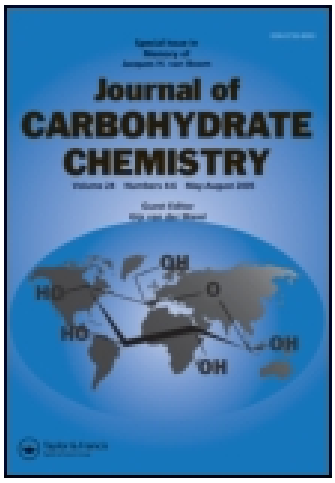

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SYNTHESIS OF A MANNOTETRAOSE—THE REPEATING UNIT OF THE CELL-WALL MANNANS OF MICROSPORUM GYPSEUM AND RELATED SPECIES OF TRYCHOPHYTON

Linsen Heng [a] , Jun Ning [a] & Fanzuo Kong [a]
[a] Research Center for Eco-Environmental Science, Academia Sinica , P.O. Box 2871, Beijing, 100085, China
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SYNTHESIS OF A MANNOTETRAOSE—THE REPEATING UNIT OF THE CELL-WALL MANNANS OF *MICROSPORUM GYPSEUM* AND RELATED SPECIES OF *TRYCHOPHYTON*

Linsen Heng, Jun Ning, and Fanzuo Kong

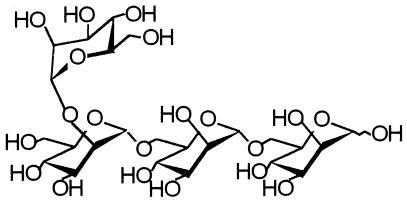
Research Center for Eco-Environmental Science, Academia Sinica.
P.O. Box 2871, Beijing 100085, China

ABSTRACT

A tetrasaccharide, α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-D-mannopyranose (**1**), the repeating unit of the cell-wall mannans of *Microsporum gypseum* and related species of *Trychophyton,* was synthesized using 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (**5**) and 2-*O*-acetyl-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (**13**) as the glycosyl donors in "the inverse Schmidt" procedure.

INTRODUCTION

Dermatophytes are a group of fungi which parasitise man and animals, and cause superficial cutaneous infections involving primarily the keratinised tissues of the epidermis, nails, and pilosebaceous follicles. The cell wall of dermatophytes is made up of chitin, a water-insoluble β-(1→3)-glucan, and water-soluble polysaccharides which are antigenically relevant. In many ascoycetous yeasts,[1] the antigenically relevant outer polysaccharides have a skeleton composed of α-(1→6)-linked mannopyranosyl residues, to most of which are attached one branching moiety, each composed of chains of various lengths containing mainly α-, β(or both)-(1→2) and/or −(1→3) links (the so-called comb-like structure, as for instance, in *Candida maltosa* and *C. Tropicalis*[2]). A more complex structure (a tree-like structure) has been reported for *C. Albicans*,[3,4] which shows an analogous backbone of α-(1→6)-linked mannopyranosyl residues with (1→2) and/or (1→3) side



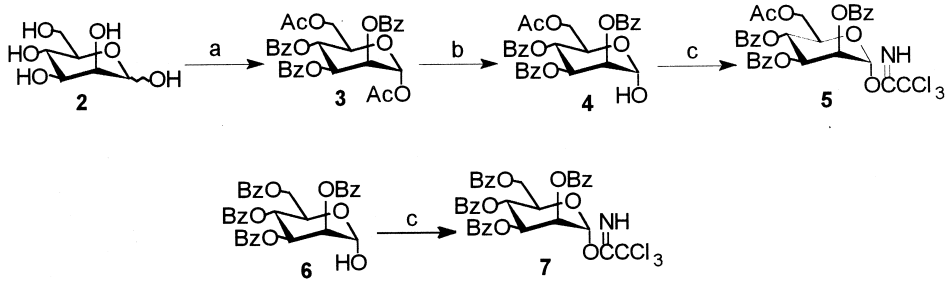
1

chains, some of which are branched. A third type of sequence has been proposed for the *C. Krusei* mannan,[5] which contains a main chain of mannopyranose with (1→2) and (1→6) linkages in a 3:1 ratio but is lightly branched, either at the 2- or 6-positions.

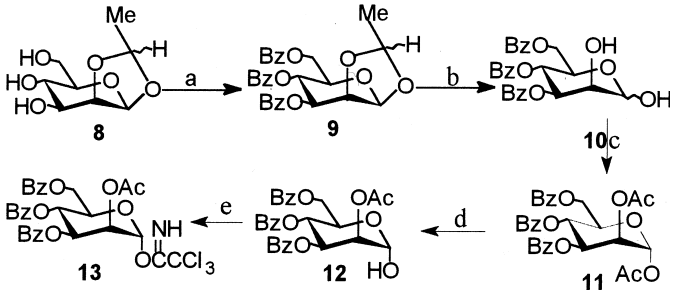
In 1995, Jiménez-Barbero et al.[6] investigated the structures of cell-wall mannans isolated from *Microsporum gypseum* and related species of *Trychophyton* and found that all of them consist of an α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-D-mannopyranose repeating tetrasaccharide. Syntheses of the fragments of polysaccharides are important for elucidation of biological functions of polysaccharides. In this paper, as a part of our continuous synthetic approach directed toward epitopes of fungal cell-wall mannans, we report the synthesis of a tetrasaccharide 1, the repeating unit of mannans isolated from *Microsporum gypseum* and related species of *Trychophyton*.

RESULTS AND DISCUSSION

Tritylation of mannose (**2**) followed by benzoylation in a one-pot manner gave the 1,2,3,4-tetra-*O*-benzoyl-6-*O*-trityl-D-mannopyranose, selective acetolysis of which using CH_2Cl_2-AcOH-Ac_2O-H_2SO_4 in a ratio of 1:1:0.6:0.175 afforded the corresponding 1,6-diacetate **3** in 71.3% yield (for three steps). The diacetate **3** was selectively deacetylated at the anomeric position with benzylamine in THF in high yield to give the corresponding 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-D-mannopyranose (**4**). Subsequent reaction of **4** with CCl_3CN/DBU in dichloromethane afforded the glycosyl donor **5**. A similar procedure gave another glycosyl donor **7** (Scheme 1).



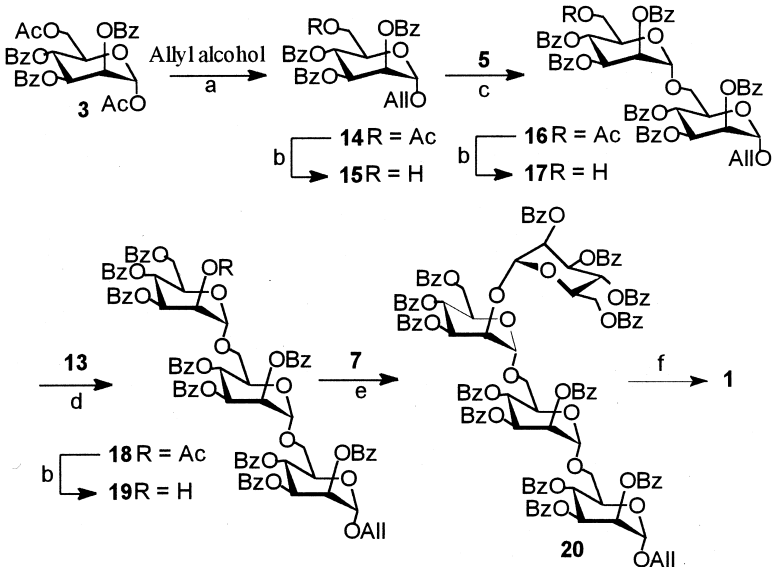
Scheme 1. Reagents and conditions: (a) i.trityl chloride (1.2 equiv), pyridine, 50°C, 32 h; ii. PhCOCl (4.8 equiv), <40°C, 24 h; iii.CH_2Cl_2/HOAc/Ac_2O/H_2SO_4 = 1/1/0.6/0.175 (v/v), rt, 20 h, 71.3% (for three steps); (b) benzylamine (3.2 equiv), THF, rt, 24 h, 86.2%.(c) CCl_3CN (2.3–3.2 equiv), DBU (0.18–0.23 equiv), rt, 5 h, 88.1%–85.6%.



Scheme 2. Reagents and conditions: (a) PhCOCl (3.3 equiv), pyridine, <40°C, 24 h, 94.8%; (b) F_3CCOOH (90%), rt, 4 h, 89.0%; (c) $(Ac)_2O$, pyridine, rt, 5 h, 100%; (d) benzylamine (4.0 equiv), THF, rt, 24 h, 88.4%.(e) CCl_3CN (3.3 equiv), DBU (0.3 equiv), rt, 5 h, 86.3%.

Benzoylation of 1,2-*O*-ethylidene-β-D-mannopyranose[7] (**8**) followed by hydrolysis with 90% CF_3COOH afforded the 3,4,6-tri-*O*-benzoyl-D-mannopyranose (**10**), subsequent acetylation with acetic anhydride in pyridine furnished the diacetate **11**. Selective removal of the 1-*O*-acetyl group with benzylamine in THF (→**12**), and then treatment with CCl_3CN/DBU in dichloromethane afforded the glycosyl donor **13**. (Scheme 2).

As shown in Scheme 3, allyl 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (**14**) was prepared by the Helferich reaction using **3** as the glycosyl donor and allyl alcohol as the acceptor.[8] Selective removal of the acetyl group of **14** in



Scheme 3. Reagents and conditions: (a) Allyl alcohol (2 equiv.), TMSOTf (0.26 equiv), CH_2Cl_2, rt, 3 h, 88%. (b) methanol/0.5% HCl, rt, 12–14 h, 93%–96%. (c) **5** (1.4 equiv), CH_2Cl_2, TMSOTf (0.08 equiv), rt, 3 h, 86.5%. (d) **13** (1.4 equiv), CH_2Cl_2, TMSOTf (0.16 equiv), rt, 3 h, 85.7%. (e) **7** (5 equiv), CH_2Cl_2, TMSOTf (0.3 equiv), rt, 3 h, 80.4%. (f) i. $PdCl_2$, CH_3OH, rt, 4 h; ii. CH_3OH satd with dry NH_3, rt, 72 h, 70.2% (two steps).

methanol solution containing 0.5% HCl gave the glycosyl acceptor **15** in a high yield. The disaccharide **16** was prepared using the "inverse Schmidt" strategy.[9] Thus the glycosyl acceptor **15** and the catalyst TMSOTf were mixed first in dry CH_2Cl_2, and after stirring for 15 min, the glycosyl donor **5** in dry dichloromethane was added dropwise within 30 min in order to give **16** in a high yield. Selective removal of the acetyl group of **16** gave the glycosyl acceptor **17**, "inverse Schmidt" coupling of which with 2-*O*-acetyl-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (**13**) afforded the trisaccharide **18** in 85.7% yield. The ^{1}H NMR spectrum of **18** showed one acetyl signal (δ 2.14), one allyl signal, both signals characteristic of the structure of the trisaccharide **18**. Selective removal of the 2-*O*-acetyl group of the trisaccharide **18** gave the glycosyl accepter **19**. The fully protected tetrasaccharide **20** was smoothly obtained using the "inverse Schmidt" method, again by coupling with 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (**7**). Deprotection of **20** using $PdCl_2$ in CH_3OH,[10] followed by treatment with NH_3 in CH_3OH, gave the title mannotetraose **1**. The bioassay of **1** is in process.

EXPERIMENTAL

General Methods. Optical rotations were determined at 25°C with a Perkin-Elmer Model 241-Mc automatic polarimeter. Melting points were determined with a "Mel-Temp" apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker ARX 400 spectrometers for solutions in $CDCl_3$. Chemical shifts are given in parts per million (ppm) downfield from internal Me_4Si. Mass spectra were recorded with a JMS-D300S mass spectrometer using a direct sample introduction technique. Thin-layer chromatography (TLC) was performed on Silica Gel HF_{254} with detection by charring with 30% (v/v) H_2SO_4 in MeOH or in some cases by UV detection. Column chromatography was conducted by elution of a column (16 × 240, 18 × 300, 35 × 400 mm) of silica gel (100–200 mesh) with EtOAc - petroleum ether (60–90°C) as the eluent. Solutions were concentrated at < 60°C under diminished pressure.

1,6-Di-*O*-acetyl-2,3,4-tri-*O*-benzoyl-α-D-mannopyranose (3). A solution of mannose **2** (15 g, 83.3 mmol) and trityl chloride (28 g, 100.5 mmol) in pyridine (100 mL) was stirred at 50°C for 32 h, at the end of which time TLC (4:1 EtOAc-methanol) indicated that the reaction was complete. The reaction mixture was cooled to 0°C, and then benzoyl chloride (46.5 mL, 400.9 mmol) was added dropwise for 30 min to keep the reaction temperature under 40°C. After 24 h, water (300 mL) was added to the reaction mixture, and stirring was continued for 30 min. The aq solution was extracted with CH_2Cl_2 (3 × 100 mL), the extract was washed with HCl (1 N) and saturated aqueous sodium bicarbonate, dried (Na_2SO_4) and concentrated to dryness. The residue without separation was dissolved in CH_2Cl_2 (50 mL), Ac_2O (50 mL) and AcOH (30 mL), the solution cooled to 10°C in an ice bath, and H_2SO_4 (8.8 mL) added dropwise over 20 min. After the addition

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was complete, the ice bath was removed and the reaction was continued for 20 h at ambient temperature. The reaction solution was poured into ice water (400 mL), stirring was continued for an additional 15 min, and the aqueous solution was extracted with chloroform (3 × 100 mL). The combined chloroform extracts were carefully washed with 10% aq $NaHCO_3$ (3 × 60 mL), dried over Na_2SO_4, and concentrated to a syrup which was subjected to column chromatography with 4:1 petroleum ether-EtOAc as the eluent. Compound **3** was obtained as a syrup (34.2 g, 71.3%); $[\alpha]_D$ + 9.5° (*c* 1.0, $CHCI_3$); ^{1}H NMR (400 MHz, $CDCI_3$): δ 8.11–7.28 (m, 15 H, 3 Ph*H*), 6.36 (d, 1 H, $J_{1,2}$ = 2.0 Hz, H-1), 6.01 (t, 1 H, $J_{3,4} = J_{4,5}$ = 10.2 Hz, H-4), 5.88 (dd, 1 H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 10.2 Hz, H-3), 5.70 (dd, 1 H, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.2 Hz, H-2), 4.34 (m, 2 H, H-5, 6a), 4.27 (dd, 1 H, $J_{6a,6b}$ = 13.4 Hz, $J_{5,6b}$ = 4.2 Hz, H-6b), 2.28, 2.08 (2 s, 6 H, 2COC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): 170.0, 167.7 (2 C, 2 *C*OCH_3), 165.1, 165.0, 164.6 (3 C, 3 *C*OPh), 133.3–127.8 (Ph), 90.2 (C-1), 70.2, 69.3, 68.8, 65.9 (4 C, C-2, 3, 4, 5), 62.0 (C-6), 20.4, 20.1 (2 C, 2 *C*OCH_3).

Anal. Calcd for $C_{31}H_{28}O_{11}$: C, 64.58; H, 4.89. Found: C, 64.67; H, 4.94.

6-*O*-Acetyl-2,3,4-tri-*O*-benzoyl-α-D-mannopyranose (4). A solution of compound **3** (5 g, 8.67 mmol) and benzylamine (3 mL, 27.4 mmol) in anhydrous THF (30 mL) was stirred at room temperature for 24 h, at the end of which time TLC (3:1 petroleum ether-EtOAc) indicated that the reaction was complete. The solution was concentrated. Purification by flash column chromatography on silica gel (3:1 petroleum ether-EtOAc) gave compound **4** as a syrup (4.0 g, 86.2%); $[\alpha]_D$ + 16.8° (*c* 1.0, $CHCI_3$); ^{1}H NMR (400 MHz, $CDCI_3$): δ 8.11–7.27 (m, 15 H, 3 Ph*H*), 5.98 (m, 2 H, H-3, 4), 5.71 (dd, 1 H, $J_{1,2}$ = 1.6Hz, $J_{2,3}$ = 2.4 Hz, H-2), 5.53 (d, 1 H, $J_{1,2}$ = 1.6 Hz, H-), 4.55 (m, 1 H, H-5), 4.33 (m, 2 H, H-6a, 6b), 2.09(s, 3 H,COC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) ; 170.6 (*C*OCH_3), 166.1, 165.2, 165.2 (3 C, 3 *C*OPh), 133.1–127.9 (Ph), 91.7 (C-1), 70.6, 69.4, 68.0, 66.5 (4 C, C-2, 3, 4, 5), 62.4 (C-6), 20.3 (*C*OCH_3).

Anal. Calcd for $C_{29}H_{26}O_{10}$: C, 65.17; H, 4.90. Found: C, 65.42; H, 4.94.

6-*O*-Acetyl-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (5). A mixture of **4** (4.0 g, 7.48 mmol), trichloroacetonitrile (2.1 mL, 20.9 mmol), and 1,8-diazabicyclo[5.4.0]undecene (DBU) (0.25 mL, 1.67 mmol) in dry dichloromethane (25mL) was stirred under nitrogen for 5 h and then concentrated *in vacuo*. The residue was purified by flash chromatography (4:1 petroleum ether-EtOAc) to give **5** (4.47 g, 88.1%) as crystals; mp 88–91°C; $[\alpha]_D$ + 20.3° (*c* 1.0, $CHCI_3$); ^{1}H NMR (400 MHz, $CDCI_3$): δ 8.87 (s, 1 H, OC(N*H*)CCI_3), 8.12–7.27 (m, 15 H, 3 Ph*H*), 6.55 (d, 1 H, $J_{1,2}$ = 2.0 Hz, H-1), 6.06 (t, 1 H, $J_{3,4} = J_{4,5}$ = 10.0 Hz, H-4), 5.93 (dd, 1 H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 10.0 Hz, H-3), 5.90 (dd, 1 H, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.2 Hz, H-2), 4.49 (m, 1 H, H-5), 4.34 (m, 2 H, H-6a, 6b), 2.07 (s, 3 H, COC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): 170.0 (*C*OCH_3), 165.0, 164.6, 159.4 (4 C, 3 *C*OPh, *C*(NH)CCl_3), 133.3–127.9 (Ph), 94.1 (C-1), 90.1 (*C*Cl_3), 70.8, 69.2, 68.3, 65.7 (4 C, C-2, 3, 4, 5), 61.9 (C-6), 20.1 (*CO**C*H$_3$).

Anal. Calcd for $C_{31}H_{26}NO_{10}CI_3$: C, 54.84; H, 3.86. Found: C, 54.72; H, 3.90.

2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (7). A mixture of 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranose **(6)**[11] (3.5 g, 5.87 mmol), trichloroacetonitrile (1.9 mL, 18.9 mmol), and 1,8-diazabicyclo[5.4.0]undecene (DBU) (0.20 mL, 1.34 mmol) in dry dichloromethane (30 mL) was stirred under nitrogen for 5 h and then concentrated *in vacuo*. The residue was purified by flash chromatography (4:1 petroleum ether-EtOAc) to give **7** (3.72 g, 85.6%) as crystals; mp 132–134°C; $[\alpha]_D$ +48.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (s, 1 H, OC(N*H*)CCl_3), 8.10–7.26 (m, 20 H, 4 Ph*H*), 6.57 (d, 1 H, $J_{1,2}$ = 1.3 Hz, H-1), 6.23 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 10.0 Hz, H-4), 5.99–5.94 (, 2 H, H-2, 3), 4.72 (dd, 1 H, $J_{5,6a}$ = 2.4 Hz, $J_{6b,6a}$ =12.3 Hz, H-6b), 4.62 (m, 1 H, H-5), 4.50 (dd, 1 H, $J_{5,6b}$ = 4.0 Hz, $J_{6b,6a}$ = 12.3 Hz, H-6b); ^{13}C NMR (100 MHz, $CDCl_3$), 165.5, 165.0, 164.9, 164.6 (4 C, 4 *C*OPh), 159.0 (*C*(NH)CCl_3), 133.2–127.9 (Ph), 94.2 (C-1), 71.1, 69.4, 68.4, 65.6 (4 C, C-2, 3, 4, 5), 61.95 (C-6).

Anal. Calcd for $C_{36}H_{28}NO_{10}CI_3$: C, 58.35; H, 3.81. Found: C, 58.44; H, 3.76.

3,4,6-Tri-*O*-benzoyl-1,2-*O*-(*S*-ethylidene)-β-D-mannopyranose (9). 1,2-*O*-(*S*-ethylidene)-β-D-mannopyranose (**8**)[7] (6.4 g, 31.1 mmol) in pyridine (30 ml) was cooled to 0°C, and then benzoyl chloride (11.9 mL, 102.5mmol) was added dropwise for 30 min to keep the reaction temperature under 40°C. After 24 h, water (300 mL) was added to the reaction mixture, and stirring was continued for 30 min. The aq solution was extracted with CH_2Cl_2 (3 × 100 mL), the extract was washed with HCl (1 N) and then saturated sodium bicarbonate, dried (Na_2SO_4) and concentrated to dryness. The residue was purified by flash chromatography (4:1 petroleum ether-EtOAc) to give **9** (15.3 g, 94.8%) as crystals; mp 123–125°C; $[\alpha]_D$ + 25.9° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400MHz, $CDCl_3$): δ 8.04–7.25 (m, 15 H, 3 Ph*H*), 6.01 (t, 1 H, $J_{3,4}$ = $J_{5,4}$ = 10.2 Hz, H-4), 5.80 (dd, 1 H, $J_{3,2}$ = 3.6 Hz, $J_{4,3}$ =10.2 Hz, H-3), 5.51 (dd, 1 H, $J_{1,2}$ = 2.0 Hz, $J_{3,2}$ = 3.6 Hz, H-2), 5.45 (q, 1 H, J = 5.0 Hz, CH_3CH), 5.36 (d, 1 H, $J_{2,1}$ = 2.0 Hz, H-1), 4.70 (m, 1 H, H-5), 4.50–4.44 (m, 2 H, H-6, 6′), 1.57 (d, 3 H, J = 5.0 Hz, CH_3CH); ^{13}C NMR (100 MHz, $CDCl_3$), 165.7, 165.5, 164.8 (3 C, 3 *C*OPh), 133.0–127.8 (Ph), 104.4 (*C*HCH_3), 96.3 (C-1), 77.06, 71.4, 71.0, 66.3 (4 C, C-2, 3, 4, 5), 62.9 (C-6), 21.1 (CH*C*H_3).

Anal. Calcd for $C_{29}H_{26}O_9$: C, 67.18; H, 5.05. Found: C, 67.33; H, 5.00.

3,4,6-Tri-*O*-benzoyl-D-mannopyranose (10). A solution of compound **9** (7.2 g, 13.9 mmol) in 90% F_3CCOOH (30 mL) was stirred at room temperature for 4 h, at the end of which time TLC (1:1 petroleum ether-EtOAc) indicated that the reaction was complete. The reaction mixture was diluted with toluene (50 mL) and then concentrated to dryness. Purification by flash column chromatography on silica gel (3:1 petroleum ether-EtOAc) gave compound **10** as a crystalline mixture of α and β forms in a ratio of 2:1 (6.1 g, 89.0%); mp 99–101°C; $[\alpha]_D$ + 40.8° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.27 (m, 15 H, 3 Ph*H*), 6.00 (t, 0.66 H, $J_{3,4}$ = $J_{5,4}$ = 9.8 Hz, H-4 of α anomer), 5.92 (t, 0.34 H, $J_{3,4}$ = $J_{5,4}$ = 9.9 Hz, H-4 of β anomer), 5.76 (dd, 0.66 H, $J_{3,2}$ = 3.2 Hz, $J_{4,3}$ = 9.8 Hz, H-2 of α anomer), 5.44 (dd, 0.34 H, $J_{3,2}$ = 3.1 Hz, $J_{4,3}$ =9.7 Hz, H-2 of β anomer), 5.43 (d, 0.66 H, $J_{2,1}$ = 1.0 Hz, H-1 of α anomer), 5.1 (d, 0.34 H, $J_{2,1}$ = 1.1 Hz, H-1 of β anomer),

4.67–4.37 (m, 4 H, H-2, 5, 6, 6′); ^{13}C NMR (100 MHz, $CDCl_3$): 166.1, 165.5, 165.3 (3 C, 3 *C*OPh), 133.3–127.9 (Ph), 94.0, (C-1), 72.2, 69.2, 68.0, 66.5 (4 C, C-2, 3, 4, 5), 63.2 (C- 6).

Anal. Calcd for $C_{27}H_{24}O_9$: C, 65.85; H, 4.91. Found: C, 66.02; H, 4.95.

1,2-Di-*O*-acetyl-3,4,6-tri-*O*-benzoyl-α-D-mannopyranose (**11**). Acetylation of **10** (3 g, 6.1 mmol) with acetic anhydride (8 mL) in pyridine (10 mL) at room temperature for 4 h gave compound **11** in a quantitative yield as crystals; mp 115–117°C; $[\alpha]_D$ + 35.9° (*c* 1.0, $CHCI_3$); ^{1}H NMR (400MHz, $CDCI_3$): δ 8.05–7.27 (m, 15 H, 3 Ph*H*), 6.24 (d, 1 H, $J_{2,1}$ = 2.0 Hz, H-1), 6.01 (t, 1 H, $J_{3,4} = J_{5,4}$ = 10 Hz, H-4), 5.80 (dd, 1 H, $J_{3,2}$ = 3.6 Hz, $J_{4,3}$ = 10.2 Hz, H-3), 5.51 (dd, 1 H, $J_{1,2}$ = 2.0 Hz, $J_{3,2}$ = 3.6 Hz, H-2), 4.63 (m, 1 H, H-5), 4.49–4.43 (m, 2 H, H-6,6′), 2.26, 2.18 (2 s, 6 H, 2 *C*OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): 169.5, 168.2 (2C, 2 *C*OCH_3), 166.0, 165.6, 165.3 (3C, 3 *C*OPh), 133.6–128.3 (Ph), 90.6 (C-1), 70.8, 69.5, 68.7, 66.4 (4 C, C-2, 3, 4, 5), 62.8 (C-6), 21.0, 20.7 (2 C, 2 CO*C*H_3).

Anal. Calcd for $C_{31}H_{28}O_{11}$: C, 64.58; H, 4.89. Found: C, 64.70; H, 4.93.

2-*O*-Acetyl-3,4,6-tri-*O*-benzoyl-α-D-mannopyranose (**12**). A solution of compound **11** (8 g, 13.8 mmol) and benzylamine (6 mL, 54.9 mmol) in anhydrous THF (50 mL) was stirred at room temperature for 24 h, at the end of which time TLC (3:1 petroleum ether-EtOAc) indicated that the reaction was complete. The solution was concentrated. Purification by flash column chromatography on silica gel (3:1 petroleum ether-EtOAc) gave compound **12** as crystals (6.56g, 88.4%); mp 89–91°C; $[\alpha]_D$ + 39.8° (*c* 1.0, $CHCI_3$); ^{1}H NMR (400 MHz, $CDCI_3$): δ 8.07–7.34 (m, 15 H, 3 Ph*H*), 5.96 (t, 1 H, $J_{3,4} = J_{5,4}$ = 10 Hz, H-4), 5.87 (dd, 1 H, $J_{3,2}$ = 3.2 Hz, $J_{4,3}$ = 10.0 Hz, H-3), 5.50 (dd, 1 H, $J_{1,2}$ = 2.0 Hz, $J_{3,2}$ = 3.2 Hz, H-2), 5.37 (d, 1 H, $J_{2,1}$ = 2.0 Hz, H-1), 4.66 (dd, 1 H, $J_{6',6}$ = 12.0 Hz, $J_{5,6}$ = 2.8 Hz, H-6), 4.60 (m, 1 H, H-5), 4.44 (dd, 1 H, $J_{6,6'}$ = 12.0 Hz, $J_{5,6'}$ = 4.4 Hz, H-6), 2.18 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$), 169.6 (*C*OCH_3), 165.9, 165.1 (3 C, 3 *C*OPh), 132.9–127.9 (Ph), 91.7 (C-1), 70.0, 69.1, 68.4, 66.6 (4 C, C-2, 3, 4, 5), 62.7 (C-6), 20.3 (CO*C*H_3).

Anal. Calcd for $C_{29}H_{26}O_{10}$: C, 65.17; H, 4.90. Found: C, 65.02; H, 4.85.

2-*O*-Acetyl-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl trichloroacetimidate (13). A mixture of **12** (4.9 g, 9.17 mmol), trichloroacetonitrile (3.0 mL, 30.0 mmol), and 1,8-diazabicyclo[5.4.0]undecene (DBU) (0.40 mL, 2.7 mmol) in dry dichloromethane (40 mL) was stirred under nitrogen for 5 h and then concentrated *in vacuo*. The residue was purified by flash chromatography (4:1 petroleum ether-EtOAc) to give **13** (5.37 g, 86.3%) as crystals; mp 87–90°C; $[\alpha]_D$ + 36.7° (*c* 1.0, $CHCI_3$); ^{1}H NMR (400 MHz, $CDCI_3$): δ 8.82 (s, 1 H, OC(N*H*)CCI_3), 8.04–7.36 (m, 15 H, 3 Ph*H*), 6.42 (d, 1 H, $J_{1,2}$ = 2.0 Hz, H-1), 6.03 (t, 1 H, $J_{3,4} = J_{4,5}$ = 10.0 Hz, H-4), 5.85 (dd, 1 H, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 10.0 Hz, H-3), 5.71 (dd, 1 H, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.4 Hz, H-2), 4.64 (dd, 1 H, $J_{6,6'}$ = 12.8 Hz, $J_{5,6}$ = 7.0 Hz, H-6), 4.56 (m, 1 H, H-5),4.46 (dd, 1 H, $J_{6',6}$ = 12.8 Hz, $J_{5,6'}$ = 2.8 Hz, H-6′), 2.17 (s, 3H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$), 169.5 (*C*OCH_3), 165.9, 165.1, 165.0,

164.9(4 C, 3 *C*OPh, *C*(NH)CCl_3), 133.2–127.9 (Ph), 95.7 (C-1), 91.7 (C(NH)*C*Cl_3), 69.9, 69.1, 68.4, 66.6 (4 C, C-2, 3, 4, 5), 62.7 (C-6), 20.3 (CO*C*H_3).

Anal. Calcd for $C_{31}H_{26}NO_{10}CI_3$: C, 54.84; H, 3.86. Found: C, 54.69; H, 3.98.

Allyl 6-*O*-Acetyl-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (14). A solution of **3** (2.5 g, 4.3 mmol) and allyl alcohol (0.6 mL, 8.8 mmol) in dry dichloromethane (40 mL) was stirred with dried molecular sieves (4 A, 1 g) under nitrogen for 15 min, and then TMSOTf (0.2 mL, 1.1 mmol) was added dropwise. After 1 h the reaction mixture was diluted with dichloromethane (50 mL) and washed with a satd sodium hydrogen carbonate solution (15 mL). The organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. Purification of the residue by flash chromatography (3:1 petroleum ether-EtOAc) gave **14** as a syrup (2.19 g, 88%); $[\alpha]_D$ + 15.9° (*c* 1.0, $CHCI_3$); ^{1}H NMR (400MHz, $CDCI_3$): δ 8.11–7.26 (m, 15 H, 3 Ph*H*), 6.12–5.91 (m, 3 H, H-3, 4,CH_2CH=CH_2), 5.68 (dd, $J_{1,2}$ = 2.0 Hz, $J_{3,2}$ = 2.8 Hz, H-2), 5.40 (dd, 1 H, ^{2}J = 1.6Hz, $^3J_{trans}$ = 17.2 Hz, CH_2CH=CH_2), 5.30 (dd, 1 H, ^{2}J = 1.6 Hz, $^3J_{cis}$ =10.4 Hz, CH_2CH=CH_2), 5.14 (d, $J_{1,2}$ = 2.0 Hz, H-1), 4.47–4.27 (m, 4 H, H-6, 6′, C*H*$_2$CH=CH_2), 4.17 (m, 1 H, H-5), 2.10 (s, 3 H,COC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$), 170.1 (*C*OCH_3), 165.7, 165.6, 165.5 (3 C,3 *C*OPh), 133.7–128.4 (Ph, CH_2CH=CH_2), 118.7 (CH_2CH=CH_2), 96.7 (C-1), 70.5, 70.0, 69.0, 68.7, 66.9 (5 C, C-2, 3, 4, 5, *C*H_2CH=CH_2), 62.8 (C-6), 20.8 (CO*C*H_3).

Anal. Calcd for $C_{32}H_{30}O_{10}$: C, 66.89; H, 5.26. Found: C, 66.93; H, 5.31.

Allyl 2,3,4-Tri-*O*-benzoyl-α-D-mannopyranoside (15). A solution of **14** (1.6 g, 2.8 mmol) in methanol solution (80 mL) containing 0.5 % HCl was stirred at room temperature for 12 h, at the end of which time TLC (2:1 petroleum ether-EtOAc) indicated that the starting material had disappeared. The mixture was carefully neutralized with triethylamine, and then concentrated to dryness. The residue was partitioned between water and CH_2Cl_2, then the organic layer dried over Na_2SO_4, and concentrated to a syrup. Purification of the residue by flash chromatography (2:1 petroleum ether-EtOAc) gave **15** as a syrup (1.42 g, 96%); $[\alpha]_D$ + 14.2° (*c* 1.0, $CHCI_3$); ^{1}H NMR (400MHz, $CDCI_3$): δ 8.12–7.24 (m, 15 H,3 Ph*H*), 6.03–5.98 (m, 2 H, H-3, CH_2CH=CH_2), 5.85 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 10.0 Hz, H-4), 5.69 (dd, $J_{1,2}$ = 1.6Hz, $J_{2,3}$ = 3.2Hz, H-2), 5.40 (dd, 1 H, ^{2}J = 1.6 Hz, $^3J_{trans}$ = 17.2 Hz, CH_2CH=CH_2), 5.29 (dd, 1 H, ^{2}J = 1.6Hz, $^3J_{cis}$ = 10.4 Hz, CH_2CH=CH_2), 5.16 (d, $J_{1,2}$ = 1.6 Hz, H-1), 4.34–4.16 (m, 2 H, C*H*$_2$CH=CH_2), 4.11 (m, 1 H, H-5), 3.83–3.79 (m, 2 H, H-6,6′); ^{13}C NMR (100 MHz, $CDCl_3$). 166.6, 165.6, 165.5 (3 C, 3 *C*OPh), 133.7–128.3 (Ph, CH_2CH=CH_2), 118.5 (Ph, CH_2CH=CH_2), 96.8 (C-1), 71.0, 70.7, 69.6, 68.8, 67.3 (5 C, C-2, 3, 4, 5, *C*H_2CH=CH_2), 61.3 (C-6).

Anal. Calcd for $C_{30}H_{28}O_9$: C, 67.66; H, 5.30. Found: C, 67.83; H, 5.37. .

Allyl 6-*O*-Acetyl-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (16). A solution of **15** (0.37 g, 0.69 mmol) and TMSOTf (10 μL, 0.055mmol) in dry dichloromethane (6 mL) was stirred with

dried molecular sieves (4 A, 0.4 g) under nitrogen for 15 min, and then **5** (0.66 g, 0.97 mmol) in dichloromethane (4 mL) was added dropwise for 20 min. After 3 h the reaction mixture was diluted with dichloromethane (30 mL) and washed with satd sodium hydrogen carbonate solution (5 mL). The organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. Purification of the residue by flash chromatography (2:1 petroleum ether-EtOAc) gave **16** as a syrup (0.63 g, 86.5%); $[\alpha]_D$ + 35.3° (*c* 1.0, $CHCI_3$); ^{1}H NMR (400 MHz, $CDCI_3$): δ 8.08–7.27 (m, 30 H, 6 Ph*H*), 6.07–5.91 (m, 5 H, H-3_A, 3_B, 4_A, 4_B, $CH_2CH{=}CH_2$), 5.77 (dd, 1 H, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.2 Hz, H-2_A), 5.74 (dd, 1 H, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.2 Hz, H-2_B), 5.50 (dd, 1 H, ^2J = 1.6 Hz, $^3J_{trans}$ = 17.2 Hz, $CH_2CH{=}CH_2$), 5.35 (dd, 1 H, ^2J = 1.6 Hz, $^3J_{cis}$= 10.4 Hz,), 5.18 (d, 1 H, $J_{1,2}$ = 1.5 Hz, H-1_A), 5.13 (d, 1 H, $J_{1,2}$ = 1.5 Hz, H-1_B), 4.45–3.76 (m, 8 H, H-5_A, 5_B, 6_A, 6_b, $6_A'$, $6_B'$, CH_2CH=CH_2), 1.92 (s, 3 H, COCH_3); ^{13}C NMR (100 MHz, $CDCl_3$), 169.5 (*C*OCH_3), 164.6, 164.5, 164.2, 164.1 (6 C, 6 *C*OPh), 132.6–127.3 (Ph, $CH_2CH{=}CH_2$). 117.6 ($CH_2CH{=}CH_2$), 96.4, 95.7 (2 C, C-1_A, 1_B), 69.5, 69.1, 68.8, 68.5, 67.9, 67.7, 65.9, 65.7, 61.5 (11 C, C-2_A, 2_B, 3_A, 3_B, 4_A, 4_B, 5_A, 5_B, 6_A, 6_B, $CH_2CH{=}CH_2$), 19.5 (CO*C*H_3).

Anal. Calcd for $C_{59}H_{52}O_{18}$: C, 67.55; H, 5.00. Found: C, 67.34; H, 4.96.

Allyl 2,3,4-Tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (17). A solution of **16** (0.55 g, 0.52 mmol) in methanol solution (25 mL) containing 0.5 % HCl was stirred at room temperature for 14 h, at the end of which time TLC (2:1 petroleum ether-EtOAc) indicated that the starting material had disappeared. The mixture was carefully neutralized with triethylamine, and then concentrated to dryness. The residue was partitioned between water and CH_2Cl_2, then the organic layer dried over Na_2SO_4, and concentrated to a syrup. Purification of the residue by flash chromatography (2:1 petroleum ether-EtOAc) gave **17** as a syrup (0.5 g, 95.6%); $[\alpha]_D$ + 31.0° (*c* 1.5, $CHCI_3$); ^{1}H NMR (400 MHz, $CDCI_3$):δ 8.17–7.26 (m, 30 H, 6 Ph*H*), 6.06–5.80 (m, 5 H, H-3_A, 3_B, 4_A, 4_B, $CH_2CH{=}CH_2$), 5.76–5.73 (m, 2 H, H-2_A, 2_B), 5.34 (dd, 1 H, ^2J = 1.6 Hz, $^3J_{trans}$ = 17.2 Hz, $CH_2CH{=}CH_2$), 5.50 (dd, 1 H, ^2J = 1.6 Hz, $^3J_{cis}$= 10.4 Hz,), 5.17 (d, 1 H, $J_{1,2}$ = 1.6 Hz, H-1_A), 5.14 (d, 1 H, $J_{1,2}$ = 1.6 Hz, H-1_B), 4.44–3.55 (m, 8 H, H-5_A, 5_B, 6_A, 6_B, $6_A'$, $6_B'$, CH_2CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$), 166.7, 165.7, 165.5, 165.4, 165.2 (6 C, 6 *C*OPh), 133.7–128.3 (Ph, $CH_2CH{=}CH_2$), 118.6 ($CH_2CH{=}CH_2$), 97.8, 96.7 (2 C, C-1_A, 1_B), 70.9, 70.6, 70.4, 70.2, 69.5, 68.9, 67.1, 67.0, 66.7, 61.0 (11 C, C-2_A, 2_B, 3_A, 3_B, 4_A, 4_B, 5_A, 5_B, 6_A, 6_B, $CH_2CH{=}CH_2$).

Anal. Calcd for $C_{57}H_{50}O_{17}$: C, 67.99; H, 5.00. Found: C, 68.11; H, 5.02.

Allyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosy-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (18). A solution of **17** (0.25 g, 0.25 mmol) and trimethylsilyl trifluoromethanesulfonate (8 μL, 0.04 mmol) in dry dichloromethane (20 mL) was stirred with dried molecular sieves (4 A, 1 g) under nitrogen for 15 min, and **13** (0.24 g, 0.35 mmol) in dry dichloromethane (10 mL) was added dropwise for 30 min. After 3 h the reaction mixture was diluted with dichloromethane (20 mL) and

washed with satd sodium hydrogen carbonate solution (8 mL). The organic layer was dried with Na_2SO_4 and concentrated in vacuo. Purification of the residue by column chromatography (2:1 petroleum ether-EtOAc) gave **18** as a syrup (0.32 g, 85.7%); $[\alpha]_D$ + 28.7° (*c* 1.0, $CHCI_3$); ^{1}H NMR (400 MHz, $CDCI_3$): δ 8.10–7.25 (m, 45 H, 9 Ph*H*), 6.21–5.88 (m, 7 H, H-3_A, 3_B, 3_C, 4_A, 4_B, 4_C, $CH_2CH{=}CH_2$), 5.84 (dd, 1 H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.2 Hz, H-2_A), 5.79 (dd, 1 H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.2 Hz, H-2_B), 5.44 (dd, 1 H, ^2J = 1.6 Hz, $^3J_{trans}$ = 17.2 Hz, $CH_2CH{=}CH_2$), 5.37 (dd, 1 H, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.2 Hz, H-2_C), 5.26 (dd, 1 H, ^2J = 1.6 Hz, $^3J_{cis}$ = 10.4 Hz, $CH_2CH{=}CH_2$), 5.20 (d, 1 H, $J_{1,2}$ = 1.6 Hz, H-1_A), 5.16 (d, 1 H, $J_{1,2}$ = 1.6 Hz, H-1_B), 4.73 (d, 1 H, $J_{1,2}$ = 1.6 Hz, H-1_C), 4.43–4.37 (m, 11 H, H-5_A, 5_B, 5_C, 6_A, 6_B, 6_C, $6_A'$, $6_B'$, $6_C'$, C*H*$_2$CH=CH$_2$), 2.07 (s, 3 H, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$), 169.5 (*C*OCH_3), 166.0, 165.7, 165.5, 165.3, 165.2 (9 C, 9 *C*OPh), 133.4–128.3 (Ph, $CH_2CH{=}CH_2$), 118.8 ($CH_2CH{=}CH_2$), 98.0, 97.2, 96.9 (3 C, C-1_A, 1_B, 1_C), 20.7 (CO*C*H_3).

Anal. Calcd for $C_{86}H_{74}O_{26}$: C, 67.80; H, 4.90. Found: C, 68.04; H, 4.96.

Allyl 3,4,6-Tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (19). A solution of **18** (0.37 g, 0.24 mmol) in methanol solution (25 mL) containing 0.5 % HCl was stirred at room temperature for 14 h, at the end of which time TLC (2:1 petroleum ether-EtOAc) indicated that the starting material had disappeared. The mixture was carefully neutralized with triethylamine, and then concentrated to dryness. The residue was partitioned between water and CH_2Cl_2, then the organic layer dried over Na_2SO_4, and concentrated to a syrup. Purification of the residue by flash chromatography (2:1 petroleum ether-EtOAc) gave **19** as a syrup (0.34 g, 93.5%); $[\alpha]_D$ + 23.0° (*c* 1.5, $CHCI_3$); ^{1}H NMR (400 MHz, $CDCI_3$):δ 8.09–7.26 (m, 45 H, 9 Ph*H*), 6.19–5.70 (m, 10 H, H-2_A, 2_B, 2_C, 3_A, 3_B, 3_C, 4_A, 4_B, 4_C, $CH_2CH{=}CH_2$), 5.48 (dd, 1 H, ^2J = 1.6 Hz, $^3J_{trans}$ = 17.2 Hz, $CH_2CH{=}CH_2$), 5.29 (dd, 1 H, ^2J = 1.6 Hz, $^3J_{cis}$ = 10.4 Hz, $CH_2CH{=}CH_2$), 5.20 (d, 1 H, $J_{1,2}$ = 1.6 Hz, H-1_A), 5.17 (d, 1 H, $J_{1,2}$ = 1.6 Hz, H-1_B), 4.75 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1_C), 4.43–4.37 (m, 11 H, H-5_A, 5_B, 5_C, 6_A, 6_B, 6_C, $6_A'$, $6_B'$, $6_C'$, C*H*$_2$CH=CH$_2$); ^{13}C NMR (100 MHz, $CDCl_3$), 166.1, 165.8, 165.7, 165.6, 165.5, 165.4, 165.3, 165.2, 165.1 (9 C, 9 *C*OPh), 133.6–27.7 (Ph, $CH_2CH{=}CH_2$), 118.5 ($CH_2CH{=}CH_2$), 97.7, 96.8, 96.4 (3 C, C-1_A, 1_B, 1_C).

Anal. Calcd for $C_{84}H_{72}O_{25}$: C, 68.10; H, 4.90. Found: C, 67.99; H, 4.94.

Allyl 2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (20). A solution of **19** (0.21 g, 0.14 mmol) and trimethylsilyl trifluoromethanesulfonate (8 μL, 0.04 mmol) in dry dichloromethane (20 mL) was stirred with dried molecular sieves (4 A, 1 g) under nitrogen for 15 min, and then **7** (0.52 g, 0.70 mmol) in dry dichloromethane (10 mL) was added dropwise for 30 min. After 3 h the reaction mixture was diluted with dichloromethane (20 mL) and washed with satd sodium hydrogen carbonate solution (8 mL). The organic layer was dried over Na_2SO_4 and

concentrated *in vacuo*. Purification of the residue by column chromatography (2:1 petroleum ether-EtOAc) gave **20** as a syrup (0.23 g, 80.4%); $[\alpha]_D$ + 14.7° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.04–7.18 (m, 65 H, 13 Ph*H*), 6.21–5.80 (m, 13 H, H-2_A, 2_B, 2_C, 2_D, 3_A, 3_B, 3_C, 3_D, 4_A, 4_B, 4_C, 4_D, $CH_2CH{=}CH_2$), 5.45 (dd, 1 H, ^2J = 1.6 Hz, $^3J_{trans}$ = 17.2 Hz, $CH_2CH{=}CH_2$), 5.28 (dd, 1 H, ^2J = 1.6 Hz, $^3J_{cis}$ = 10.4 Hz, $CH_2CH{=}CH_2$), 5.24 (d, 1 H, $J_{1,2}$ = 1.6 Hz, H-1_A), 5.22 (d, 1 H, $J_{1,2}$ = 1.6 Hz, H-1_B), 5.05 (d, 1 H, $J_{1,2}$ = 1.6 Hz, H-1_C), 4.87 (d, 1 H, $J_{1,2}$ = 1.6 Hz, H-1_D), 4.43–4.37 (m, 14 H, H-5_A, 5_B, 5_C, 5_D, 6_A, 6_B, 6_C, 6_D, $6_A'$, $6_B'$, $6_C'$, $6_D'$, $CH_2CH{=}CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$), 166.2, 165.9, 165.7, 165.6, 165.5, 165.4, 165.2, 165.0, 164.8 (13 C, 13 *C*OPh), 133.4–128.3 (Ph, $CH_2CH{=}CH_2$), 118.4 ($CH_2CH{=}CH_2$), 99.7, 98.1, 98.0, 97,6 (4 C, C-1_A, 1_B, 1_C, 1_D).

Anal. Calcd for $C_{118}H_{98}O_{34}$: C, 68.80; H, 4.79. Found: C, 68.97; H, 4.74.

α-D-Mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-α-D-mannopyranosyl-(1→6)-D-mannopyranose (1). A mixture of compound **20** (0.1 g, 0.048 mmol) and $PdCl_2$ (0.02 mg) in dry methanol (10 mL) was stirred vigorously for 4 h at room temperature, TLC (1:1 petroleum ether-EtOAc) indicated that the reaction was complete, then filtered through Celite. The filtrate was concentrated to dryness. The resulting compound was dissolved in methanol (20 mL) satd with dry NH_3 and stirred at room temperature for 72 h, at the end of which time TLC (1:1.5 Methanol-EtOAc) indicated that the reaction was complete. The solution was concentrated to dryness and was chromatographed (methanol) on a column of Sephadex LH-20 to afford **1** (0.023 g, 70.2%) as an amorphous mass; $[\alpha]_D$ + 3.1° (*c* 0.1, MeOH); ^1H NMR (400 MHz, D_2O): δ 5.09, 5.01, 4.91, 4.89 (4 d, 4 H, $J_{1,2}$ = 1.5 Hz, H-1_A, 1_B, 1_C, 1_D); ^{13}C NMR (100 MHz, D_2O), δ 100.3, 100.1, 99.8, 98.6 (4 C, C-1_A, 1_B, 1_C, 1_D). ESMS Calcd for $C_{24}H_{42}O_{21}$: 666.58 (M). Found: 665.4 (M-H).

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REFERENCES

1. Gorin, P.A.J.; Spencer, J.F.T. Structural Chemistry of Fungal Polysaccharides. Adv. Appl. Microbiol. **1970**, *13*, 25–42.
2. Bovina, E.V.; Deryabin, V.V.; Gagloev, V.N.; Serebryakov, N.G. Carbon-13 NMR Study of Mannans Produced by *Candida maltosa* and *Candida tropicalis*. Prikl. Biokhim. Mikrobiol. **1988**, *24* (2), 218–225.
3. Suzuki, M.; Fukazawa, Y. Immunochemical Characterization of *Candida albicans* Cell Wall Antigens: Specific Determinant of *Candida albicans* Serotype A Mannan. Microbiol. Immunol. **1982**, *26* (5), 387–402.

4. Kogan, G.; Pavliak, V.; Masler, L. Structural Studies of Mannans from the Cell Wall of the Pathogenic Yeasts *Candida albicans* Serotypes A and B and *Candida parapsilosis*. Carbohydr. Res. **1988**, *172* (2), 243–253.
5. Kogan, G.; Pavliak, V.; Sandula, J.; Masler, L. Novel Structure of the Cellular Mannan of the Pathogenic Yeast *Candida Krasei*. Carbohydr. Res. **1988**, *184*, 171–182.
6. Jiménez-Barbero, J.; Prieto, A.; Gómez-Miranda, B.; Leal, J.A.; Bernabé, M. Chemical Structure of Fungal Cell-Wall Polysaccharides Isolated from *Microsporum gypseum* and Related Species of *Microsporum* and *Trychophyton*. Carbohydr. Res. **1995**, *272* (1), 121–128.
7. Betaneli, V.I.; Ovchinnikov, M.V.; Backinowsky, L.V.; Kochetkov, N.K. A Convenient Synthesis of 1,2-*O*-Benzylidene and 1,2-*O*-Ethylidene Derivatives of Carbohydrates. Carbohydr. Res. **1982**, *107* (2), 285–291.
8. Helferich, B.; Schmitz-Hillebrecht, E. A New Method for the Synthesis of Glucosides of the Phenols. Ber. **1933**, *66B*, 378–383.
9. Schmidt, R.R.; Toepfer, A. Glycosylation with Highly Reactive Glycosyl Donors: Efficiency of the Inverse Procedure. Tetrahedron Lett. **1991**, *32* (28), 3353–3356.
10. a) Boss, R.; Scheffold, R. Cleavage of Allyl Ether with Palladium/Carbon. Angew. Chem. **1976**, *88* (17), 578–579; b) Ogawa, T.; Nakabayashi, S. Synthetic Studies on Cell-Surface Glycans. Part 8. Synthesis of a Hexasaccharide Unit of a Complex Type of Glycan Chain of a Glycoprotein. Carbohydr. Res.**1981**, *93* (1), C1–C5.
11. Nikolaev, A.V.; Ivanova, I.A. Shibaev, V.N.; Kochetkov, N.K. Application of the Hydrogenphosphonate Approach in the Synthesis of Glycosyl Phosphosugar Linked through Secondary Hydroxyl Groups. Carbohydr. Res. **1990**, *204*, 65–78.

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MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016