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Synthesis of *p*-Nitrophenyl 4-*O*-(α-D-Mannopyranosyl)-α-L-rhamnoside and *p*-Acetamidophenyl 4-*O*-(β-D-Mannopyranosyl)-α-L-rhamnoside

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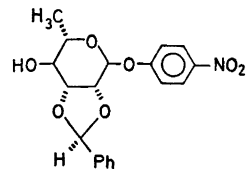
p-Nitrophenyl 4-*O*-(α-D-mannopyranosyl)-α-L-rhamnoside has been synthesized by condensation of 3,4,6-tri-*O*-acetyl-1,2-*O*-methylorthoacetyl-β-D-mannose and *p*-nitrophenyl 2,3-*O*-benzylidene-(H-*endo*)-α-L-rhamnoside followed by removal of protecting groups. *p*-Acetamidophenyl 4-*O*-(β-D-mannopyranosyl)-α-L-rhamnoside has been synthesized *via* condensation of 3,4,6-tri-*O*-benzyl-1,2-*O*-methylorthoacetyl-α-D-glucose and *p*-nitrophenyl 2,3-*O*-benzylidene-(H-*endo*)-α-L-rhamnoside, deblocking, C-2-oxidation of the D-glucose moiety, stereoselective reduction to the corresponding D-mannose derivative and removal of protecting groups.

The structural element α-D-Man-(1→4)-α-L-Rha- occurs in the O-specific side chains of *Salmonella* serogroup A lipopolysaccharides,[1] and the structural element β-D-Man-(1→4)-α-L-Rha- occurs in the serogroups D_2 and E lipopolysaccharides.[2,3] For immunochemical studies the corresponding disaccharides, linked to aglycones containing functional groups through which they could be attached to proteins, thus giving artificial antigens, were needed. The syntheses of two such glycosides are reported in the present communication. During the course of this work the corresponding free disaccharides have been prepared by Bebault and Dutton.[4,5]

RESULTS AND DISCUSSION

The aglycone used in both syntheses was *p*-nitrophenyl 2,3-*O*-benzylidene-(H-*endo*)-α-L-rhamnopyranoside (II, see below). Treatment of *p*-nitrophenyl α-L-rhamnopyranoside [6] with α,α-dibromotoluene in pyridine [7] yielded a mixture of the 2,3-benzylidene-(H-*endo*)- and (H-*exo*)-derivatives which, after acetylation, were separated by column chromatography on silica gel. The structures of these *O*-acetates were assigned from the chemical shifts of the benzylidene protons in NMR,[8] δ 6.28 and 5.98, respectively. In the subsequent glycoside syntheses, fair to good yields were obtained with the H-*endo* (II) but not with the H-*exo* isomer (II a). In molecular models, the hydroxyl group at C-4 in the latter seems to be less accessible because of the bulky phenyl group.



II

Reaction between 3,4,6-tri-*O*-acetyl-1,2-*O*-methylorthoacetyl-β-D-mannose [9] and II in nitromethane, as devised by Kochetkov *et. al.*,[10] followed by deacetylation and hydrolysis under mild conditions, yielded *p*-nitrophenyl 4-*O*-(α-D-mannopyranosyl)-α-L-rhamnoside (V). The yield, based upon the amount of orthoester used, was 35 %.

β-D-Mannopyranosides are less accessible than the corresponding α-D-mannopyranosides. For the synthesis of the other disaccharide,

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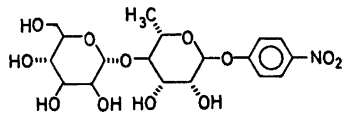


V

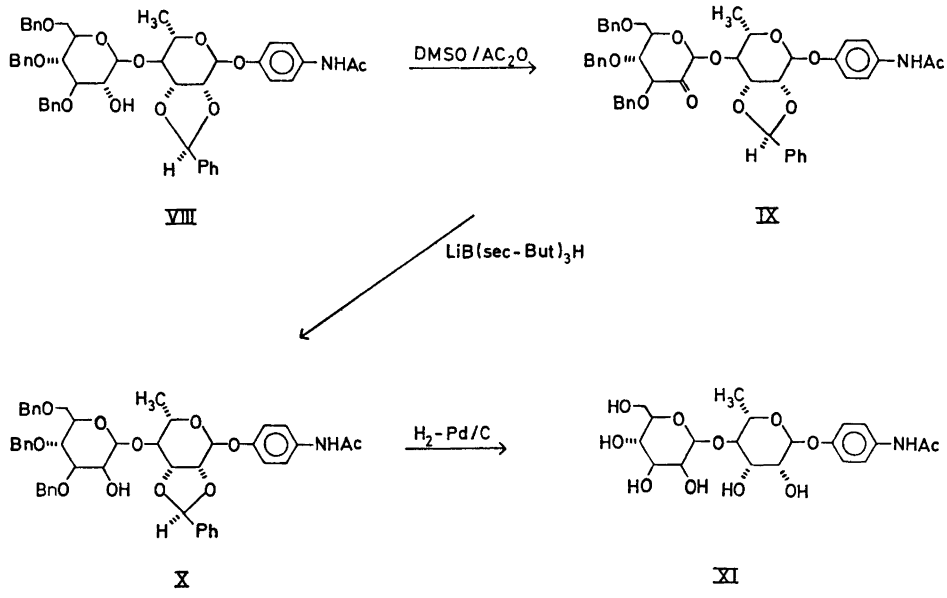
the corresponding β-D-glucopyranoside with a free hydroxyl group at C-2 was first prepared and then transferred into the β-D-mannopyranoside by oxidation to the keto derivative followed by stereoselective reduction.[11] The orthoester glycoside synthesis using benzyl ether protecting groups in the orthoester has proved suitable for preparing such β-D-glucopyranosides.[12] The method has recently been used in the synthesis of a trisaccharide containing a β-D-mannopyranose residue.[13]

Reaction of the aglycone (II) and 3,4,6-tri-*O*-benzyl-1,2-*O*-methylorthoacetyl-α-D-glucose [10,12] in nitromethane using mercuric bromide as catalyst gave the expected disaccharide derivative VI in 16 % yield. Since the presence of the *p*-nitrophenyl group in this derivative was expected to cause complications in later steps, this group was transferred into a *p*-acetamidophenyl group by selective reduction followed by *N*-acetylation. The *O*-deacetylated derivative (VIII) was oxidized to the hexulose derivative (IX) by dimethyl sulfoxide-acetic anhydride.[14] As IX was labile it was not purified, but directly reduced, using lithium tri-*sec*-butylborohydride [15] in tetrahydrofuran. The pure β-D-mannopyranoside (X) was obtained in a yield of 78 %, based on VIII. Removal of the protecting groups by catalytic hydrogenation yielded the disaccharide derivative XI.

The disaccharide derivatives V and XI both yielded equimolecular parts of D-mannose and L-rhamnose on acid hydrolysis. That V is a α- and XI a β-D-mannopyranoside is evident from their modes of syntheses and from the chemical shifts of the anomeric protons assigned to these residues, δ 4.98 and 4.90 respectively. The rather small difference in optical rotation between the compounds, $[\alpha]_{578}$ −90° for the α-mannoside and $[\alpha]_{578}$ −105° for the β-mannoside, may be explained by the larger negative contribution to the optical rotation by the *p*-nitrophenyl-α-L-rhamnoside moiety in V than by the *p*-acetamidophenyl-α-L-rhamnoside moiety in XI.

EXPERIMENTAL

General methods. Elemental analyses were performed by Dr. A. Bernhardt's laboratory.



VIII IX X XI

Scheme 1.

Melting points are corrected. Concentrations were performed at reduced pressure at temperatures not exceeding 40 °C. NMR spectra were recorded on Varian A 60 A, HA-100 and XL-100 instruments. Interpretations were made on a first order basis. For deuteriochloroform and tetradeuteriomethanol solutions TMS was used as internal standard and for deuterium oxide solutions 3-(trimethylsilyl)-1,1,2,2,3,3-hexadeuteriopropanesulfonic acid sodium salt. TLC was performed on silica gel F_{254} plates (Merck). For visualization of the compounds UV-light or spraying with sulfuric acid followed by heating at 120 °C was used. Column chromatography was performed on silica gel (< 0.08 mm, Merck). The following solvent systems were used; A (ethyl acetate-light petroleum, 1:2), B (diethyl ether-hexane, 3:1), C (methanol-ethyl acetate, 1:9), D (ethyl acetate-toluene, 1:1), E (ethyl acetate-toluene, 1:4), F (ethyl acetate-toluene, 2:1). For GLC a Perkin-Elmer 990 instrument was used. Separations were performed on an ECNSS-M column (180 × 0.15 cm, 3 % on Gas Chrom Q) at 190 °C. Optical rotations were recorded on a Perkin-Elmer 141 instrument and IR in a Perkin-Elmer 257 instrument.

p-*Nitrophenyl-4*-O-*acetyl-2,3*-O-*benzylidene-(H*-endo-*and H*-exo-*)*-α-L-*rhamnoside (I and I a)*. *p*-Nitrophenyl-α-L-rhamnopyranoside [6] (20 g) was dissolved in pyridine (400 ml). α,α-Dibromotoluene (24 ml) was added and the mixture was refluxed for 75 min. Acetic anhydride (160 ml) was added and the solution was left for 1 h at room temperature. The solution was poured into water (3 l), and the mixture was extracted with chloroform (5 × 600 ml). The organic layer was washed with water (1000 ml), aqueous sodium hydrogen carbonate (4 × 600 ml) and water (3 × 1000 ml), dried over magnesium sulfate and evaporated. The crude product was chromatographed on a silica gel column (solvent system A) to yield the H-*endo*-isomer (I) (12.4 g, 42 %) and the H-*exo*-isomer (I a) (9.1 g, 31 %), both crystalline after evaporation. After crystallization from methanol the H-*endo*-isomer showed m.p. 84 – 87 °C, $[\alpha]_{578}^{23}$ −74° (*c* 1.0, chloroform). (Found: C 60.6; H 5.08; N 3.50. Calc. for $C_{21}H_{21}O_8N$: C 60.7; H 5.11; N 3.37). NMR ($CDCl_3$, 60 MHz): δ 8.21 and 7.17 (2 H each, both d, $J_{H,H}$ 9.5 Hz, *p*-$NO_2C_6H_4O$), 7.3 – 7.7 (5 H, m, other aromatics), 6.28 (1 H, s, benzylidene proton), 5.90 (1 H, s, $J_{1,2}$ < 1 Hz, H-1), 5.14 (1 H, q, $J_{3,4}$ 8.0 Hz, $J_{4,5}$ 9.5 Hz, H-4), 4.69 (1 H, q, $J_{2,3}$ 5.6 Hz, $J_{3,4}$ 8.0 Hz, H-3), 4.39 (1 H, $J_{2,3}$ 5.0 Hz, H-2), 3.88 (1 H, oct, $J_{4,5}$ 9.5 Hz, $J_{5,6}$ 6.5, H-5), 2.13 (3 H, s, $OCOCH_3$), 1.19 (3 H, d, $J_{5,6}$ 6.5 Hz, H-6).

The H-*exo*-isomer was crystallized from chloroform-hexane and showed m.p. 153 – 154 °C. $[\alpha]_{578}$ −65° (*c* 1.1, chloroform). (Found: C 60.6; H 5.12; N 3.49. Calc. for $C_{21}H_{21}O_8N$: C 60.7; H 5.11; N 3.37). NMR ($CDCl_3$, 60 MHz): δ 8.23 and 7.18 (2 H each, both d, $J_{H,H}$ 9.5 Hz, *p*-$NO_2C_6H_4O$), 7.3 – 7.7 (5 H, m, other aromatics), 5.98 (1 H, s, benzylidene proton), 5.93 (1 H, s, $J_{1,2}$ < 1 Hz, H-1), 4.85-5.20 (1 H, m, H-4), 3.87 (1 H, oct, $J_{4,5}$ 10.0 Hz, $J_{5,6}$ 6.5 Hz, H-5), 2.10 (3 H, s, $OCOCH_3$), 1.14 (3 H, d, $J_{5,6}$ 6.5 Hz, H-6).

I a in the presence of 0.17 mol Eu $(DPM)_3$/mol I a ($CDCl_3$, 60 MHz): δ 8.25 and 7.23 (2 H each, both d, $J_{H,H}$ 9.5 Hz, *p*-$NO_2C_6H_4O$), 7. 65 – 7.90 (2 H, m, other aromatics), 7.20 – 7.40 (3 H, m, other aromatics), 6.13 (1 H, s, benzylidene proton), 6.04 (1 H, s $J_{1,2}$ < 1 Hz, H-1), 5.89 (1 H, q, $J_{3,4}$ 6.5 Hz, $J_{4,5}$ 10.0 Hz, H-4), 4.92 (1 H, trip, $J_{2,3}$ 6.5 Hz, $J_{3,4}$ 6.5 Hz, H-3), 4.66 (1 H, d, $J_{2,3}$ 6.5 Hz, H-2), 4.17 (1 H, oct, $J_{4,5}$ 10.0 Hz, $J_{5,6}$ 6.5 Hz, H-5), 2.52 (3 H, s, $OCOCH_3$), 1.38 (3 H, d, $J_{5,6}$ 6.5 Hz, H-6).

p-*Nitrophenyl 2,3*-O-*benzylidene-H*-endo)-α-L-*rhamnopyranoside (II)*. I (12.2 g) was dissolved in methanol (100 ml) and 3 % methanolic ammonia (50 ml) was added. The solution was left at room temperature for three days. Evaporation yielded II (10.9 g, 99 %) as a syrup which slowly crystallized. Crystallization from diethyl ether-hexane yielded the pure substance, m.p. 78 – 82 °C. $[\alpha]_{578}^{23}$ −65.0° (*c* 1.0, chloroform). A satisfactory elemental analysis could not be obtained for this compound. NMR ($CDCl_3$, 100 MHz): δ 8.16 and δ 7.10 (2 H each, both d, $J_{H,H}$ 9.0 Hz, *p*-$NO_2C_6H_4O$), 7.2 – 7.6 (5 H, m, other aromatics), 6.18 (1 H, s, benzal proton), 5.84 (1 H, s, $J_{1,2}$ < 1 Hz, H-1), 4.54 (1 H, q, $J_{2,3}$ 5.0 Hz, $J_{3,4}$ 7.0 Hz, H-3), 4.32 (1 H, d, $J_{2,3}$ 5.0 Hz, H-2), 1.28 (3 H, d, $J_{5,6}$ 5.0 Hz, H-6).

p-*Nitrophenyl 2,3*-O-*benzylidene-(H*-exo)-α-L-*rhamnopyranoside (II a)*. I a (1.0 g) was dissolved in methanol (30 ml) and dichloromethane (10 ml). Barium oxide (0.20 g) was added and the mixture was refluxed for 1 h. The solvents were evaporated and the residue was suspended in ethyl acetate. After filtration and evaporation II a was obtained as a syrup (0.90 g, 100 %) which slowly crystallized. Crystallization from ethanol yielded the pure substance, m.p. 128 – 130 °C. $[\alpha]_{578}^{23}$ −143° (*c* 1.7, chloroform). (Found: C 61.2; H 5.19; N 3.88. Calc. for $C_{19}H_{17}NO_7$: C 61.1; H 5.13; N 3.75). NMR ($CDCl_3$, 60 MHz): δ 8.21 and 7.16 (2 H each, both d, $J_{H,H}$ 9.5 Hz, *p*-$NO_2C_6H_4O$), 7.3 – 7.7 (5 H, m, other aromatics), 5.98 (1 H, s, benzylidene proton), 5.93 (1 H, s, $J_{1,2}$ < 1 Hz, H-1), 1.17 (3 H, d, $J_{5,6}$ 5.5 Hz, H-6).

p-*Nitrophenyl 2,3*-O-*benzylidene-H*-endo)-*4*-O-(α-D-*mannopyranosyl*)-α-L-*rhamnoside* (IV). II (4.72 g) and 3,4,6-tri-*O*-acetyl-1,2-*O*-methylorthoacetyl-β-D-mannose [9] (4.0 g) were dissolved in nitromethane (100 ml), mercuric bromide (0.36 g) was added and the mixture was distilled. The volume was kept constant by addition of nitromethane. After 1 h, when examination by TLC (solvent system B) indicated a complete reaction, yielding the acetylated disaccharide derivative III, the solvent was evaporated. The residue was suspended in

methanolic ammonia (100 ml, 1.67 %) and left at room temperature overnight. After filtration and evaporation a crude syrup (6.32 g) was obtained. Chromatography on a silica gel column (solvent system C) yielded IV (2.07 g, 35 %) as a slowly crystallizing syrup. Crystallization from 2-propanol yielded the pure substance, m.p. 108–114 °C. $[\alpha]_{578}^{23}$ −19° (*c* 0.7, methanol). (Found: C 55.9; H 5.49; N 2.67. Calc. for $C_{25}H_{29}NO_{13}$: C 56.1; H 5.45; N 2.67). NMR (CD_3OD, 100 MHz) δ 8.20 and 7.24 (2 H each, both d, $J_{H,H}$ 9.0 Hz, *p*-$NO_2C_6H_4O$), 7.3–7.6 (5 H, m, other aromatics), 6.21 (1 H, s, benzal proton), 5.93 (1 H, s, $J_{1,2} < 1$ Hz, H-1 L-rhamnosyl residue), 4.97 (1 H, s, $J_{1,2} < 1$ Hz, H-1 D-mannosyl residue), 4.37 (1 H, d, $J_{2,3}$ 5.0 Hz, H-2 L-rhamnosyl residue), 1.26 (3 H, d, $J_{5,6}$ 6.5 Hz, H-6 L-rhamnosyl residue).

p-*Nitrophenyl 4*-O-*(α*-D-*mannopyranosyl)*-α-L-*rhamnoside (V)*. IV (1.0 g) was dissolved in 50 % aqueous acetic acid (50 ml) and the solution was kept at 100 °C for 30 min and evaporated. The residue was suspended in water (50 ml) and extracted with diethyl ether (3 × 30 ml). The water phase was evaporated to yield crude V (0.78 g). After acetylation with acetic anhydride (10 ml) and pyridine (12 ml) at room temperature overnight, a syrup (1·21 g) was obtained, which was chromatographed on a silica gel column (solvent system D) to yield a chromatographically homogeneous hexaacetate (0.93 g, 76 %) that did not crystallize. After deacetylation with 5 % methanolic ammonia pure V (0.60 g, 100 %) was obtained as a slowly crystallizing syrup. Crystallization from a small volume of water afforded the pure compound with 1 mol of water, m.p. 126–128 °C. $[\alpha]_{578}^{23}$ −90° (*c* 0.5, water). (Found: C 46.4; H 5.45; N 3.09. Calc. for $C_{18}H_{25}NO_{12}$·H_2O: C 46.5; H 5.84; N 3.01). NMR (D_2O, 100 MHz): δ 8.21 and δ 7.20 (2 H each, both d, $J_{H,H}$ 9.0 Hz, *p*-$NO_2C_6H_4O$); δ 5.67 (1 H, d, $J_{1,2}$ 2 Hz, H-1 L-rhamnosyl residue), 4.98 (1 H, d, $J_{1,2}$ 1 Hz, H-1 D-mannosyl residue), 1.25 (3 H, d, $J_{5,6}$ 6.0 Hz, H-6 L-rhamnosyl residue).

p-*Nitrophenyl 4*-O-*(2*-O-*acetyl-3,4,6-tri*-O-*benzyl-β*-D-*glucosyl)-2,3*-O-*benzylidene-(H*-endo)-α-L-*rhamnoside (VI)*. II (7.72 g) and 3,4,6-tri-*O*-benzyl-1,2-*O*-methylorthoacetyl-α-D-glucose [12] were dissolved in nitromethane (125 ml). Solvent was distilled off and the volume was kept constant by addition of nitromethane. The reaction was monitored by TLC (solvent system E). After 6 h when no further reesterification appeared to take place, mercuric bromide (0.23 g) was added and the mixture was refluxed for 15 h. After filtration and evaporation a crude syrup was obtained, which after chromatography on a silica gel column yielded VI (2.16 g, 16 %) as a syrup, which slowly crystallized. Crystallization from methanol yielded the pure substance, m.p. 137–139 °C. $[\alpha]_{578}^{23}$ −51° (*c* 0.4, chloroform). (Found: C 68.0; H 5.86; N 1.81. Calc. for $C_{48}H_{49}NO_{13}$: C 68.0, H 5.83; N 1.65). NMR ($CDCl_3$, 100 MHz): δ 8.16 and 7.10 (2 H each, both d, $J_{H,H}$ 9.0 Hz, *p*-$NO_2C_6H_4O$), 7.2–7.5 (20 H, m, other aromatics), 6.13 (1 H, s, benzylidene proton), 5.80 (1 H, s, $J_{1,2} < 1$ Hz, H-1 L-rhamnosyl residue), 4.28 (1 H, d, $J_{2,3}$ 6 Hz, H-2 L-rhamnosyl residue), 1.98 (3 H, s, $OCOCH_3$), 1.30 (3 H, d, $J_{5,6}$ 5.0 Hz, H-6 L-rhamnosyl residue).

p-*Acetamidophenyl 4*-O-*(2*-O-*acetyl-3,4,6-tri*-O-*benzyl-β*-D-*glucosyl)-2,3*-O-*benzylidene-(H*-endo)-α-L-*rhamnoside (VII)*. VI (1.4 g) was hydrogenated at room temperature and atmospheric pressure in the presence of Adams' catalyst (0.15 g) using tetrahydrofuran (30 ml) as solvent. When hydrogen consumption had ceased, acetic anhydride (5 ml) and pyridine (8 ml) were added. After 1 h at room temperature, the solution was filtered and evaporated. VII was obtained as a chromatographically homogeneous syrup (1.42 g, 99 %), which slowly crystallized. Crystallization from methanol yielded the pure substance, m.p. 193–195 °C. $[\alpha]_{578}^{23}$ −37° (*c* 0.7, chloroform). (Found: C 70.0; H 6.31; N 1.74. Calc. for $C_{50}H_{53}NO_{12}$: C 69.8; H 6.21; N 1.62). NMR ($CDCl_3$, 100 MHz): δ 6.97 (2 H, d, $J_{H,H}$ 9.0 Hz, *p*-$AcNHC_6H_4O$, other 2 H in other aromatics), 7.1–7.6 (22 H, m, other aromatics), 6.11 (1 H, s, benzylidene proton), 5.65 (1 H, s, $J_{1,2} < 1$, H-1 L-rhamnosyl residue), 4.26 (1 H, d, $J_{2,3}$ 5.0 Hz, H-2 L-rhamnosyl residue), 2.13 (3 H, s, *N*-$COCH_3$), 1.98 (3 H, s, $OCOCH_3$), 1.31 (3 H, d, $J_{5,6}$ 6.0 Hz, H-6 L-rhamnosyl residue).

p-*Acetamidophenyl 4*-O-*(3,4,6-tri*-O-*benzyl-β*-D-*glucosyl)-2,3*-O-*benzylidene-(H*-endo)-α-L-*rhamnoside (VIII)*. VII (1.3 g) was dissolved in a mixture of methanol and dichloromethane (1:1, 40 ml), barium oxide (0.20 g) was added. The mixture was refluxed for 1 h, cooled and the solvent was evaporated. The residue was suspended in ethyl acetate (30 ml) and filtered. After evaporation to dryness, IX was obtained as a crude syrup. After purification on silica gel (solvent system F) a homogeneous syrup (1.0 g, 79 %) which slowly crystallized was obtained. Crystallization from methanol afforded the pure compound, m.p. 175–178 °C. $[\alpha]_{578}^{23}$ −53° (*c* 0.5, chloroform). (Found: C 70.3; H 6.24; N 1.85. Calc. for $C_{43}H_{51}NO_{11}$: C 70.5; H 6.28; N 1.71). NMR ($CDCl_3$, 100 MHz): δ 6.96 (2 H, d, $J_{H,H}$ 9.0 Hz, *p*-$AcNHC_6H_4O$, other 2 H in other aromatics), 7.1–7.6 (22 H, m, other aromatics), 6.14 (1 H, s, benzylidene proton), 5.66 (1 H, s, $J_{1,2} < 1$ Hz, H-1 L-rhamnosyl residue), 4.28 (1 H, d, $J_{2,3}$ 5.0 Hz, H-2 L-rhamnosyl residue), 2.12 (3 H, s, *N*-$COCH_3$), 1.33 (3 H, d, $J_{5,6}$ 5.0 Hz, H-6 L-rhamnosyl residue).

p-*Acetamidophenyl 4*-O-*(3,4,6-tri*-O-*benzyl-β*-D-arabino-*hexoside-2-ulose)-2,3*-O-*benzylidene-(H*-endo)-α-L-*rhamnoside (IX)*. VIII (0.80 g) was dissolved in dimethyl sulfoxide (80 ml) and acetic anhydride (4 ml). The solution was kept at room temperature under nitrogen for two days and the reagents were removed by

lyophilization. The crude product was used without purification in the following step. IR (KBr) showed, *inter alia*, a strong absorption at 1750 cm^{-1} (C=O, ketone).

p-*Acetamidophenyl 4-O-(3,4,6-tri-O-benzyl-β-D-mannosyl)-2,3-O-benzylidene-(H-endo)-α-L-rhamnoside(X)*. A solution of IX (from 0.80 g VIII) in tetrahydrofuran (10 ml) was added, under nitrogen, to a stirred M solution of lithium tri-*sec*-butylborohydride in tetrahydrofuran (5 ml) at −75 °C. The solution was kept for 3 h at −75 °C. Excess reagent was decomposed by the addition of methanol, after which the alkylboranes were oxidized with 35 % aqueous hydrogen peroxide. The solution was removed from the salts by decantation and concentrated. The crude syrup was chromatographed on a silica gel column (solvent system F), to yield X as a chromatographically homogeneous syrup (0.62 g, 78 %) which crystallized from 95 % ethanol to yield the pure substance, m.p. 162−165 °C. $[\alpha]_{578}^{23}$ −62° (*c* 0.7, chloroform). (Found: C 70.6; H 6.33; N 1.72. Calc. for $C_{48}H_{51}NO_{11}$: C 70.5; H 6.28; N 1.71). NMR ($CDCl_3$, 100 MHz): δ 6.94 (2 H, d, $J_{H,H}$ 9.0 Hz, *p*-$AcNHC_6H_4O$, other 2 H in other aromatics); δ 7.1−7.6 (22 H, m, other aromatics), 6.10 (1 H, s, benzylidene proton), 5.66 (1 H, s, $J_{1,2}<1$ Hz, H-1 L-rhamnosyl residue), 4.93 (1 H, s, $J_{1,2}<1$ Hz, H-1 D-mannosyl residue), 4.29 (1 H, d, $J_{2,3}$ 6.0 Hz, H-2 L-rhamnosyl residue), 2.11 (3 H, s, *N*-$COCH_3$), 1.33 (3 H, d, $J_{5,6}$ 6.0 Hz, H-6 L-rhamnosyl residue).

p-*Acetamidophenyl 4-O-(β-D-mannopyranosyl)-α-L-rhamnoside (XI)*. X (0.32 g) was hydrogenated at room temperature and atmospheric pressure in the presence of 10 % palladium on charcoal (0.35 g) using 95 % ethanol (100 ml) as solvent. After processing, XII (0.17 g) was obtained. Crystallization from ethanol afforded the pure substance, m.p. 153−155 °C. $[\alpha]_{578}^{23}$ −105° (*c* 0.5, water). (Found: C 52.2; H 6.44; N 3.22. Calc. for $C_{20}H_{29}NO_{11}$: C 52.3; H 6.36; N 3.05). NMR (D_2O, 100 MHz): δ 7.31 and 7.06 (2 H each, both d, $J_{H,H}$ 9.0 Hz, *p*-$AcNHC_6H_4O$), 5.48 (1 H, s, $J_{1,2}<1$ Hz, H-1 L-rhamnosyl residue), 4.90 (1 H, s, $J_{1,2}<1$ Hz, H-1 D-mannosyl residue), 2.15 (3 H, s, *N*-$COCH_3$), 1.30 (3 H, d, $J_{5,6}$ 6.0 Hz, H-6 L-rhamnosyl residue).

Sugar analysis of compounds V and XI. Samples (≃5 mg) were hydrolysed (0.25 M sulfuric acid, 100 °C, 14 h), neutralized ($BaCO_3$), and the sugars were transformed into their alditol acetates by reduction (sodium borohydride) and acetylation (acetic anhydridepyridine, 1:1). The mixtures were analysed on GLC.[16]

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