Lett.*, (1975) 4287–4290; K. TORI, T. HIRATA, O. KOSHITANI, AND T. SUGA, *ibid.*, (1976) 1311–1314; K. YAMASAKI, H. KOHDA, T. KOBAYASHI, R. KASAI, AND O. TANAKA, *ibid.*, (1976) 1005–1008; K. TORI, S. SEO, Y. YOSHIMURA, M. NAKAMURA, Y. TOMITA, AND H. ISHII, *ibid.*, (1976) 4167–4170.
12 E. E. LEE AND J. O. WOOD, *Carbohydr. Res.*, 75 (1979) 322–324.