

Glycosylation Using Hemiacetal Sugar Derivatives: Synthesis of *O*-α-D-Rhamnosyl-(1 → 3)-*O*-α-D-rhamnosyl-(1 → 2)-D-rhamnose and *O*-α-D-Tyvelosyl-(1 → 3)-*O*-α-D-mannosyl-(1 → 4)-L-rhamnose

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O-α-D-Rhamnopyranosyl-(1 → 3)-*O*-α-D-rhamnopyranosyl-(1 → 2)-D-rhamnopyranose, a repeating trisaccharide of the O-specific polysaccharides (OPSs) of *Pseudomonades*, and *O*-α-D-tyvelopyranosyl-(1 → 3)-*O*-α-D-mannopyranosyl-(1 → 4)-L-rhamnopyranose, a trisaccharide composing the OPSs of *Salmonella typhi*, were synthesized by in-situ activating glycosylation reactions using hemiacetal sugar derivatives. Allyl 2,4-di-*O*-benzyl-α-D-rhamnopyranoside was prepared via the direct ditritylation of allyl α-D-mannopyranoside. 3-*O*-Acetyl-2,4-di-*O*-benzyl-D-rhamnopyranose was used as a precursor for the moiety of D-tyvelose (3,6-dideoxy-D-*arabino*-hexose, 3,6-dideoxy-D-mannopyranose, 3-deoxy-D-rhamnose) of the salmonella trisaccharide.

Glycosylation is the fundamental reaction for assembling sugar units artificially. Modern currently developed methods for glycosylation have been effectively used to synthesize various oligosaccharidal substances.[1] In-situ-activation methods using hemiacetal sugar derivatives (lactols) as donors (DOH in Eq. 1) simplify the glycosylation of a given acceptor (AOH),

$$\mathrm{DOH} + \mathrm{AOH} + \mathrm{Reagent(s)} \rightarrow \mathrm{DOA} \quad (1)$$

because they are free from the preparation of any activated intermediates.[2,3] Recently, using such methods,[2,4] we carried out α-selective syntheses of D-mannooligosaccharides[2] and L-rhamnooligosaccharides.[5c] This article presents new applications of our methods for α-selective syntheses of a trisaccharide **1** (Fig. 1) consisting of the rare sugar D-rhamnose (6-deoxy-D-mannose) and a trisaccharide **2** containing tyvelose (3-deoxy-D-rhamnose), as described below.

Several years ago, we published the syntheses of dityrityl derivatives[6] of hexopyranosides (**B** in Fig. 2) and dihydroxy derivatives (**C**) therefrom.[6a] Later, we reported that **C** in *gluco*-form was useful as a precursor for partially protected 6-deoxy-D-glucose (D-quinovose) (**D**).[5b,7] This paper now shows that dityrityl D-mannosides are good starting materials for preparing monohydroxy derivatives of D-rhamnose,[8a,b] as shown in Fig. 2; i.e., a D-mannoside **A** was converted into an acceptor form **D** of D-rhamnose by successive reactions of ditritylation, benzylation, detritylation, monotosylation, and reduction. Furthermore, the selective removal of a protecting group (R) from **D**, of which the OH group was pre-masked with a protecting group (Q), gave a donor form **E** of D-rhamnose.

As described above, we planned to synthesize **1** and **2** starting from the D-mannoside **3**,[5a] as summarized in Fig. 1, to show the utility of **B** in the *manno*-form. From **3**, we prepared four synthons: three D-rhamnose derivatives (**4**, **5**, and **6**) and one D-mannosyl donor **8**. The saccharide **1** is the common repeating linear trisaccharide of the O-specific polysaccharides (OPSs) of *Pseudomonades*, which are opportunistic pathogens[8c,f,h] and phytopathogens.[8d,h,j,k] A recent paper[8i] informed that the OPSs of phytopathogenic *Xanthomonades* also contain **1** as a repeating unit of the branched-chain stem polysaccharide. Although a polymer of **1**[9a] and **1**-bovin serum albumin conjugate[9b] were synthesized, **1** itself has never been synthesized or characterized. On the other hand, **2** is a common trisaccharide composing repeating tetrasaccharide units of the OPSs of *Salmonella typhi*,[10] causing an acute enteric infectious disease, typhus,[10a] and has not been synthesized. As described below, we will show that the D-rhamnose donor **6** was useful as a precursor of the immunodominant α-D-tyvelosyl moiety[11] at the non-reducing end of **2**, avoiding any difficulties due to the instability of tyvelosyl halides[11b–d] and, especially, the uncontrollable selectivity in glycosylation with the benzyl-protected tyvelosyl chloride.[11e]

The synthesis of **1** began with the preparation of **4** (Fig. 3). Compound **3**[5a] was converted into the 6-OH derivative **10**,[12a,b] via conventional monotritylation,[12c] benzylation, and detritylation. This compound was monotosylated and reduced with $LiAlH_4$[5b,7] to afford the D-rhamnose derivative **11** in 37% yield from **3**. The deallylation of **11** with $PdCl_2$[13] gave **4** in 54% yield.

Direct tritylation without the tin-mediation[14a] of **3**, readily prepared from D-mannose,[5a] with trityl chloride (2.3 mol. amt.)[6a] in pyridine at 55 °C, afforded the 3,6-disubstituted **12**[14a] in 67% yield. In contrast, a similar tritylation was conducted, but at 100 °C gave the 2,6-disubstituted **13** in 27% yield as a major ditritylated derivative, as previously observed in the cases of methyl and benzyl α-D-mannnosides.[6a] Benzylation followed by detritylation of **12** gave the diol **14**[14a] in 56% yield. This was tosylated selectively[5b,7] and reduced with $LiAlH_4$ to afford **5** in 34% yield. To our knowledge,[9] this is the shortest route to a versatile 3-OH derivative of D-rhamnose from D-mannose. Acetylation of **5**, followed by removal of the

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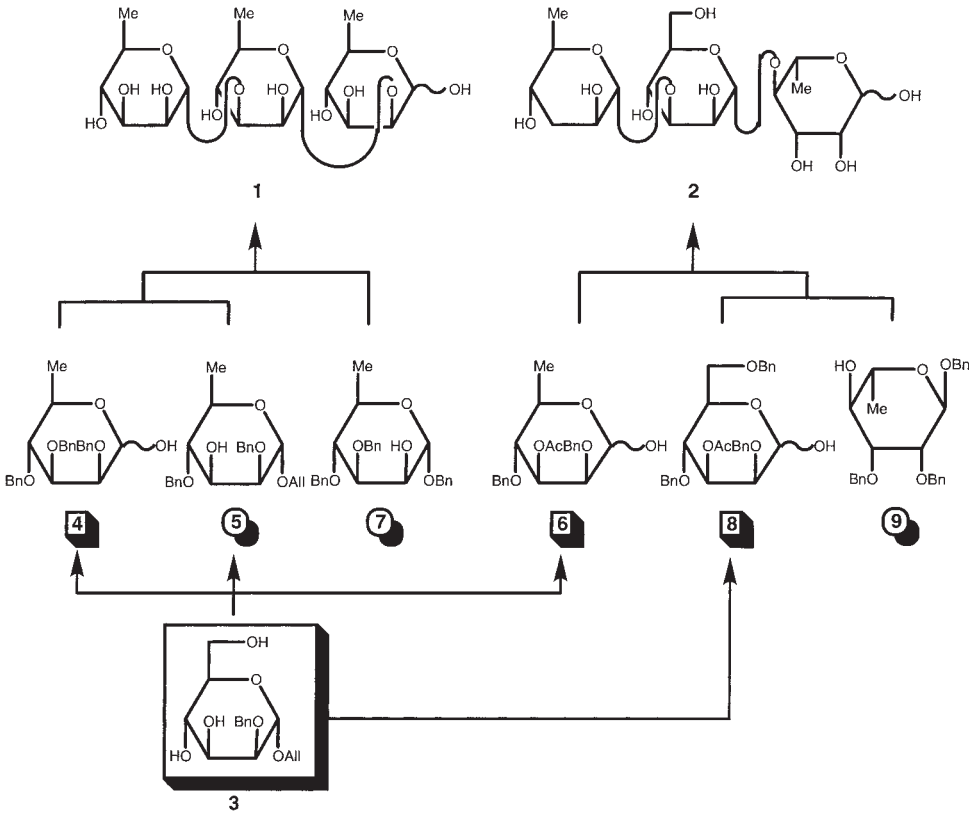

Fig. 1. Synthetic scheme for α-D-Rha*p*-(1 → 3)-α-D-Rha*p*-(1 → 2)-D-Rha*p*-OH (**1**) and α-D-Tyv*p*-(1 → 3)-α-D-Man*p*-(1 → 4)-L-Rha*p*-OH (**2**). A code with square shade is a donor, whereas that with round shade is an acceptor.

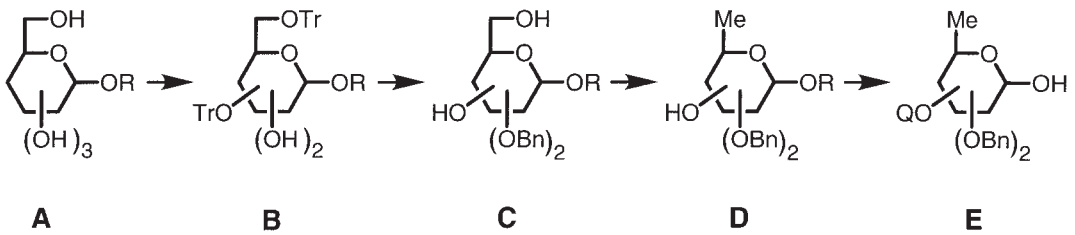

Fig. 2. A route to partially benzylated 6-deoxyhexoses.

allyl group, furnished **6**. Through a similar sequence of reactions, **13** was converted into the diol **15**,[14b,c] and then into the D-rhamnose derivative **16**. The diol **17**, prepared before by means of a ditritylation reaction at 100 °C,[6a] was readily converted into the acceptor **7** in 35% yield, through monotosylation and subsequent reduction.

We have previously observed that a solvent-free benzylation[15a] of methyl α-D-mannopyranoside in benzyl chloride in the presence of 4.5 mol. amt. of KOH at 140 °C[15b] afforded mainly the 3-OH derivative.[15c] A similar reaction was applied to **3** to give the desired 3-OH compound **18** in 31% yield; minor products were the 4-OH derivative **19**[5a] (19%) and the diol **20**[14d] (17%). Compound **18**, thus obtained only in two steps from D-mannose, was then transformed into the donor **8** via acetylation and deallylation. Through a known method,[16a,b] the acceptor **9** (Fig. 1) was prepared from benzyl α-L-rhamnopyranoside.[5c,16c]

α-Selective condensations of **4** and **5** (Fig. 4) were performed with the TCTM system,[4c,5b] composed of trimethylsilyl bromide (Me_3SiBr), $CoBr_2$, tetrabutylammonium bromide (*n*-Bu_4NBr), and molecular sieves 4A (MS4A), in 1,2-dichloroethane.[5b] The desired disaccharide derivative **21** was produced in 57% yield. The β-linked by-product was isolated in 23% yield. The ^1H and ^{13}C NMR spectra of the filtrate of a reaction mixture of **4** and the TCTM system in CD_2Cl_2 showed a quantitative conversion of **4** into **a** (Fig. 3),[4b] indicating that glycosylation proceeds via **a**.

Mild deallylation using $PdCl_2$[13] converted **21** into **22** in 63% yield. This donor was condensed with **7** in the presence of the TCTM system to selectively produce the protected trisaccharide **23** in 42% yield. In its NMR spectra observed in $CDCl_3$, the values of one-bond-coupling of the anomeric centers of the interglycosidic linkages[17] indicated the α-linked structure; the $J_{C1,H1}$ values were 168.9 Hz for the $C1^{II}$-$H1^{II}$ bond and 169.3 Hz for the $C1^{III}$-$H1^{III}$ bond. The linkage positions were analyzed by NOE experiments: the irradiation on $H1^{II}$ at 5.08 ppm enhanced the signal of $H2^{I}$ at 4.07 ppm, whereas that of $H1^{III}$ at 5.18 ppm did the signal of $H3^{II}$ at

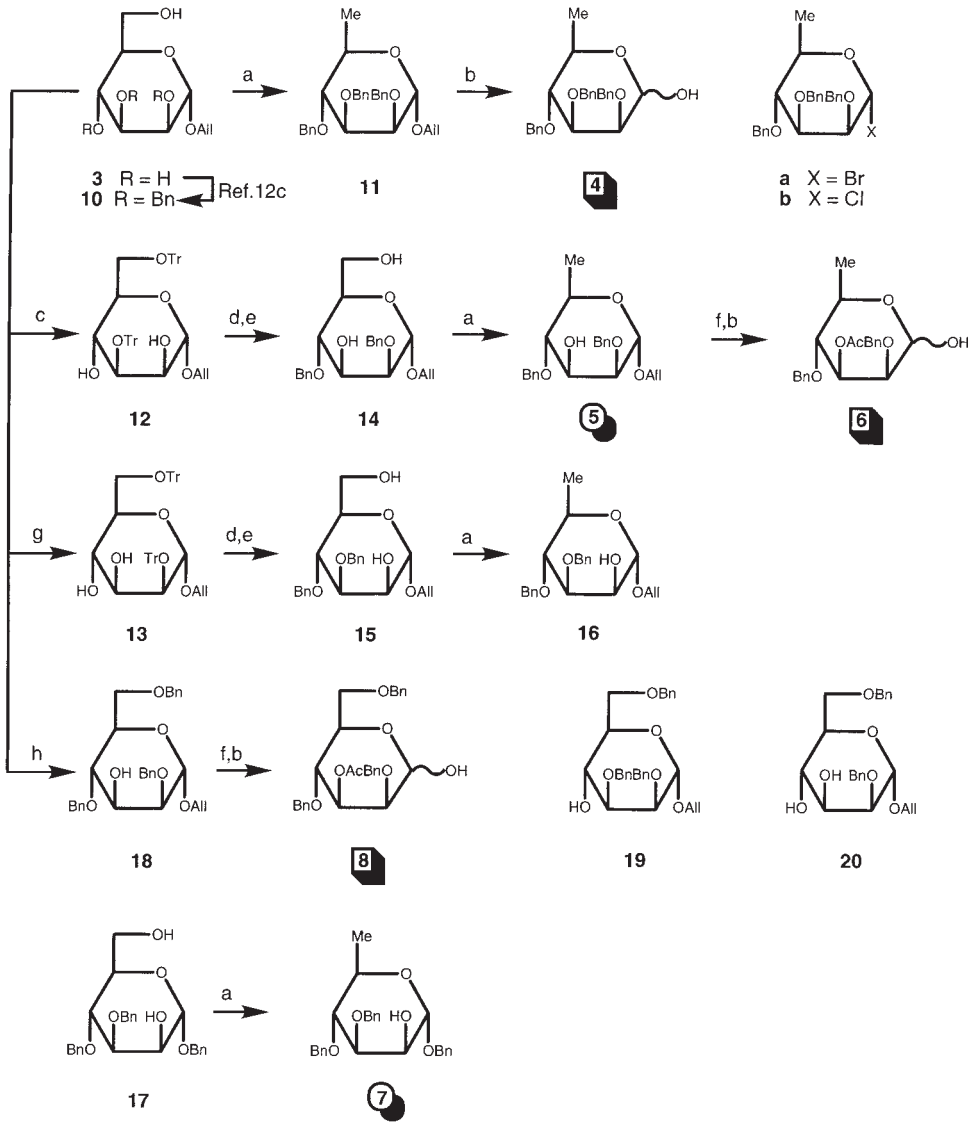

Fig. 3. Synthesis of partially benzylated D-rhamnose derivatives: a. (i) TsCl + pyridine (Py), −10 °C → room temperature (rt), (ii) $LiAlH_4/Et_2O$, 0 °C → reflux; b. $PdCl_2$ + NaOAc/aq AcOH (95%), rt; c. TrCl (2.3 eq) + Py, 55 °C; d. BnBr + NaH/DMF, 0 °C → rt; e. CF_3CO_2H + MeOH/$CHCl_3$, rt; f. Ac_2O + Py, rt; g. TrCl (3.0 eq) + Py, 100 °C; h. BnCl + KOH, 140 °C.

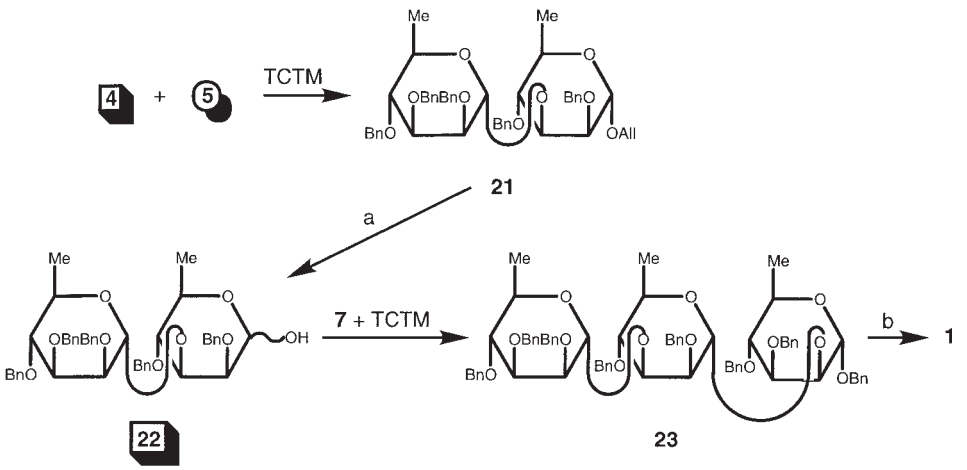

Fig. 4. Synthesis of α-D-Rha*p*-(1 → 3)-α-D-Rha*p*-(1 → 2)-D-Rha*p*-OH (**1**) (TCTM = Me_3SiBr + $CoBr_2$ + *n*-Bu_4NBr + MS4A): a. $PdCl_2$ + NaOAc/aq AcOH (95%), rt; b. H_2, Pd-C(10%)/MeOH, rt.

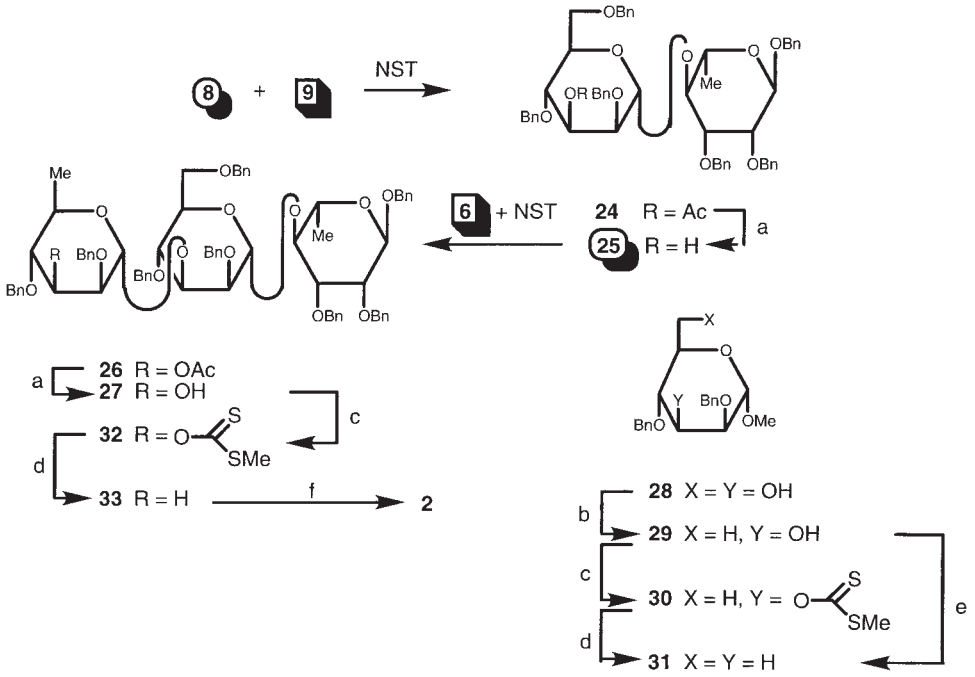

Fig. 5. Synthesis of α-D-Tyv*p*-(1 → 3)-α-D-Man*p*-(1 → 4)-L-Rha*p*-OH (**2**) (NST = NsCl + AgOTf + Et_3N): a. dil NaOMe, rt; b. (i) TsCl + Py, −10 °C → rt, (ii) $LiAlH_4/Et_2O$, 0 °C → reflux; c. (i) NaH/THF, rt, (ii) CS_2/THF, rt, (iii) MeI/THF, rt; d. *n*-Bu_3SnH + AIBN(cat.)/PhMe, N_2, 110 °C; e. (i) Tf_2O + Py/CH_2Cl_2, −30 °C → 20 °C, (ii) *n*-Bu_4NBH_4/PhMe, 50 °C; f. H_2, Pd-C(10%)/MeOH, rt.

4.14 ppm. Total debenzylation gave **1**. Its ^{13}C NMR determined in D_2O agreed well with those reported for the L-form.[18] The observed specific rotation of **1**, being the D-form, was +54° in H_2O; the absolute value agreed with the reported value of the L-form of **1**, −52°,[18] within the experimental errors.

The synthesis of **2** started from condensations of **8** and **9** using an NST system,[4a,5a] composed of *p*-nitrobenzenesulfonyl chloride (NsCl), silver trifluoromethanesulfonate (AgOTf), and triethylamine (Et_3N) (Fig. 5). The α-linked disaccharide **24** was selectively formed in 92% yield. Deacetylation of **24** with methanolic NaOMe gave the acceptor **25**. The final α-selective rhamnosylation of **25** with **6** was conducted in the presence of the TCTM system to afford the trisaccharide **26** selectively only in 25% yield. It appears that the presence of OAc group at C-3 in **6** makes it disarmed to give such a low yield. It was, however, found that the NST system[4a] performed this condensation to selectively form **26** in 90% yield. We considered that the in-situ generated 1-*O*-sulfonates[4d] of **6** is reactive enough despite the presence of the disarming 3-OAc group.[4e] It is known that the 1-OH group is transformed into the 1-Cl group upon a reaction with sulfonyl chloride and a base.[4f–j] We observed that **4** disappeared in the presence of a 1.3 mol. amt. of NsCl and Et_3N in CD_2Cl_2 in a NMR-tube at room temperature to generate the chloride **b** (Fig. 3). It is conceivable that the reactive intermediate of the NST system might have been the 1-OTf derivative generated from the 1-chloride, such as **b** and AgOTf.[4e] However, the possibility of the intervention of 1-ONs as a reactive intermediate giving glycosides directly could not be omitted. In the NMR spectra of **26** observed in $CDCl_3$, the $J_{C1,H1}$ values[17] were 167.8 Hz for the $C1^{II}$-$H1^{II}$ bond and 170.0 Hz for the $C1^{III}$-$H1^{III}$ bond, indicating their α-glycosidic structure. The NOE experiments proved the $C1^{II}$-to-$O4^{I}$ linkage and the $C1^{III}$-to-$O3^{II}$ linkage.

Deacetylation of **26** afforded **27**. Before deoxygenating the D-rhamnosyl moiety of **27** into the antigenic D-tyvelosyl one,[10a,19] we tried to convert a model D-rhamnoside derivative **29**, obtained from a diol **28**,[6a] into a tyvelose derivative **31**. The reduction of a dithiocarbonate of **30** with *n*-Bu_3SnH in toluene with an initiator[20a–d] gave **31** in 48% yield; the starting **29** was obtained in 45% yield.[20e] Deoxygenation via triflate of **29** and its reduction with *n*-Bu_4NBH_4[21a–c] also gave **31** (43%); the parent alcohol **29** was concurrently formed in 25% yield.[21d] Ultrasonication[21a,b] did not give **31**, but afforded only **29** quantitatively.

The trisaccharide derivative **27** was then converted into the dithiocarbonate **32**. The reduction of **32** with *n*-Bu_3SnH in boiling toluene containing an initiator afforded the desired product **33** in 29% yield; the starting **27** was yielded in 38%. The NMR spectra of **33** in $CDCl_3$ clearly showed deoxygenation at the $C\text{-}3^{III}$ position giving a methylene group; the δ-value of $C\text{-}3^{III}$ was 29.5 and those of $H\text{-}3^{III}$ were 1.80 and 2.23. Deoxygenation of **32** via a triflate only gave a complex mixture of many products. The total debenzylation of **33** afforded **2**. The ^1H and ^{13}C NMR spectra determined in D_2O was consistent with its structure: (1) the δ-value of $C\text{-}3^{III}$ was 35.8 and those of $H\text{-}3^{III}$ were 1.85 and 2.02, (2) the $J_{C1,H1}$ value[17] of $C1^{II}$ was 169.5 Hz and that of $C1^{III}$ was 170.0 Hz, and (3) GHMBC experiments showed closs-couplings, indicating the $C1^{II}$-to-$O4^{I}$ linkage and the $C1^{III}$-to-$O3^{II}$ linkage.

In summary, the ditritylated D-mannopyranosides are of use as starting materials for preparing monohydroxy derivatives, **5** and **7**, of D-rhamnose. The donor **6** is useful as a precursor of

tyvelosyl residue in the glycoside **2**. All of the condensations of the building blocks in this study were performed by one-pot-one-stage in-situ activation glycosylation using sugar derivatives in the hemiacetal form.

Experimental[2]

The solvent systems for column chromatography on silica gel (Kanto Chemical, No. 37047; gradient elusion) and thin-layer chromatography (TLC)(Merck, DC-Plastikfolien Kieselgel 60 F 254, Art. 5735) were AcOEt–MeOH (EM), hexane–AcOEt (HE), and PhMe–2-butanone (TK). Hydrogenolytic debenzylation was carried out using a Parr-3911 hydrogenation apparatus under 340 kPa of H_2 at room temperature. Evaporation was carried out under reduced pressure. The melting points were determined on a Yanaco Micro Melting Point Apparatus (Yanagimoto). The optical rotations were measured on a JASCO DIP-180 Digital Polarimeter at room temperature. The ^{1}H and ^{13}C NMR spectra were recorded with a Varian VXR300 spectrometer or a Varian XL-400 spectrometer, along with the measurements of the H,H-COSY, C,H-COSY, and DEPT spectra. The $J_{C1,H1}$ values[17] were determined by gated decoupling with the NOE experiment. The assignments of the spectra of **1**, **2**, **23**, **26**, and **33** were made by auxiliary measurements of HOHAHA, HMQC, HMBC, GHMQC, and differential NOE spectra. The elemental analyses were carried out with a Yanaco CHN Corder MT-5. The LRMS and the HRMS were recorded with a JEOL JMS-AX505H spectrometer, a JEOL JMS-AX505HA spectrometer, and a JEOL JMS-700, respectively. The abbreviations used here for the assigned substituents are: All (allyl), Bn (benzyl), Ns (*p*-nitrobenzenesulfonyl), Tf (trifluoromethanesulfonyl), Tr (triphenylmethyl), and Ts (*p*-toluenesulfonyl).

Commercial NsCl (Wako) was passed through a silica-gel column eluted with benzene, evaporated to dryness, and stored in a dry box in a refrigerator. Syrupy donor and acceptors were purified by chromatography using the HE system and stored in a refrigerator. Commercial AgOTf (Aldrich), Me_3SiBr (Tokyo Kasei), $CoBr_2$ (Wako), *n*-Bu_4NBr (Wako), TsCl (Wako), $LiAlH_4$ (Wako), and anhydrous pyridine (Tokyo Kasei) were used without purification. Acceptor **9** was prepared by a known method[16a,b] from benzyl α-L-rhamnopyranoside.[5c,16c]

The preparation of an acetate for the determination of the NMR spectra was carried out as follows: a sample (ca. 20 mg) was treated with Ac_2O (0.2 mL) and pyridine (0.2 mL) at room temperature overnight, quenched with MeOH (0.2 mL), evaporated to dryness, and chromatographed using the HE system to give a chromatographically pure acetate.

Allyl 2,3,4-Tri-*O*-benzyl-α-D-mannopyranoside (10). To a stirred solution of allyl 6-*O*-trityl-α-D-mannopyranoside (5.0 g, 11 mmol), prepared from **3**[5a] by a known method,[12c] in *N*,*N*-dimethylformamide (DMF, 37.5 mL) containing BnBr (14.2 mL, 119 mmol), NaH (ca. 60% dispersion in oil, 2.235 g, 56 mmol) was added at 0 °C. After the resulting mixture was stirred for 20 min, it was stirred at 20 °C for 1 h. After the addition of MeOH (3.0 mL) at 0 °C and stirring at room temperature, the mixture was evaporated on a boiling water bath. Chromatography with TK system (20:1) afforded a syrup (5.156 g). This (1.019 g, 1.4 mmol) was treated with aq AcOH (80%, 7.9 mL) at 95 °C for 0.5 h. Evaporation and chromatography with TK system (10:1) gave **10** (627.7 mg, 60%); $[\alpha]_D^{25}$ +38° (*c* 0.6, $CHCl_3$) (Ref. 12a, $[\alpha]_D$ +37° (*c* 0.45, $CHCl_3$); Ref. 12b, $[\alpha]_D$ +31.2° (*c* 1.03, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.68 (dt, $J_{4,5}$ = 9.0 Hz, $J_{5,6a} = J_{5,6b}$ = 4.0 Hz, H5), 3.79 (dd, $J_{5,6a}$ = 4.0 Hz, $J_{6a,6b}$ = 11.5 Hz, H2), 3.83 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2), 3.85 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.0 Hz, H3), 3.98 (t, $J_{3,4} = J_{4,5}$ = 9.0 Hz, H4), 4.86 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.84 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 62.4 (C6), 67.9 (All), 72.3 (C5), 74.9 (C3), 75.0 (C2), 80.2 (C4), 97.5 (C1, $J_{C1,H1}$ = 167.5 Hz), 117.3, 133.6 (All). Found: C, 73.24; H, 7.01%. Calcd for $C_{30}H_{34}O_6$: C, 73.45; H, 6.79%.

Allyl 2,3,4-Tri-*O*-benzyl-α-D-rhamnopyranoside (11). To a stirred solution of **10** (0.510 g, 1.04 mmol) in pyridine (2.5 mL, 31 mmol) at −15 °C (bath temperature), TsCl (247.2 mg, 1.3 mmol) was added. The bath temperature was allowed to rise up to 25 °C. The mixture was kept standing overnight and evaporated to dryness. Chromatography using the TK system (100:1→10:1) gave a syrupy tosylate (0.536 g, 80%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.41 (s, Ts), 3.77 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2), 3.83 (~t, $J_{3,4}$ = 8.5 Hz, $J_{4,5}$ = 9.0 Hz, H4), 3.88 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 8.5 Hz, H3), 4.23 (dd, $J_{5,6a}$ = 5.0 Hz, $J_{6a,6b}$ = 10.5 Hz, H6a), 4.28 (dd, $J_{5,6b}$ = 2.5 Hz, $J_{6a,6b}$ = 10.5 Hz, H6b), 4.80 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.80 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6 (Ts), 67.0 (All), 69.3 (C6), 70.2 (C5), 74.2 (C4), 74.7 (C2), 80.1 (C3), 97.0 (C1, $J_{C1,H1}$ = 168.7 Hz), 144.5 (Ts), 117.4, 133.5 (All). This (0.518 g, 0.80 mmol) was dissolved in dry Et_2O (13 mL). To a stirred solution at 0 °C, $LiAlH_4$ (Wako, 1.447 g, 38 mmol) was added in three portions. The mixture was stirred at 0 °C for 0.5 h under anhydrous conditions and then under reflux for 0.5 h. After a careful addition of EtOAc (15.3 mL), the mixture was evaporated to dryness. Chromatography using TK system (100:1→20:1) afforded **11** (294.7 mg, 62 %); $[\alpha]_D^{23}$ +12° (*c* 0.3, CH_2Cl_2) (Ref. 22, L-form, $[\alpha]_D$ −15.1° (*c* 2.01, CH_2Cl_2)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.34 (q, $J_{5,6}$ = 6.0 Hz, H6), 3.63 (t, $J_{3,4} = J_{4,5}$ = 9.0 Hz, H4), 3.72 (dq, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 6.0 Hz, H5), 3.81 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2), 3.89 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.0 Hz, H3), 4.81 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.84 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6), 67.7 (All), 68.1 (C5), 75.1 (C2), 80.2 (C3), 80.6 (C4), 97.2 (C1, $J_{C1,H1}$ = 166.6 Hz), 117.1, 133.9 (All). HRMS (FAB) Found: *m*/*z* 497.2323. Calcd for $C_{30}H_{34}NaO_5$ $[M + Na]^+$: 497.2304.

2,3,4-Tri-*O*-benzyl-D-rhamnopyranose (4). A mixture of **11** (600.0 mg, 1.27 mmol), $PdCl_2$ (Wako, 311.7 mg, 1.8 mmol), NaOAc (573.5 mg, 7.0 mmol), and aq AcOH (95%, 47.2 mL) was stirred at room temperature overnight. After the addition of allyl alcohol (0.95 mL) at 0 °C, the mixture was stirred at room temperature for 0.5 h and evaporated to dryness. Chromatography using TK system (100:1→2:1) afforded **4** (298.3 mg, 54%), mp 92–93 °C, $[\alpha]_D^{23}$ +14° (*c* 1.0, H_2O) (Ref. 22, L-form, mp 88–89 °C; Ref. 23a, L-form, mp 90–92 °C, $[\alpha]_D$ −15.4° ($CHCl_3$); Ref. 23b, L-form, mp 90 °C, $[\alpha]_D^{20}$ −15.0° (*c* 1.0, $CHCl_3$); Ref. 23c, L-form, mp 94–95 °C, $[\alpha]_D^{20}$ −12° (*c* 0.5, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) (60% α) δ 1.33 (q, $J_{5,6}$ = 6.0 Hz, H6α), 1.35 (q, $J_{5,6}$ = 6.0 Hz, H6β), 3.37 (dq, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 6.0 Hz, H5β), 3.57 (t, $J_{3,4} = J_{4,5}$ = 9.0 Hz, H4β), 3.64 (t, $J_{3,4} = J_{4,5}$ = 9.0 Hz, H4α), 3.82 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2α), 3.85 (dd, $J_{1,2}$ = 1.0 Hz, $J_{2,3}$ = 2.0 Hz, H2β), 3.93 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.0 Hz, H3α), 3.93 (dq, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 6.0 Hz, H6α), 4.62 (d, $J_{1,2}$ = 1.0 Hz, H1β), 5.18 (d, $J_{1,2}$ = 2.0 Hz, H1α); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6β), 18.1 (C6α), 68.3 (C5α), 71.6 (C5β), 75.3 (C2α), 76.7 (C2β), 79.8 (C3α), 80.0 (C4β), 80.1 (C4α), 83.1 (C3β), 93.1 (C1α, $J_{C1,H1}$ = 168.1 Hz), 93.4 (C1β, $J_{C1,H1}$ = 160.0 Hz). Found: C, 74.28; H, 6.96%. Calcd for $C_{27}H_{30}O_5$: C, 74.63; H, 6.96%.

Allyl 3,6- and 2,6-Di-*O*-trityl-α-D-mannopyranosides (12

and 13). A mixture of **3** (8.804 g, 40 mmol), TrCl (25 g, 90 mmol), and pyridine (44 mL, 54 mmol) was stirred at 55 °C overnight. After the addition of Et_3N (44 mL), the mixture was evaporated to dryness and chromatographed with the TK system (100:1→3:1) to give **12** (18.84 g, 67 %), $[\alpha]_D^{23}$ +32° (*c* 1.3, $CHCl_3$) (Ref. 14a, $[\alpha]_D^{25}$ +33° (*c* 1, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.73 (br s, OH), 2.07 (br s, OH), 2.78 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2), 3.34 (dd, $J_{5,6a}$ = 5.5 Hz, $J_{5a,5b}$ = 10.0 Hz, H6a), 3.37 (dd, $J_{5,6b}$ = 4.0 Hz, $J_{6a,6b}$ = 10.0 Hz, H6b), 3.63 (m, $J_{4,5}$ = 8.5 Hz, $J_{5,6a}$ = 5.5 Hz, $J_{5,6b}$ = 4.9 Hz, H5), 3.89 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 8.5 Hz, H3), 3.96 (t, $J_{3,4}$ = $J_{4,5}$ = 8.5 Hz, H4), 4.63 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.80 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 64.6 (C6), 67.4 (All), 68.0 (C4), 69.1 (C2), 71.4 (C5), 74.8 (C3), 86.8, 87.3 (Tr), 99.4 (C1, $J_{C1,H1}$ = 167.0 Hz), 116.3, 133.8 (All). Found: C, 79.83; H, 6.39%. Calcd for $C_{47}H_{44}O_6$: C, 80.09; H, 6.29%.

Further elution afforded **13** (3.73 g, 13%), $[\alpha]_D^{25}$ 0° (*c* 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.21 (s, OH), 2.41 (s, OH), 3.43 (dd, $J_{5,6a}$ = 4.0 Hz, $J_{61,6b}$ = 10.0 Hz, H6a), 3.55 (dd, $J_{5,6b}$ = 4.0 Hz, $J_{5,6a}$ = 10.0 Hz, H6b), 3.55 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.0 Hz, H3), 3.56 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2), 3.65 (∼dt, $J_{4,5}$ = 9.0 Hz, $J_{5,6a}$ = 4.0 Hz, $J_{5,6b}$ = 3.0 Hz, H5), 4.35 (t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4), 4.46 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.67 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 63.3 (C6), 67.6 (All), 69.6 (C3), 71.2 (C5), 71.3 (C2), 73.5 (C3), 86.6, 88.4 (Tr), 96.8 (C1), 117.0, 133.7 (All). Found: C, 79.37; H, 6.50%. Calcd for $C_{47}H_{44}O_6 \cdot H_2O$: C, 79.08; H, 6.35%.

After a mixture of **3** (2.87 g, 13 mmol), TrCl (10.9 g, 39 mmol), and pyridine (15 mL, 185 mmol) was stirred at 100 °C overnight, followed by addition of Et_3N (15 mL), evaporation and chromatography afforded **12** (<1 g, <11%) and then **13** (2.50 g, 27%).

The NMR data of the acetate of **12**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.54 (s, Ac), 2.23 (s, Ac), 2.99 (dd, $J_{5,5a}$ = 2.5 Hz, $J_{6a,6b}$ = 10.5 Hz, H6a), 3.14 (dd, $J_{5,6b}$ = 6.0 Hz, $J_{6a,6b}$ = 10.5 Hz, H6b), 3.58 (ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 6.0 Hz, H5), 3.91 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 10.0 Hz, H3), 4.26 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2), 4.74 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.39 (t, $J_{3,4}$ = $J_{4,5}$ = 10.0 Hz, H4), 5.80 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.9, 21.3 (Ac), 63.2 (C6), 67.7 (All), 67.8 (C4), 69.9 (C3), 70.9 (C5), 71.9 (C2), 86.5, 87.4 (Tr), 95.8 (C1, $J_{C1,H1}$ = 170.0 Hz), 169.7, 170.3 (Ac), 116.3, 133.5 (All).

The NMR data of the acetate of **13**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.76 (s, Ac), 1.87 (s, Ac), 3.14 (dd, $J_{5,5a}$ = 4.5 Hz, $J_{6a,6b}$ = 10.5 Hz, H6a), 3.30 (dd, $J_{5,6b}$ = 2.0 Hz, $J_{6a,6b}$ = 10.5 Hz, H6b), 3.84 (ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.5 Hz, $J_{5,6b}$ = 2.0 Hz, H5), 3.86 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 10.0 Hz, H2), 4.12 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.14 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 10.0 Hz, H3), 5.96 (t, $J_{3,4}$ = $J_{4,5}$ = 10. Hz, H4), 5.67 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.5, 21.0 (Ac), 62.5 (C6), 67.0 (C4), 68.0 (All), 70.2 (C5), 71.3 (C3), 71.8 (C2), 86.8, 88.0 (Tr), 97.1 (C1), 117.2, 133.7 (All), 169.2, 170.1 (Ac).

Allyl 2,4-Di-*O*-benzyl-α-D-mannopyranoside (14). To a stirred mixture of **12** (8.686 g, 12.3 mmol), BnBr (4.4 mL, 37 mmol), and DMF (43.3 mL) at 0 °C, NaH (ca. 60% dispersion in oil, 1.472 g, 37 mmol) was added. The resulting mixture was stirred at 0 °C for 0.5 h, and then at room temperature for 2 h. After a careful addition of MeOH (5.2 mL) at 0 °C, the mixture was evaporated to dryness at 95 °C and chromatographed using the TK system (100:1→20:1) to give a syrup (9.05 g). This (8.78 g, 9.9 mmol) was dissolved in $CHCl_3$ (125 mL) containing MeOH (37.6 mL). After the addition of CF_3CO_2H (12.5 mL) under stirring, the solution was kept standing at room temperature for 0.5 h. Evaporation to dryness and chromatography with the TK system (100:1→10:1) yielded **14** (2.656 g, 56%), $[\alpha]_D^{24}$ +35° (*c* 0.5, $CHCl_3$) (Ref. 14a, $[\alpha]_D^{25}$ +28° (*c* 1.25, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.27 (br s, 2H, OH), 3.64 (ddd, $J_{4,5}$ = 8.5 Hz, $J_{5,6a}$ = 4.0 Hz, $J_{5,6b}$ = 3.0 Hz, H5), 3.67 (t, $J_{3,4}$ = $J_{4,5}$ = 8.5 Hz, H4), 3.76 (dd, $J_{1,2}$ = 2.0 H, $J_{2,3}$ = 3.5 Hz, H2), 3.79 (dd, $J_{5,6a}$ = 4.0 Hz, $J_{6a,6b}$ = 11.5 Hz, H6a), 3.86 (dd, $J_{5,6b}$ = 3.0 Hz, $J_{6a,6b}$ = 11.5 Hz, H6b), 4.03 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 8.5 Hz, H3), 4.91 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.85 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 62.3 (C6), 68.0 (All), 71.5 (C5), 71.7 (C3), 76.6 (C4), 78.5 (C5), 96.3 (C1), 117.5, 133.5 (All). Found: C, 68.68; H, 6.91%. Calcd for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05%.

The NMR data of the acetate of **14**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.99 (s, Ac), 2.08 (s, Ac), 3.90 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.5 Hz, H2), 3.92 (t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4), 3.95 (ddd, $J_{4,5}$ = 9.0 Hz, $J_{5,6a}$ = 5.0 Hz, $J_{5,6b}$ = 2.5 Hz, H5), 4.30 (dd, $J_{5,6a}$ = 5.0 Hz, $J_{6a,6b}$ = 12.5 Hz, H6a), 4.35 (dd, $J_{5,6b}$ = 2.5 Hz, $J_{6a,6b}$ = 12.5 Hz, H6b), 4.89 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.28 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.0 Hz, H3), 5.87 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.8, 21.0 (Ac), 63.4 (C6), 68.1 (All), 69.8 (C5), 72.9 (Bn), 73.4 (C4), 73.8 (C3), 74.7 (Bn), 75.9 (C2), 96.7 (C1), 117.6, 133.5 (All), 170.0, 170.7 (Ac).

Allyl 3,4-Di-*O*-benzyl-α-D-mannopyranoside (15). In a similar manner as that for the transformation of **12** into **14**, **13** (1.49 g, 2.1 mmol) was derived into **15** (0.606 g, 72%), $[\alpha]_D^{22}$ +45° (*c* 0.3, $CHCl_3$) (Ref. 14b, $[\alpha]_D^{23}$ +56° (*c* 0.45, $CHCl_3$). Ref. 14c, $[\alpha]_D^{20}$ +109.5° (*c* 1.16, $CHCl_3$). A large difference in the specific rotation was not clarified, but our ^{1}H NMR data shown below agree well with those in Ref. 14c); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.68 (dt, $J_{4,5}$ = 9.0 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 3.0 Hz, H5), 3.80 (dd, $J_{5,6a}$ = 3.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H6a), 3.85 (dd, $J_{5,6b}$ = 3.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H6b), 3.91 (t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4), 3.92 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.0 Hz, H3), 4.05 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2), 4.92 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.87 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 61.9 (C6), 68.1 (All), 68.5 (C2), 71.7 (C5), 74.0 (C4), 80.0 (C3), 98.4 (C1), 117.5, 133.6 (All). HRMS (FAB) Found: *m/z* 423.1815. Calcd for $C_{23}H_{28}NaO_6$ $[M + Na]^+$: 423.1784.

NMR data of the acetate of **15**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.07 (s, Ac), 2.15 (s, Ac), 3.74 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4), 3.88 (ddd, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = 2.0 Hz, $J_{5,6b}$ = 4.5 Hz, H5), 4.03 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.5 Hz, H3), 4.31 (dd, $J_{5,6a}$ = 2.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H6a), 4.36 (dd, $J_{5,6b}$ = 4.5 Hz, $J_{6a,6b}$ = 12.0 Hz, H6b), 4.86 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.39 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.5 Hz, H2), 5.87 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.9, 21.0 (Ac), 63.4 (C6), 68.3 (All), 68.6 (C2), 69.7 (C5), 74.1 (C4), 78.1 (C3), 96.9 (C1, $J_{C1,H1}$ = 168.5 Hz), 118.0, 133.2 (All), 170.3, 170.8 (Ac).

Allyl 2,4-Di-*O*-benzyl-α-D-rhamnopyranoside (5). To a stirred mixture of **14** (2.429 g, 6.1 mmol) and dry pyridine (15.2 mL, 188 mmol) at −15 °C (bath temperature), TsCl (2.267 g, 1.2 mmol) was added, and the bath temperature was allowed to rise up to 25 °C. After being kept standing overnight, MeOH (2.0 mL) was added into the mixture at 0 °C under stirring. The mixture was evaporated to dryness, followed by chromatography using the TK system (100:1→10:1) to give a syrup (1.978 g); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.36 (d, $J_{3,OH}$ = 9.5 Hz, OH), 2.41 (s, Ts), 3.54 (∼t, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 10.0 Hz, H4), 3.72 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.5 Hz, H2), 3.74 (ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.0 Hz, $J_{5,6b}$ = 3.0 Hz, H5), 3.98 (dt, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = $J_{3,OH}$ = 9.5 Hz, H3), 4.22 (dd, $J_{5,6a}$ = 4.0 Hz, $J_{6a,6b}$ = 10.5 Hz, H6a), 4.28 (dd, $J_{5,6b}$ = 3.0 Hz, $J_{6a,6b}$ = 10.5 Hz, H6b), 4.87 (d, $J_{1,2}$ = 2.0 Hz,

H1), 5.81 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6 (Ts), 68.0 (All), 69.2 (C6), 69.3 (C5), 71.8 (C3), 76.0 (C4), 78.3 (C2), 95.8 (C1), 117.5, 133.4 (All), 144.6 (Ts). This (544.4 mg, 0.98 mmol) was dissolved in dry Et_2O (14 mL) and cooled at 0 °C (bath temperature). Then, $LiAlH_4$ (232.3 mg, 6.1 mmol) was added in two portions to the stirring solution. The mixture was efficiently stirred at 0 °C for 10 min, at 20 °C for 10 min, and at 40 °C under reflux for 30 min. After a careful addition of EtOAc (3 mL) under cooling, the mixture was evaporated to dryness and chromatographed using the TK system (100:1→10:1) to give **5** (220.3 mg, 34%), $[\alpha]_D^{24}$ +5° (*c* 1.2, CH_2Cl_2) (Ref. 5h, L-form, $[\alpha]_D^{22}$ −2° (*c* 0.5, CH_2Cl_2). Ref. 24a, L-form, $[\alpha]_D^{25}$ +0.5° (*c* 0.5, CH_2Cl_2)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.34 (q, $J_{5,6}$ = 6.0 Hz, H6), 2.33 (d, $J_{3,OH}$ = 9.5 Hz, OH), 3.34 (t, $J_{3,4} = J_{4,5}$ = 9.5 Hz, H4), 3.71 (dq, $J_{4,5}$ = 9.5 Hz, $J_{4,5}$ = 6.0 Hz, H5), 3.76 (dd, $J_{2,3}$ = 4.0 Hz, $J_{3,4}$ = 9.5 Hz, H2), 3.98 (dt, $J_{2,3}$ = 4.0 Hz, $J_{3,4} = J_{3,OH}$ = 9.5 Hz, H3), 4.87 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.86 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6), 67.3 (C5), 67.8 (All), 71.7 (C3), 78.7 (C2), 82.3 (C4), 96.1 (C1), 117.2, 133.7 (All). Found: C, 71.65; H, 7.26%. Calcd for $C_{23}H_{28}O_5$: C, 71.85; H, 7.34%.

Allyl 3,4-Di-*O*-benzyl-α-D-rhamnopyranoside (16). This was synthesized via an essentially same procedure as that used in the conversion of diol **14** into **5**. A treatment of **15** (0.510 g, 1.3 mmol) with TsCl (0.480 g, 2.5 mmol) and pyridine (3.2 mL, 40 mmol) afforded a syrup (314.5 mg); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.42 (s, Ts), 3.69 (dd, $J_{3,4}$ = 9.0 Hz, $J_{4,5}$ = 10.0 Hz, H4), 3.81 (~dt, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.0 Hz, $J_{5,6b}$ = 3.0 Hz, H5), 3.88 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.0 Hz, H3), 4.02 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2), 4.21 (dd, $J_{5,6a}$ = 4.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H6a), 4.25 (dd, $J_{5,6b}$ = 4.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H6b), 4.84 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.83 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6 (Ts), 68.05 (All), 68.10 (C2), 69.0 (C6), 69.4 (C5), 73.4 (C4), 80.1 (C3), 98.1 (C1, $J_{C1,H1}$ = 169.5 Hz), 144.7 (Ts), 117.7, 133.3 (All). This (227.5 mg, 0.41 mmol) was reduced with $LiAlH_4$ (60 mg, 1.6 mmol) in Et_2O (5.6 mL) to give **16** (87.9 mg, 25%), $[\alpha]_D^{23}$ +51° (*c* 0.3, $CHCl_3$) (Ref. 24b, L-form, $[\alpha]_D^{20}$ −35° (*c* 1, $CHCl_3$); Ref. 24c, L-form, $[\alpha]_D^{20}$ −47.2° (*c* 1.4, $CHCl_3$); Ref. 24d, L-form, $[\alpha]_D$ −43.6° (*c* 1, $CHCl_3$)); ^{1}H NMR($CDCl_3$, 300 MHz) δ 1.32 (q, $J_{5,6}$ = 6.0 Hz, H6), 3.47 (t, $J_{3,4} = J_{4,5}$ = 9.5 Hz, H4), 3.73 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.0 Hz, H5), 3.89 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.5 Hz, H3), 4.07 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2), 4.87 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.86 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.9 (C6), 67.4 (C5), 67.9 (All), 68.6 (C2), 80.1 (C3), 80.6 (C4), 98.2 (C1, $J_{C1,H1}$ = 168.4 Hz), 117.3, 133.8 (All). HRMS (FAB) Found: *m/z* 407.1827. Calcd for $C_{23}H_{28}NaO_5$ $[M + Na]^+$: 407.1834.

NMR data of the acetate of **16**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.34 (q, $J_{5,6}$ = 6.0 Hz, H6), 2.16 (s, Ac), 3.45 (t, $J_{3,4} = J_{4,5}$ = 10.0 Hz, H4), 3.74 (dq, $J_{4,5}$ = 10.0 Hz, $J_{5,6}$ = 6.0 Hz, H5), 3.97 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 10.0 Hz, H3), 4.78 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.40 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.5 Hz, H2), 5.86 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.9 (C6), 21.1 (Ac), 67.8 (C5), 68.0 (All), 69.1 (C2), 78.1 (C3), 80.1 (C4), 96.8 (C1, $J_{C1,H1}$ = 168.0 Hz), 117.5, 133.5 (All), 170.3 (Ac).

Benzyl 3,4-Di-*O*-benzyl-α-D-rhamnopyranoside (7). In a similar manner as that described for **5** derived from diol **14**, this was synthesized via essentially the same procedure as in the case of **5**. The tosylation of diol **17**[6a] (129.1 mg, 0.29 mmol) with TsCl (107 mg, 0.56 mmol) and pyridine (0.72 mL, 8.9 mmol) afforded a syrup (139.8 mg); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.42 (s, Ts), 3.84 (ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 4.0 Hz, H5), 3.71 (dd, $J_{3,4}$ = 9.0 Hz, $J_{4,5}$ = 10.0 Hz, H4), 3.85 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.0 Hz, H3), 4.21 (dd, $J_{5,6a}$ = 2.5 Hz, $J_{6a,6b}$ = 10.5 Hz, H6a), 4.25 (dd, $J_{5,6a}$ = 4.0 Hz, $J_{6a,6b}$ = 10.5 Hz, H6b), 4.30 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.5 Hz, H2), 4.87 (d, $J_{1,2}$ = 2.0 Hz, H1); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6 (Ts), 68.2 (C2), 69.0 (C6), 69.6 (C5), 73.6 (C4), 80.1 (C3), 98.3 (C1), 144.7 (Ts). This (85.0 mg, 0.14 mmol) was then subjected to reduction with $LiAlH_4$ (23.7 mg, 0.62 mmol) in Et_2O (2.5 mL) to give **7** (26.3 mg, 35%), $[\alpha]_D^{25}$ +52° (*c* 0.9, $CHCl_3$) (Ref. 16a, L-form, $[\alpha]_D$ −58° (*c* 0.6, $CHCl_3$); Ref. 18b, $[\alpha]_D$ −49° (*c* 1, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.33 (q, $J_{5,6}$ = 6.0 Hz, H6), 3.48 (t, $J_{3,4} = J_{4,5}$ = 9.5 Hz, H4), 3.82 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.0 Hz, H5), 3.90 (dd, $J_{2,3}$ = 3.5 Hz, H3), $J_{3,4}$ = 9.5 Hz, H3), 4.08 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.5 Hz, H2), 4.91 (d, $J_{1,2}$ = 2.0 Hz, H1); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.9 (C6), 67.6 (C5), 68.7 (C2), 80.0 (C4), 80.2 (C3), 99.3 (C1). Found: C, 73.54; H, 6.89%. Calcd for $C_{27}H_{30}O_5 \cdot 0.5H_2O$: C, 73.11; H, 7.05%.

3-*O*-Acetyl-2,4-di-*O*-benzyl-α-D-rhamnopyranose (6). A mixture of **5** (0.335 g, 0.87 mmol), pyridine (0.5 mL, 6.2 mmol), and Ac_2O (0.5 mL, 5.3 mmol) was kept standing overnight. After the addition of MeOH (1.6 mL) under cooling, the mixture was evaporated to dryness and chromatographed with the TK system (100:1→20:1) to give a syrup (369 mg); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.34 (q, $J_{5,6}$ = 6.0 Hz, H6), 1.97 (s, Ac), 3.64 (t, $J_{3,4} = J_{4,5}$ = 9.5 Hz, H4), 3.81 (dq, $J_{4,5}$ = 9.5 Hz, $J_{4,5}$ = 6.0 Hz, H5), 3.88 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.5 Hz, H2), 4.81 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.24 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.5 Hz, H3), 5.86 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6), 21.0 (Ac), 67.8 (C5), 67.9 (All), 73.8 (C3), 76.3 (C2), 79.2 (C4), 96.8 (C1), 117.3, 133.7 (All), 170.1 (Ac). This (0.121 g, 0.28 mmol) was treated with $PdCl_2$ (70 mg, 0.40 mmol) and NaOAc (257.6 mg, 3.1 mmol) in aq AcOH (95%, 21.2 mL) at room temperature overnight. After the addition of allyl alcohol (42 mL) under cooling, evaporation to dryness and chromatography with the TK system (100:1→10:1) gave **6** (55.0 mg, 50%), $[\alpha]_D^{25}$ −23° (*c* 3.1, $CHCl_3$) (Ref. 23c, L-form, $[\alpha]_D$ +20° (*c* 1.0, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) (70% α), δ 1.33 (q, $J_{5,6}$ = 6.0 Hz, H6α), 1.37 (q, $J_{5,6}$ = 6.0 Hz, H6β), 1.97 (s, Acα), 1.99 (s, Acβ), 3.43 (br, OHα), 3.45 (q, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.0 Hz, H5β), 3.61 (t, $J_{3,4} = J_{4,5}$ = 9.5 Hz, H4β), 3.65 (t, $J_{3,4} = J_{4,5}$ = 9.5 Hz, H4α), 3.77 (br d, $J_{1,OH}$ = 10.0 Hz, OHβ), 3.89 (dd, $J_{1,2}$ = 2.0 Hz, $J_{5,6}$ = 3.5 Hz, H2α), 3.95 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.0 Hz, H2β), 4.03 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.0 Hz, H5α), 4.77 (br d, $J_{1,2}$ = 1.5 Hz, $J_{1,OH}$ = 10.0 Hz, H1β), 4.96 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.5 Hz, H3β), 5.15 (d, $J_{1,2}$ = 2.0 Hz, H1α), 5.28 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.5 Hz, H3α); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.9 (C6β), 18.0 (C6α), 20.9 (Acβ), 21.0 (Acα), 67.8 (C5α), 71.5 (C5β), 73.3 (C3α), 76.1 (C3β), 76.5 (C2α), 77.5 (C2β), 78.3 (C4β), 79.1 (C4α), 92.5 (C1α), 93.3 (C1β), 170.2 (Ac). Found: C, 68.20; H, 6.80%. Calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78%.

Allyl 2,4,6-Tri-*O*-benzyl-α-D-mannopyranoside (18). A mixture of **3** (0.978 g, 4.4 mmol), powdered KOH (0.996 g, 17.8 mmol), and BnCl (19.6 mL, 170 mmol) was strongly stirred at 140 °C for 4.5 h. The mixture was evaporated at 95 °C and chromatographed with the TK system (100:1→10:1) to give **18** (682.3 mg, 31%), followed by the elution of allyl 2,3,6-tri-*O*-benzyl-α-D-mannopyranoside **19** (408.4 mg, 19%), which was identified with a sample prepared previously.[5a] Further elution with the TK system (1:1) afforded allyl 2,6-di-*O*-benzyl-α-D-mannopyranoside **20** (296.1 mg, 17%).

18: $[\alpha]_D^{25}$ +22° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.03 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 8.5 Hz, H3), 5.00 (d, $J_{1,2}$ = 2.0 Hz, H1), 5.88 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 67.9 (All), 69.2

(C6), 71.1 (C5), 71.8 (C3), 76.7 (C4), 78.5 (C5), 96.1 (C1, $J_{C1,H1} = 167.0$ Hz), 117.3, 133.7 (All). Found: C, 73.22; H, 6.81%. Calcd for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99%.

20: $[\alpha]_D^{24}$ +11° (*c* 1.4, $CHCl_3$) (Ref. 14d, $[\alpha]_D^{23}$ +7.2° (*c* 2.1, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.96 (d, $J_{1,2} = 2.0$ Hz, H1), 5.88 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 67.9 (All), 69.8 (C4), 70.3 (C6), 70.8 (C5), 71.5 (C3), 73.0, 73.5 (Bn), 77.9 (C2), 96.2 (C1), 117.3, 133.6 (All), 137.6, 138.1 (Bn). Found: C, 68.38; H, 7.06%. Calcd for $C_{23}H_{28}O_6 \cdot 0.25H_2O$: C, 68.21; H, 7.09%.

NMR data of the acetate of **18**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.96 (s, Ac), 3.71 (dd, $J_{5,6a} = 1.5$ Hz, $J_{6a,6b} = 10.5$ Hz, H6a), 3.80 (dd, $J_{5,6b} = 4.0$ Hz, $J_{6a,6b} = 10.5$ Hz, H6b), 3.85 (ddd, $J_{4,5} = 9.5$ Hz, $J_{5,6a} = 1.5$ Hz, $J_{5,6b} = 4.0$ Hz, H5), 3.89 (dd, $J_{1,2} = 2.0$ H, $J_{2,3} = 3.0$ Hz, H2), 4.06 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4), 4.93 (d, $J_{1,2} = 2.0$ Hz, H1), 5.27 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz, H3, 5.87 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.0 (Ac), 68.0 (All), 69.0 (C6), 71.5 (C5), 73.6 (C4), 73.9 (C3), 76.1 (C2), 96.9 (C1), 117.4, 133.7 (All), 170.1 (Ac).

NMR data of the acetate of **20**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.91 (s, Ac), 2.00 (s, Ac), 3.55 (dd, $J_{5,6a} = 3.5$ Hz, $J_{6a,6b} = 11.0$ Hz, H6a), 3.61 (dd, $J_{5,6b} = 5.0$ Hz, $J_{6a,6b} = 11.0$ Hz, H6b), 3.84 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2), 3.93 (ddd, $J_{4,5} = 10.0$ Hz, $J_{5,6a} = 3.5$ Hz, $J_{5,6b} = 5.0$ Hz, H5), 4.90 (d, $J_{1,2} = 2.0$ Hz, H1), 5.26 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 10.0$ Hz, H3), 5.41 (t, $J_{3,4} = J_{4,5} = 10.0$ Hz, H4), 5.88 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.7, 20.8 (Ac), 67.6 (C4), 68.1 (All), 69.5 (C6), 70.0 (C5), 71.5 (C3), 73.1, 73.5 (Bn), 75.6 (C2), 96.9 (C1), 117.6, 133.5 (All), 138.0, 137.8 (Bn), 170.1 (Ac).

3-*O*-Acetyl-2,4,6-tri-*O*-benzyl-D-mannopyranose (8). A mixture of **18** (453.1 mg, 0.92 mmol), pyridine (2.0 mL, 25 mmol), and Ac_2O (2.0 mL, 21 mmol) was kept standing overnight at room temperature. After the addition of MeOH (2 mL) under cooling, evaporation and chromatography using the TK system (100:1→10:1) yielded the acetate (438.3 mg). This (373.4 mg, 0.70 mmol) was dissolved in aq AcOH (95%, 32 mL) containing NaOAc (384 mg, 4.7 mmol) and $PdCl_2$ (209 mg, 1.2 mmol) was added. The mixture was stirred at 60 °C for 2 h. Evaporation and chromatography using the TK system (100:1→10:1) gave **8** (313.4 mg, 81%), $[\alpha]_D^{23}$ −8° (*c* 1.5, $CHCl_3$) (Ref. 23c. $[\alpha]_D$ −8° (*c* 1.0, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) (75% α) δ 1.95 (s, Acβ), 1.96 (s, Acα), 3.42 (br s, OHα), 3.49 (ddd, $J_{4,5} = 10.0$ Hz, $J_{5,6a} = 2.0$ Hz, $J_{5,6b} = 4.0$ Hz, H5β), 3.68 (dd, $J_{5,6a} = 3.0$ Hz, $J_{6a,6b} = 10.5$ Hz, H6aα), 3.71 (dd, $J_{5,6b} = 4.0$ Hz, $J_{6a,6b} = 10.5$ Hz, H6bα), 3.73 (dd, $J_{5,6a} = 2.0$ Hz, $J_{6a,6b} = 11.0$ Hz, H6aβ), 3.77 (dd, $J_{5,6b} = 4.0$ Hz, $J_{6a,6b} = 11.0$ Hz, H6bβ), 3.88 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2α), 3.92 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3.0$ Hz, H2β), 3.95 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4α), 4.01 (t, $J_{3,4} = J_{4,5} = 10.0$ Hz, H4β), 4.10 (ddd, $J_{4,5} = 9.5$ Hz, $J_{5,6a} = 3.0$ Hz, $J_{5,6b} = 4.0$ Hz, H5α), 4.77 (br d, $J_{1,2} = 1.5$ Hz, $J_{1,OH} = 9.0$ Hz, H1β), 4.97 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 10.0$ Hz, H3β), 5.25 (d, $J_{1,2} = 2.0$ Hz, H1α), 5.31 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz, H3α); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.9 (Acβ), 21.0 (Acα), 68.8 (C6β), 69.3 (C6α), 71.3 (C5α), 72.8 (C4β), 73.4 (C3α), 73.8 (C4α), 75.2 (C5β), 76.3 (C2α and C3β), 77.3 (C2β), 92.5 (C1α), 93.6 (C1β), 170.1 (Ac). Found: C, 70.58; H, 6.45%. Calcd for $C_{29}H_{32}O_7$: C, 70.71; H, 6.55%.

Allyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-rhamnopyranosyl)-(1 → 3)-2,4-di-*O*-benzyl-D-rhamnopyranosides (21). To a stirred mixture of **4** (86.5 mg, 0.20 mmol), **5** (58.9 mg, 0.15 mmol), $CoBr_2$ (43.6 mg, 0.20 mmol), *n*-Bu_4NBr (64.3 mg, 0.20 mmol), molecular sieve 4A (215 mg), and $(CH_2Cl)_2$ (0.61 mL), Me_3SiBr (25.9 μL, 0.20 mmol) was added. The mixture was stirred at room temperature overnight under anhydrous conditions. After the addition of PhMe (3 mL) and powdered $NaHCO_3$ (0.2 mg), the mixture was stirred for 15 min and then transferred onto the top of a silica-gel column, which was eluted with the TK system (100:1→10:1) to give **21** (69.4 mg, 57%) and the β-linked isomer (28.0 mg, 23%).

21: $[\alpha]_D^{26}$ +30° (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.28 (d, $J_{5,6} = 6.0$ Hz, H6^I), 1.31 (d, $J_{5,6} = 6.0$ Hz, H6^{II}), 3.58 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, H4^I), 3.64 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, H4^{II}), 3.73 (dq, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 6.0$ Hz, H5^I), 3.76 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^I), 3.79 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{II}), 3.85 (dq, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 6.0$ Hz, H5^{II}), 4.13 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, H3^I), 4.81 (d, $J_{1,2} = 2.0$ Hz, H1^I), 5.18 (d, $J_{1,2} = 2.0$ Hz, H1^{II}), 5.87 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.9 (C6^{II}), 18.1 (C6^I), 67.8 (All), 68.2 (C5^I), 68.7 (C5^{II}), 75.8 (C2^{II}), 77.9 (C3^I), 78.0 (C2^I), 79.9 (C3^{II}), 80.5 (C4^{II}), 80.9 (C4^I), 96.8 (C1^I, $J_{C1,H1} = 166.5$ Hz), 99.8 (C1^{II}, $J_{C1,H1} = 170.0$ Hz), 116.9, 133.9 (All). Found: C, 74.74; H, 7.05%. Calcd for $C_{50}H_{56}O_9$: C, 74.98; H, 7.05%.

The β-linked isomer: $[\alpha]_D^{25}$ +2° (*c* 2.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.35 (d, $J_{5,6} = 6.0$ Hz, H6^{II}), 1.36 (d, $J_{5,6} = 6.0$ Hz, H6^I), 3.26 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6.0$ Hz, H5^{II}), 3.38 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz, H3^{II}), 3.60 (dd, $J_{3,4} = 8.0$ Hz, $J_{4,5} = 9.0$ Hz, H4^I), 3.63 (dd, $J_{3,4} = 9.5$ Hz, $J_{4,5} = 9.0$ Hz, H4^{II}), 3.75 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^I), 3.76 (dq, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 6.0$ Hz, H5^I), 3.78 (d, $J_{1,2} = 90$ Hz, $J_{2,3} = 3.0$ Hz, H2^{II}), 4.18 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 8.0$ Hz, H3^I), 4.36 (s, $J_{1,2} = 0$ Hz, H1^{II}), 4.89 (d, $J_{1,2} = 2.0$ Hz, H1^I), 5.89 (m, All); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6^{II}), 18.2 (C6^I), 67.8 (All), 67.9 (C5^I), 72.1 (C5^{II}), 75.0 (C2^{II}), 75.2 (C2^I), 77.0 (C3^I), 80.2 (2C, C4^I and C4^{II}), 82.3 (C3^{II}), 96.9 (C1^I, $J_{C1,H1} = 166.7$ Hz), 98.9 (C1^{II}, $J_{C1,H1} = 152.3$ Hz); 117.4, 133.9 (All). Found: C, 74.93; H, 7.07%. Calcd for $C_{50}H_{56}O_9$: C, 74.98; H, 7.05%.

NMR Study Detecting 2,3,4-Tri-*O*-benzyl-α-D-rhamnopyranosyl Bromide (a). To a stirred mixture of **4** (15.5 mg, 0.036 mmol), $CoBr_2$ (9.4 mg, 0.043 mmol), *n*-Bu_4NBr (13.8 mg, 0.043 mmol), MS4A (41 mg), and CD_2Cl_2 containing TMS (1%) (Aldrich, 1.0 mL), Me_3SiBr (5.6 μL, 0.043 mmol) was added at room temperature. After 1 h, the mixture was filtered through a pad of Celite and the ^{1}H NMR spectrum of the filtrate was determined at 300 MHz.

Separately, the bromide **a** was generated as follows: a mixture of **4** (15.5 mg, 0.036 mmol), $AcBr$[25] (4.5 μL, 0.056 mmol), and CD_2Cl_2 containing TMS (1%) (1 mL) was kept standing at room temperature. The ^{1}H NMR spectrum of the solution was determined after 1 h. The spectrum showed that **4** was completely exhausted and **a** was the sole product. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 1.33 (d, $J_{5,6} = 6.5$ Hz, H6), 3.62 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4), 3.86 (ddq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6.5$ Hz, $J_{1,5} = 1.0$ Hz, H5), 4.01 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2), 4.25 (dd, $J_{2,3} = 3.0$ Hz, $J_{4,5} = 9.5$ Hz, H3), 6.45 (dd, $J_{1,2} = 2.0$ Hz, $J_{1,5} = 1.0$ Hz, H1); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 17.5 (C6), 73.1 (C5), 78.5 (C3), 79.4 (C2), 79.7 (C4), 88.9 (C1, $J_{C1,H1} = 181.5$ Hz).

The ^{1}H NMR spectrum of the above-described filtrate was identical with that of **a** at δ 3.8–7.5, indicating a quantitative conversion of **4** into **a**.

To a solution of **4** (15.5 mg, 0.036 mmol) in CD_2Cl_2 containing TMS (1%) (1 mL), Me_3SiBr (5.6 μL, 0.043 mmol) alone was added. The mixture was kept standing for 1 h at room temperature. The ^{1}H NMR spectra of the obtained reaction mixture showed that ca. 30% of **4** remained unreacted, based on the integral value of H6 of **a** (δ 1.33, d, $J_{5,6} = 6.5$ Hz) and those of **4**

(δ 1.27, d, $J_{1,2} = 6.0$ Hz for the α-anomer and δ 1.29, d, $J_{1,2} = 6.0$ Hz for the β-anomer).

NMR Study Detecting 2,3,4-Tri-*O*-benzyl-α-D-rhamnopyranosyl Chloride (b). A solution of **4** (20.0 mg, 0.046 mmol) in $SOCl_2$ (1.0 mL, 13.2 mmol) was kept standing at room temperature overnight.[4k] After evaporation to dryness at 25 °C, the ^{1}H and ^{13}C NMR spectra showed that **4** was completely transformed into the 1-chloride **b**. ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 1.34 (d, $J_{5,6} = 6.5$ Hz, H6), 3.63 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4), 3.96 (ddq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6.5$ Hz, $J_{1,5} = 1.0$ Hz, H5), 3.97 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2), 4.15 (dd, $J_{2,3} = 3.0$ Hz, $J_{4,5} = 9.5$ Hz, H3), 6.09 (br d, $J_{1,2} = 2.0$ Hz, $J_{1,5} = 1.0$ Hz, H1); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ 17.6 (C6), 71.4 (C5), 78.5 (C3), 79.4 (C2), 79.7 (C4), 92.1 (C1, $J_{C1,H1} = 180.0$ Hz).

To a solution of **4** (20.0 mg, 0.046 mmol) and NsCl (13.3 mg, 0.060 mmol) in CD_2Cl_2 (with TMS (1%), ca. 0.5 mL) in a NMR-tube, Et_3N (8.4 μL, 0.060 mmol) was added at room temperature. After 0.5 h, the ^{1}H NMR spectrum of the clear solution showed that **4** disappeared completely and the diagnostic isolated signals of H1 (δ 6.09, br d, $J_{1,2} = 2.0$ Hz, $J_{1,5} = 1.0$ Hz) and H3 (δ 4.15, dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz) of **b** were clearly observed.

***O*-(2,3,4-Tri-*O*-benzyl-α-D-rhamnopyranosyl)-(1 → 3)-2,4-di-*O*-benzyl-D-rhamnopyranose (22).** A mixture of **21** (69.7 mg, 0.087 mmol), NaOAc (76.8 mg, 0.94 mmol), $PdCl_2$ (42.4 mg, 0.24 mmol), and aq AcOH (95%, 3.3 mL) was stirred at room temperature overnight. After the addition of allyl alcohol (32 μL) under cooling, the mixture was evaporated to dryness and chromatographed using the TK system (100:1→10:1) to afford **22** (41.8 mg, 63%), $[\alpha]_D^{23}$ +16° (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) (63% α) δ 1.26 (d, $J_{5,6} = 6.0$ Hz, H6$^I\alpha$), 1.29 (d, $J_{5,6} = 6.0$ Hz, H6^{II}), 1.33 (d, $J_{5,6} = 6.0$ Hz, H6$^I\beta$), 3.36 (dq, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 6.0$ Hz, H5$^I\beta$), 3.54 (~t, $J_{3,4} = 9.5$ Hz, $J_{4,5} = 9.0$ Hz, H4$^{II}\beta$), 3.57 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4$^{II}\alpha$), 3.62 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4$^I\alpha$), 3.65 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, H4$^I\beta$), 3.74 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{II}), 3.76 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2$^I\beta$), 3.77 (dd, $J_{1,2} = 2.0$ Hz, $J_{5,6} = 3.0$ Hz, H2$^I\alpha$), 3.79 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, H3$^I\beta$), 3.83 (dd, $J_{2,3} = 3.0$ Hz, $J_{5,6} = 9.0$ Hz, H3$^{II}\beta$), 3.74 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz, H4$^{II}\alpha$), 3.86 (dq, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 6.0$ Hz, H5$^{II}\beta$), 3.88 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6.0$ Hz, H5$^{II}\alpha$), 3.93 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6.0$ Hz, H5$^I\alpha$), 4.15 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz, H3$^I\alpha$), 4.64 (d, $J_{1,2} = 2.0$ Hz, H1$^I\beta$), 5.15 (d, $J_{1,2} = 2.0$ Hz, H1$^I\alpha$), 5.17 (d, $J_{1,2} = 2.0$ Hz, H1$^{II}\alpha$), 5.22 (d, $J_{1,2} = 2.0$ Hz, H1$^{II}\beta$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.8 (C6$^I\beta$), 18.0 (C6$^I\alpha$), 18.07 (C6$^{II}\alpha$), 18.12 (C6$^{II}\beta$), 68.4 (C5$^I\alpha$), 68.8 (C5$^{II}\alpha$), 69.3 (C5$^{II}\beta$), 71.7 (C5$^I\beta$), 75.75 (C2$^I\beta$), 75.82 (C2$^I\alpha$), 77.1 (C3$^I\alpha$), 78.1 (C3$^I\beta$), 79.0 (C2^{II}), 79.5 (C3$^{II}\beta$), 79.8 (C3$^{II}\alpha$), 80.3 (C4$^I\beta$), 80.5 (C4$^I\alpha$), 80.6 (C4$^{II}\alpha$), 80.9 (C4$^{II}\beta$), 92.0 (C1$^I\beta$), 93.3 (C1$^I\alpha$), 99.7 (C1$^{II}\beta$), 99.8 (C1$^{II}\alpha$). Found: C, 73.67; H, 6.82%. Calcd for $C_{47}H_{52}O_9 \cdot 0.5H_2O$: C, 73.32; H, 6.94%.

Benzyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-rhamnopyranosyl)-(1 → 3)-*O*-(2,4-di-*O*-benzyl-α-D-rhamnopyranosyl)-(1 → 2)-3,4-di-*O*-benzyl-α-D-rhamnopyranoside (23). To a stirred mixture of **7** (33.7 mg, 0.078 mmol), **22** (47 mg, 0.062 mmol), $CoBr_2$ (21.6 mg, 0.099 mmol), *n*-Bu_4NBr (32.0 mg, 0.099 mmol), molecular sieve 4A (94 mg), and $(CH_2Cl)_2$ (0.55 mL), Me_3SiBr (13.0 mL, 0.10 mmol) was added and the mixture was stirred for 16 h at room temperature. After the addition of PhMe (2 mL) and powdered $NaHCO_3$ (0.1 g), the mixture was chromatographed with the TK system (100:1→10:1) to give **23** (30.8 mg, 42%), $[\alpha]_D^{24}$ +21° (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.18 (d, $J_{5,6} = 6.0$ Hz, H6^{II}), 1.26 (d, $J_{5,6} = 6.0$ Hz, H6^{III}), 1.30 (d, $J_{5,6} = 6.0$ Hz, H6^I), 3.44 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, H4^I), 3.52 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, H4^{II}), 3.62 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^{III}), 3.71 (dq, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 6.0$ Hz, H5^I), 3.74 (dq, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 6.0$ Hz, H5^{II}), 3.78 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{III}), 3.78 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6.0$ Hz, H5^{III}), 3.81 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^{II}), 3.87 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz, H3^{III}), 3.90 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, H3^I), 4.07 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, H2^I), 4.14 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, H3^{II}), 4.80 (d, $J_{1,2} = 2.0$ Hz, H1^I), 5.08 (d, $J_{1,2} = 2.0$ Hz, H1^{II}), 5.18 (d, $J_{1,2} = 2.0$ Hz, H1^{III}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.8 (C6^I), 17.9 (C6^{II}), 18.0 (C6^{III}), 68.2 (C5^I), 68.5 (C5^{III}), 68.6 (C6^{II}), 74.6 (C2^I), 77.0 (C3^{II}), 77.91 (C2^{II}), 79.94 (2C, C3^I and C2^{III}), 80.4 (C4^{III}), 80.5 (C4^I), 80.8 (C4^{II}), 98.1 (C1^I, $J_{C1,H1} = 169.9$ Hz), 99.0 (C1^{II}, $J_{C1,H1} = 168.9$ Hz), 99.5 (C1^{III}, $J_{C1,H1} = 169.3$ Hz). Found: C, 75.37; H, 6.90%. Calcd for $C_{74}H_{80}O_{13}$: C, 75.49; H, 6.85%.

***O*-α-D-Rhamnopyranosyl-(1 → 3)-*O*-α-D-rhamnopyranosyl-(1 → 2)-D-rhamnopyranose (1).** The hydrogenation of **23** (20.5 mg, 0.017 mmol) over Pd on C (10%, 34 mg) in MeOH (6 mL) was carried out at room temperature overnight. Filtration of the catalyst, evaporation, and chromatography with EM system (100:1→2:1) gave **1** (7.0 mg, 88%), $[\alpha]_D^{24}$ +54° (*c* 0.3, H_2O) (Ref. 18b, $[\alpha]_D$ −52° (*c* 0.5, H_2O)); ^{1}H NMR (D_2O, 400 MHz) (α-anomer) δ 1.24 (6H, d, $J_{5,6} = 6.5$ Hz, H6^I and H6^{II}), 1.27 (3H, d, $J_{5,6} = 6.5$ Hz, H6^{III}), 3.43 (dd, $J_{3,4} = 10.0$ Hz, $J_{4,5} = 9.5$ Hz, H4^{III}), 3.45 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^I), 3.50 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^{II}), 3.76 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6.5$ Hz, H5^{II}), 3.81 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.5$ Hz, H3^{II}), 3.81 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 10.0$ Hz, H3^{III}), 3.82 (2H, dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6.5$ Hz, H5^I and H5^{III}), 3.86 (dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.5$ Hz, H3^I), 3.88 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3.0$ Hz, H2^I), 4.03 (dd, $J_{1,2} = 1.5$ Hz, $J_{5,6} = 3.0$ Hz, H2^{III}), 4.12 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.5$ Hz, H2^{II}), 4.92 (d, $J_{1,2} = 2.0$ Hz, H1^{II}), 5.01 (d, $J_{1,2} = 2.0$ Hz, H1^{III}), 5.20 (d, $J_{1,2} = 1.5$ Hz, H1^I); ^{13}C NMR (D_2O, 100 MHz) δ 19.1 (2C, C6^{II} and C6^{III}), 19.3 (C6^I), 71.1 (C5^I), 71.8 (C5^{III}), 71.9 (C5^{II}), 72.4 (C3^I), 72.5 (C2^{II}), 72.8 (2C, C2^{III} and C3^{III}), 74.0 (C4^{II}), 74.6 (C4^{III}), 75.0 (C4^I), 81.6 (C3^I), 81.8 (C2^I), 95.0 (C1^I, $J_{C1,H1} = 169.0$ Hz), 104.4 (C1^{II}, $J_{C1,H1} = 170.0$ Hz), 104.8 (C1^{III}, $J_{C1,H1} = 170.0$ Hz). HRMS (FAB) Found: *m/z* 479.1778. Calcd for $C_{18}H_{32}NaO_{13}$ $[M + Na]^+$: 479.1741.

Benzyl *O*-(3-*O*-Acetyl-2,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1 → 4)-2,3-di-*O*-benzyl-α-L-rhamnopyranoside (24). To a stirred mixture of **8** (166.3 mg, 0.34 mmol), **9** (125.5 mg, 0.29 mmol), NsCl (160.1 mg, 0.72 mmol), AgOTf (185.8 mg, 0.72 mmol), and CH_2Cl_2 (2.2 mL), Et_3N (100.8 μL, 0.72 mmol) was added at −60 °C (bath temperature), and the mixture was stirred. The bath temperature was allowed to rise up to 0 °C (ca. 0.3 °C per min) and the mixture was stirred for 16 h at room temperature. After the addition of PhMe (5 mL) and powdered $NaHCO_3$ (0.34 mg), the mixture was chromatographed with the TK system (100:1→10:1) to give **24** (240.9 mg, 92%), $[\alpha]_D^{24}$ −2° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.15 (d, $J_{5,6} = 6.0$ Hz, H6^I), 1.99 (s, Ac), 3.29 (br s, 2H, H6^{II}), 3.70 (dq, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 6.0$ Hz, H5^I), 3.78 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.0$ Hz, H3^I), 3.80 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, H4^I), 3.83 (2H, dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.5$ Hz, H2^I and H2^{II}), 4.08 (br s, H5^{II}), 4.10 (~t, $J_{3,4} = 9.0$ Hz, $J_{5,6} = 9.5$ Hz, H4^{II}), 4.85 (d, $J_{1,2} = 2.0$ Hz, H1^I), 5.21 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.0$ Hz, H3^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.1 (C6^I), 21.1 (Ac), 68.4 (2C, C5^I and C6^{II}), 71.6 (C5^{II}), 73.3 (C3^I), 74.0 (C3^{II}), 74.6 (C4^{II}), 75.6 (C4^I), 78.2 (C2^{II}), 78.5 (C2^{II}), 97.3 (C1^I, $J_{C1,H1} = 166.0$ Hz), 98.6 (C1^{II}, $J_{C1,H1} = 168.0$ Hz), 170.0 (Ac). Found: C, 73.91; H, 6.69%. Calcd for $C_{56}H_{60}O_{11}$:

C, 73.99; H, 6.65%.

Benzyl *O*-(2,4,6-Tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-2,3-di-*O*-benzyl-α-L-rhamnopyranoside (25). A mixture of **24** (230.0 mg, 0.25 mol), MeOH (10 mL), 1,4-dioxane (1.0 mL), and dil NaOMe (7%, 0.3 mL) was stirred at room temperature overnight. After the addition of AcOH (0.1 mL), evaporation and chromatography with the TK system (100:1→10:1) furnished **25** (196.3 mg, 89%), $[\alpha]_D^{24}$ −8° (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.18 (d, $J_{5,6}$ = 6.0 Hz, H6^{I}), 2.29 (d, $J_{3,OH}$ = 9.0 Hz, OH), 3.31 (dd, $J_{5,6a}$ = 2.0 Hz, $J_{6a,6b}$ = 11.0 Hz, H6a^{II}), 3.36 (dd, $J_{5,6b}$ = 3.0 Hz, $J_{5,6}$ = 11.0 Hz, H6b^{II}), 3.66 (dq, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 6.0 Hz, H5^{I}), 3.70 (dd, $J_{1,2}$ = 1.5 Hz, $J_{5,6}$ = 3.5 Hz, H2^{II}), 3.76 (dt, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = $J_{3,OH}$ = 9.0 Hz, H3^{I}), 3.82 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2^{I}), 3.84 (t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4^{I}), 3.93 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 10.0 Hz, H3^{II}), 3.99 (t, $J_{3,4}$ = $J_{4,5}$ = 10.0 Hz, H4^{II}), 4.85 (d, $J_{1,2}$ = 2.0 Hz, H1^{I}), 5.11 (d, $J_{1,2}$ = 1.5 Hz, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.3 (C6^{I}), 68.4 (C5^{I}), 68.6 (C6^{II}), 71.3 (C5^{II}), 71.8 (C3^{II}), 74.6 (C4^{I}), 76.4 (C4^{II}), 78.1 (C2^{I}), 78.2 (C2^{II}), 78.5 (C3^{I}), 97.4 (C1^{I}, $J_{C1,H1}$ = 167.5 Hz), 97.7 (C1^{II}, $J_{C1,H1}$ = 167.5 Hz). Found: C, 74.84; H, 6.82%. Calcd for $C_{54}H_{58}O_{10}$: C, 74.80; H, 6.74%.

Benzyl *O*-(3-*O*-Acetyl-2,4-di-*O*-benzyl-α-D-rhamnopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-2,3-di-*O*-benzyl-α-L-rhamnopyranoside (26). To a stirred mixture of **6** (34.4 mg, 0.089 mmol), **25** (58.0 mg, 0.067 mmol), NsCl (40.1 mg, 0.18 mmol), AgOTf (46.5 mg, 0.18 mmol), and CH_2Cl_2 (0.40 mL), Et_3N (25.2 μL, 0.18 mmol) was added and the mixture was stirred for 16 h at room temperature. After the addition of PhMe (3 mL) and powdered $NaHCO_3$ (0.2 g), the mixture was chromatographed with the TK system (100:1→10:1) to give **26** (74.2 mg, 90%), $[\alpha]_D^{22}$ +11° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.14 (d, $J_{5,6}$ = 6.0 Hz, H6^{I}), 1.26 (d, $J_{5,6}$ = 6.0 Hz, H6^{III}), 1.94 (s, Ac), 3.29 (dd, $J_{5,6a}$ = 2.0 Hz, $J_{6a,6b}$ = 11.0 Hz, H6^{II}), 3.34 (dd, $J_{5,6b}$ = 3.0 Hz, $J_{6a,6b}$ = 11.0 Hz, H6b^{II}), 3.61(t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^{III}), 3.62 (dq, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 6.0 Hz, H5^{I}), 3.68 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2^{II}), 3.80 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.0 Hz, H3^{II}), 3.81 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2^{I}), 3.83 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.0 Hz, H5^{III}), 3.84 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.0 Hz, H3^{I}), 3.85 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2^{III}), 4.00 (ddd, $J_{4,5}$ = 9.0 Hz, $J_{5,6a}$ = 2.0 Hz, $J_{5,6b}$ = 3.0 Hz, H5^{II}), 4.09 (2H, $J_{3,4}$ = $J_{4,5}$ = 6.0 Hz, H4^{I} and H4^{II}), 4.84 (d, $J_{1,2}$ = 2.0 Hz, H1^{I}), 5.06 (d, $J_{1,2}$ = 2.0 Hz, H2^{II}), 5.17 (d, $J_{1,2}$ = 2.0 Hz, H1^{III}), 5.32 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.5 Hz, H3^{III}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.1 (C6^{III}), 18.3 (C6^{I}), 21.1 (Ac), 68.3 (C5^{III}), 68.4 (C5^{I}), 68.6 (C6^{II}), 72.4 (C5^{II}), 73.5 (C3^{III}), 74.6 (C3^{II}), 75.2 (C3^{I}), 77.0 (C2^{III}), 77.1 (C2^{II}), 78.0 (C4^{II}), 78.5 (C2^{I}), 78.6 (C3^{I}), 79.2 (C4^{III}), 97.4 (C1^{I}, $J_{C1,H1}$ = 169.0 Hz), 98.7 (C1^{II}, $J_{C1,H1}$ = 167.8 Hz), 99.6 (C1^{III}, $J_{C1,H1}$ = 170.0 Hz), 170.1 (Ac). HRMS (FAB) Found: *m*/*z* 1257.5548. Calcd for $C_{76}H_{82}O_{15}Na$ $[M + Na]^+$: 1257.5551.

The condensation of **6** (55.9 mg, 0.145 mmol) and **25** (94.7 mg, 0.109 mmol) in $(CH_2Cl)_2$ in the presence of Me_3SiBr (18.5 μL, 0.143 mmol), $CoBr_2$ (31.2 mg, 0.143 mmol), *n*-Bu_4NBr (45.9 mg, 0.143 mmol), and MS4A (109.7 mg) afforded **26** (32.9 mg, 25%).

Benzyl *O*-(2,4-Di-*O*-benzyl-α-D-rhamnopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-2,3-di-*O*-benzyl-α-L-rhamnopyranoside (27). A mixture of **26** (230.2 mg, 0.19 mmol), MeOH (30 mL), 1,4-dioxane (2 mL), and dil NaOMe (7%, 1 mL) was stirred at room temperature overnight. After the addition of AcOH (0.4 mL), evaporation and chromatography with the TK system (100:1→10:1) afforded **27** (211.0 mg, 95%), $[\alpha]_D^{23}$+15° (*c* 1.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.18 (d, $J_{5,6}$ = 6.0 Hz, H6^{I}), 1.32 (d, $J_{5,6}$ = 6.0 Hz, H6^{III}), 2.02 (br s, OH), 3.35 (dd, $J_{5,6a}$ = 2.5 Hz, $J_{6a,6b}$ = 9.0 Hz, H6a^{II}), 3.36 (t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4^{III}), 3.38 (dd, $J_{5,6b}$ = 2.5 Hz, $J_{6a,6b}$ = 9.0 Hz, H6b^{II}), 3.69 (dq, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 6.0 Hz, H5^{III}), 3.72 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2^{II}), 3.76 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.5 Hz, H2^{III}), 3.83 (dq, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 6.0 Hz, H5^{I}), 3.85 (2H, dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.0 Hz, H3^{I} and H3^{II}), 3.88 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.0 Hz, H2^{I}), 4.06 (dt, $J_{4,5}$ = 9.0 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 2.5 Hz, H5^{II}), 4.06 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.0 Hz, H3^{III}), 4.10 (t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4^{II}), 4.14 (t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4^{I}), 4.90 (d, $J_{1,2}$ = 2.0 Hz, H1^{I}), 5.10 (d, $J_{1,2}$ = 2.0 Hz, H1^{II}), 5.27 (d, $J_{1,2}$ = 1.5 Hz, H1^{III}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6^{III}), 18.2 (C6^{I}), 67.7 (C5^{III}), 68.4 (C5^{I}), 68.6 (C6^{II}), 71.5 (C3^{III}), 71.8 (C5^{II}), 74.5 (C3^{II}), 75.3 (C3^{III}), 77.4 (C2^{II}), 77.6 (C4^{I}), 78.5 (C2^{I}), 78.6 (C3^{I}), 79.2 (C2^{III}), 82.3 (C4^{III}), 97.4 (C1^{I}, $J_{C1,H1}$ = 166.0 Hz), 98.7 (C1^{II}, $J_{C1,H1}$ = 167.9 Hz), 98.8 (C1^{III}, $J_{C1,H1}$ = 167.2 Hz). Found: C, 74.18; H, 6.75%. Calcd for $C_{74}H_{80}O_{14}$: C, 74.47; H, 6.76%.

Methyl 2,4-Di-*O*-benzyl-α-D-rhamnopyranoside (29). This was prepared as described for **5**. The tosylation of methyl 2,4-di-*O*-benzyl-α-D-mannopyranoside (**28**)[6a] (0.371 g, 0.99 mmol) with TsCl (246 mg, 1.3 mmol) and pyridine (2.3 mL, 28 mmol), followed by chromatography with the TK system, afforded a tosylate (378 mg). This (314.3 mg, 0.60 mmol) was reduced with $LiAlH_4$ (94.8 mg, 2.5 mmol) in Et_2O (8.3 mL) for 30 min at reflux temperature followed by chromatography with the TK system, to give **29** (129.7 mg, 44%); $[\alpha]_D^{23}$ +14° (*c* 0.8, $CHCl_3$) (Ref. 26, $[\alpha]_D^{16}$ +14.8° (*c* 1.9, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.34 (d, $J_{5,6}$ = 6.0 Hz, H6), 3.32 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4), 3.33 (s, OMe), 3.66 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.0 Hz, H5), 3.72 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.5 Hz, H2), 3.93 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.5 Hz, H3), 4.71 (d, $J_{1,2}$ = 1.5 Hz, H1); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6), 54.7 (Me), 67.0 (C5), 71.7 (C3), 78.7 (C2), 82.3 (C4), 98.0 (C1). Found: C, 70.31; H, 7.31%. Calcd for $C_{21}H_{26}O_5$: C, 70.03; H, 7.26%.

Methyl 2,4-Di-*O*-benzyl-α-D-tyvelopyranoside (31). A. A mixture of **29** (37.0 mg, 0.10 mmol), imidazol (0.4 mg, 0.006 mmol), NaH (60% in oil, 10.7 mg, 0.27 mmol), and THF (0.51 mL) was stirred at room temperature for 1.5 h. To this, CS_2 (32 μL, 0.53 mmol) was added and the mixture was further stirred at room temperature for 3.5 h. After the addition of MeI (32 μL, 0.51 mmol), the mixture was stirred overnight at room temperature. Neutralization with AcOH (10 μL), evaporation and chromatography with the TK system afforded methyl 2,4-di-*O*-benzyl-3-*O*-(methylthio)thiocarbonyl-α-D-rhamnopyranoside (**30**) (45.4 mg, 98%); $[\alpha]_D^{24}$ +10° (*c* 0.7, $CHCl_3$) (Ref. 20c, L-form, $[\alpha]_D$ − 4.4° ($CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.37 (d, $J_{5,6}$ = 6.0 Hz, H6), 2.54 (s, SMe), 3.34 (s, OMe), 3.79 (dq, $J_{4,5}$ = 9.0 Hz, $J_{5,6}$ = 6.0 Hz, H5), 3.85 (t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, H4), 4.14 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.5 Hz, H2), 4.66 (d, $J_{1,2}$ = 2.0 Hz, H1), 6.02 (d, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.0 Hz, H3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6), 19.2 (SMe), 54.7 (OMe), 67.6 (C5), 75.1 (C2), 78.8 (C4), 83.2 (C3), 99.2 (C1), 215.1 (C=S). Found: C, 61.11; H, 6.23%. Calcd for $C_{23}H_{28}O_5S_2$: C, 61.58; H, 6.29%. This (24.5 mg, 0.055 mmol) was heated in PhMe (1.5 mL), containing *n*-Bu_3SnH (18.6 μL, 0.071 mmol) and azobisisobutyronitrile (AIBN, 0.4 mg, 0.002 mmol), at 115 °C (bath temperature) under N_2 for 3 h. Chromatography using the HE system afforded **31** (9.0 mg, 47%); $[\alpha]_D^{22}$ +66° (*c* 0.4, $CHCl_3$) (Ref. 20c, L-form, $[\alpha]_D$ −58° ($CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.31 (d, $J_{5,6}$ = 6.0 Hz, H6), 1.71 (ddd, $J_{2,3a}$ = 3.0 Hz, $J_{3a,3e}$ = 13.0 Hz, $J_{3a,4}$ = 11.0 Hz, H3a), 2.22 (dddd, $J_{1,3e}$ = 1.0

Hz, $J_{2,3e} = 3.0$ Hz, $J_{3a,3e} = 13.0$ Hz, $J_{3e,4} = 4.0$ Hz, H3e), 3.36 (s, OMe), 3.45 (ddd, $J_{3a,4} = 11.0$ Hz, $J_{3e,4} = 4.0$ Hz, $J_{4,5} = 9.0$ Hz, H4), 3.58 (dt, $J_{1,2} = 1.5$ Hz, $J_{2.3a} = J_{2,3e} = 3.0$ Hz, H2), 3.71 (dq, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 6.0$ Hz, H5), 4.58 (br, H1); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.1 (C6), 54.5 (Me), 68.0 (C5), 29.5 (C3), 75.0 (C2), 75.4 (C4), 98.2 (C1, $J_{C1,H1} = 165.0$ Hz). HRMS (FAB) Found: m/z 365.1700. Calcd for $C_{21}H_{26}NaO_4$ $[M + Na]^+$: 365.1729.

The slower-moving starting material **29** (9.0 mg, 45%) was recovered.

B. To a stirred mixture of **29** (24.1 mg, 0.067 mmol), pyridine (134.9 μL, 1.67 mmol), and CH_2Cl_2 (1.14 mL) at −30 °C (bath temperature), Tf_2O (Tokyo Kasei, 202.5 μL, 1.23 mmol) was added, and the temperature was gradually raised to 20 °C during 40 min. After stirring was continued for 30 min at 20 °C, hexane (2 mL) and H_2O (33.7 μL, 1.9 mmol) were added to the mixture at −10 °C. After being stirred for 15 min at 20 °C, the mixture was transferred onto a silica-gel column and developed with the TK system (100:1→10:1) to give a triflate (22.0 mg). This was dissolved into PhMe (1.1 mL) containing n-Bu_4NBH_4 (Aldrich, 115.5 mg, 0.45 mmol), and the mixture was stirred overnight for 50 °C. Chromatography with the TK system (100:1→10:1) gave **31** (9.9 mg, 43%) and **29** (6.0 mg, 25%).

When reduction was conducted under ultrasonical treatments, **31** did not form and **29** was quantitatively obtained.

Benzyl *O*-[2,4-Di-*O*-benzyl-3-*O*-(methylthio)thiocarbonyl-α-D-rhamnopyranosyl]-(1 → 3)-(2,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1 → 4)-2,3-di-*O*-benzyl-α-L-rhamnopyranoside (32). To a stirred mixture of **27** (185.3 mg, 0.16 mmol), imidazol (1.8 mg, 0.03 mmol), and THF (1.56 mL), NaH (ca. 60% in oil dispersion, 32.4 mg, 0.81 mmol) was added. The mixture was stirred at room temperature for 1.5 h. To this mixture, CS_2 (96.5 μL, 1.6 mmol) was added. The mixture was stirred at room temperature for 3.5 h to give a yellow mixture. Then, MeI (96.5 mL, 1.5 mmol) was added. The mixture was further stirred at room temperature overnight. After the addition of AcOH (46.2 μL, 0.81 mmol) to the resulting heterogeneous mixture, the mixture was evaporated and chromatographed with the TK system (100:1→10:1) to give **32** (186.3 mg, 93%), $[\alpha]_D^{22}$ +6° (*c* 1.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.14 (d, $J_{5,6} = 6.0$ Hz, $H6^{III}$), 1.29 (d, $J_{5,6} = 6.0$ Hz, $H6^{I}$), 2.55 (s, SMe), 3.29 (dd, $J_{5,6a} = 2.0$ Hz, $J_{6a,6b} = 11.0$ Hz, $H6a^{II}$), 3.39 (dd, $J_{5,6b} = 3.0$ Hz, $J_{5,6} = 11.0$ Hz, $H6b^{II}$), 3.65 (dq, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 6.0$ Hz, $H5^{I}$), 3.70 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, $H2^{II}$), 3.80 (2H, dd, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 9.0$ Hz, $H3^{I}$ and $H3^{II}$), 3.82 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, $H2^{I}$), 3.82 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, $H4^{III}$), 3.88 (dq, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 6.0$ Hz, $H5^{III}$), 4.00 (ddd, $J_{4,5} = 9.0$ Hz, $J_{5,6a} = 2.0$ Hz, $J_{5,6b} = 3.0$ Hz, $H5^{II}$), 4.10 (2H, t, $J_{3,4} = J_{4,5} = 9.0$ Hz, $H4^{I}$ and $H4^{II}$), 4.14 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, $H2^{III}$), 4.85 (d, $J_{1,2} = 2.0$ Hz, $H1^{I}$), 5.08 (d, $J_{1,2} = 2.0$ Hz, $H1^{II}$), 5.22 (d, $J_{1,2} = 2.0$ Hz, $H1^{III}$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 ($C6^{I}$), 18.3 ($C6^{III}$), 19.2 (SMe), 68.4 (2C, $C5^{I}$ and $C5^{III}$), 68.6 ($C6^{II}$), 72.4 ($C5^{II}$), 74.6 ($C3^{II}$), 75.2 ($C4^{I}$), 76.6 ($C2^{III}$), 77.4 ($C2^{II}$), 77.9 ($C4^{II}$), 78.4 ($C3^{I}$), 78.6 ($C4^{III}$), 78.8 ($C2^{I}$), 82.9 ($C3^{III}$), 96.8 ($C1^{II}$, $J_{C1,H1} = 167.0$ Hz), 97.4 ($C1^{I}$, $J_{C1,H1} = 166.5$ Hz), 99.3 ($C1^{III}$, $J_{C1,H1} = 165.0$ Hz), 215.0 (C=S). Found: C, 71.00; H, 6.39%. Calcd for $C_{76}H_{82}O_{14}S_2$: C, 71.11; H, 6.44%.

Benzyl *O*-(2,4-Di-*O*-benzyl-α-D-tyvelopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1 → 4)-2,3-di-*O*-benzyl-α-L-rhamnopyranoside (33). A mixture of **32** (81.9 mg, 0.064 mmol), n-Bu_3SnH (33.4 μL, 0.127 mmol), and PhMe (5.7 mL) was stirred at room temperature under N_2 for 20 min. After the addition of AIBN (2.0 mg, 0.012 mmol), the mixture was stirred at 110 °C under N_2 for 2 h. The mixture was evaporated and chromatographed with the TK system (100:1→10:1) to give **33** (21.9 mg, 29%), $[\alpha]_D^{23}$ +15° (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.11 (d, $J_{5,6} = 6.0$ Hz, $H6^{I}$), 1.25 (d, $J_{5,6} = 6.0$ Hz, $H6^{III}$), 1.80 (ddd, $J_{2,3ax} = 3.0$ Hz, $J_{3ax,4} = 11.0$ Hz, $J_{3ax,3eq} = 13.0$ Hz, $H3ax^{III}$), 2.23 (dt, $J_{2,3eq} = J_{3eq,4} = 4.0$ Hz, $J_{3ea,3eq} = 13.0$ Hz, $H3eq^{III}$), 3.27 (dd, $J_{5,6a} = 2.0$ Hz, $J_{6a,6b} = 11.0$ Hz, $H6a^{II}$), 3.30 (dd, $J_{5,6b} = 3.0$ Hz, $J_{6a,6b} = 11.0$ Hz, $H6b^{II}$), 3.46 (ddd, $J_{3eq,4} = 4.0$ Hz, $J_{3ax,4} = 11.0$ Hz, $J_{4,5} = 9.0$ Hz, $H4^{III}$), 3.62 (dd, $J_{1,2} = 0$ Hz, $J_{2,3ax} = 3.0$ Hz, $J_{2,3eq} = 4.0$ Hz, $H2^{III}$), 3.64 (dq, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 6.0$ Hz, $H5^{I}$), 3.70 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, $H2^{II}$), 3.76 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, $H4^{I}$), 3.79 (dd, $J_{2,3} = 2.0$ Hz, $J_{3,4} = 9.0$ Hz, $H3^{I}$), 3.80 (t, $J_{1,2} = J_{2,3} = 2.0$ Hz, $H2^{I}$), 3.85 (dq, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 6.0$ Hz, $H5^{III}$), 3.97 (∼t, $J_{4,5} = 9.5$ Hz, $J_{5,6a} = 2.0$ Hz, $J_{5,6b} = 3.0$ Hz, $H5^{II}$), 4.04 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, $H4^{II}$), 4.15 (dd, $J_{2,3} = 2.0$ Hz, $J_{3,4} = 9.5$ Hz, $H3^{II}$), 4.83 (d, $J_{1,2} = 2.0$ Hz, $H1^{I}$), 5.03 (d, $J_{1,2} = 2.0$ Hz, $H1^{II}$), 5.10 (s, $H1^{III}$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.1 ($C6^{III}$), 18.2 ($C6^{I}$), 29.5 ($C3^{III}$), 68.4 ($C5^{I}$), 68.6 ($C6^{II}$), 68.7 ($C5^{III}$), 72.2 ($C5^{II}$), 74.5 ($C2^{I}$), 75.3 ($C4^{II}$), 75.4 ($C4^{III}$), 75.6 ($C2^{III}$), 76.2 ($C3^{II}$), 77.5 ($C2^{II}$), 78.5 ($C3^{I}$), 78.6 ($C4^{I}$), 97.4 ($C1^{I}$, $J_{C1,H1} = 167.5$ Hz), 98.7 ($C1^{III}$, $J_{C1,H1} = 166.7$ Hz), 98.8 ($C1^{II}$, $J_{C1,H1} = 166.7$ Hz). HRMS (FAB) Found: m/z 1199.5491. Calcd for $C_{74}H_{80}NaO_{13}$ $[M + Na]^+$: 1199.5497.

Further elution with TK system (10:1), **27** (28.7 mg, 38%) was recovered.

***O*-α-D-Tyvelopyranosyl-(1 → 3)-*O*-α-D-mannopyranosyl-(1 → 4)-L-rhamnopyranose (2).** Hydrogenation of **29** (23.6 mg, 0.020 mmol) over Pd on C (10%, 69 mg) in MeOH (6 mL) was carried out at room temperature overnight. Filtration of the catalyst, evaporation, and chromatography with the EM system (100:1→2:1) afforded **2** (7.2 mg, 79%), $[\alpha]_D^{25}$ +86° (*c* 0.4, H_2O); ^{1}H NMR (D_2O, 400 MHz) (70%) δ 1.22 (3H, d, $J_{5,6} = 6.5$ Hz, $H6^{III}$), 1.27 (3H, d, $J_{5,6} = 6.5$ Hz, $H6^{I}$), 1.85 (ddd, $J_{2,3ax} = 3.0$ Hz, $J_{3ax,4eq} = 13.0$ Hz, $J_{3ax,4} = 11.0$ Hz, $H3ax^{III}$), 2.02 (∼dt, $J_{2,3eq} = 3.0$ Hz, $J_{3ax,3eq} = 13.0$ Hz, $J_{3eq,4} = 4.5$ Hz, $H3eq^{III}$), 3.42 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, $H4^{I}\beta$), 3.48 (dq, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 6.5$ Hz, $H5^{I}\beta$), 3.49 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, $H4^{I}\alpha$), 3.59 (ddd, $J_{3ax,4} = 11.0$ Hz, $J_{3eq,4} = 4.5$ Hz, $J_{4,5} = 9.5$ Hz, $H4^{III}$), 3.68 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.0$ Hz, $H3^{I}\beta$), 3.75 (dd, $J_{5,6a} = 5.0$ Hz, $J_{6a,6b} = 12.0$ Hz, $H6a^{II}$), 3.76 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6.5$ Hz, $H5^{III}$), 3.78 (dt, $J_{4,5} = 9.0$ Hz, $J_{5,6a} = J_{5,6b} = 5.0$ Hz, $H5^{II}$), 3.82 (dd, $J_{5,6b} = 5.0$ Hz, $J_{6a,6b} = 12.0$ Hz, $H6b^{II}$), 3.86 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.0$ Hz, $H3^{I}\alpha$ and $H3^{II}$), 3.89 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.5$ Hz, $H2^{I}\alpha$), 3.93 (t, $J_{3,4} = J_{4,5} = 9.0$ Hz, $H4^{II}$), 3.94 (dq, $J_{4,5} = 9.0$ Hz, $J_{5,6} = 6.5$ Hz, $H5^{I}\alpha$), 4.03 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.0$ Hz, $H2^{III}$), 4.04 (dd, $J_{1,2} = 2.0$ Hz, $J_{2,3} = 3.5$ Hz, $H2^{II}$), 4.84 (d, $J_{1,2} = 2.0$ Hz, $H1^{III}$), 4.93 (d, $J_{1,2} = 2.0$ Hz, $H1^{II}$), 5.07 (d, $J_{1,2} = 2.0$ $H1^{I}\alpha$), 5.08 (d, $J_{1,2} = 1.5$ Hz, $H1^{I}\beta$); ^{13}C NMR (D_2O, 100 MHz) δ 19.2 ($C6^{III}$), 19.5 ($C6^{I}$), 35.8 ($C3^{III}$), 63.1 ($H6^{II}$), 68.3 ($H5^{II}$), 69.3 ($H4^{III}$), 69.7 ($H5^{I}\alpha$), 69.9 ($C2^{III}$), 71.4 ($H3^{I}\alpha$), 72.6 ($C5^{III}$), 72.7 ($C2^{II}$), 73.5 ($C2^{I}\alpha$ and $C5^{I}\beta$), 74.0 ($C2^{I}\beta$), 74.1 ($C3^{I}\beta$), 75.8 ($C4^{II}$), 80.4 ($C3^{II}$), 83.8 ($H4^{I}\beta$), 84.2 ($C4^{I}\alpha$), 96.0 ($C1^{I}\beta$, $J_{C1,H1} = 159.0$ Hz), 96.2 ($C1^{I}\alpha$, $J_{C1,H1} = 169.0$ Hz), 103.7 ($C1^{III}$, $J_{C1,H1} = 169.5$ Hz), 103.8 ($C1^{II}$, $J_{C1,H1} = 170.0$ Hz). HRMS (FAB) Found: m/z 479.1762. Calcd for $C_{18}H_{32}NaO_{13}$ $[M + Na]^+$: 479.1741.

References

1 a) B. G. Davis, *J. Chem. Soc., Perkin Trans. 1*, **2000**, 2137.

b) G. Capozzi, S. Menichetti, and C. Nativi, *Methods Princ. Med. Chem.*, **7** (New Trends in Synthetic Medicinal Chemistry), 221 (2000). c) S. J. Danishefsky and J. R. Allen, *Angew. Chem., Int. Ed.*, **39**, 836 (2000). d) K. Toshima, *Carbohydr. Res.*, **327**, 15 (2000). e) O. Seitz, *CHEMBIOCHEM*, **1**, 214 (2000). f) M. Nits and D. R. Bundle, "Glycosciences," ed by B. Fraser-Reid, K. Tatsuta, and J. Thiem, Springer-Verlag, Berlin, Heidelberg, New York (2001), Vol. II, p. 1497. g) G. Magnusson and U. J. Nilsson, "Glycosciences," ed by B. Fraser-Reid, K. Tatsuta, and J. Thiem, Springer-Verlag, Berlin, Heidelberg, New York (2001), Vol. II, p. 1543. h) K. C. Nicolaou and H. J. Mitchell, *Angew. Chem., Int. Ed.*, **40**, 1576 (2001).

2 M. Hirooka, M. Terayama, E. Mitani, S. Koto, A. Miura, K. Chiba, A. Takabatake, and T. Tashiro, *Bull. Chem. Soc. Jpn.*, **75**, 1301 (2002).

3 a) Ref. 4 of the foregoing report. b) M. J. Ford and S. V. Ley, *Synlett*, **1990**, 255. c) S. Suda and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **66**, 1211 (1993). d) N. Morishima and Y. Mori, *Bioorg. Med. Chem.*, **4**, 1799 (1996). e) H. M. Nguyen, Y. Chen, S. G. Duron, and D. Y. Gin, *J. Am. Chem. Soc.*, **123**, 8766 (2001). f) H. Yamada and T. Hayashi, *Carbohydr. Res.*, **337**, 581 (2002). g) H. Jona, H. Mandai, W. Charasiri, K. Takeuchi, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **75**, 291 (2002). Early examples: h) A. M. Gakhokidze, *Zh. Obshch. Khim.*, **11**, 117 (1941). i) A. M. Gakokidze and N. K. Kutidze, *Zh. Obshch. Khim.*, **22**, 247 (1952). j) F. Micheel and A. Böckmann, *Makromol. Chem.*, **51**, 97 (1962).

4 a) S. Koto, T. Sato, N. Morishima, and S. Zen, *Bull. Chem. Soc. Jpn.*, **53**, 1761 (1980). b) S. Koto, N. Morishima, and S. Zen, *Bull. Chem. Soc. Jpn.*, **55**, 1543 (1982). c) S. Koto, N. Morishima, C. Kusuhara, S. Sekido, T. Yoshida, and S. Zen, *Bull. Chem. Soc. Jpn.*, **55**, 2995 (1982). d) S. Koto, N. Morishima, M. Owa, and S. Zen, *Carbohydr. Res.*, **130**, 73 (1984). e) R. Eby and C. Schuerch, *Carbohydr. Res.*, **34**, 79 (1974). f) R. S. Tipson, *Adv. Carbohydr. Chem.*, **8**, 107 (1953). g) K. Hess and L. Kinze, *Chem. Ber.*, **70**, 1139 (1937). h) B. Helferich and A. Gnüchtel, *Chem. Ber.*, **71**, 712 (1938). i) A. L. Bernoulli and H. Stauffer, *Helv. Chim. Acta*, **23**, 615 (1940). j) H. J. Jennings, *Can. J. Chem.*, **46**, 2799 (1968). k) P. W. Austin, F. E. Hardy, J. G. Buchanan, and J. Baddiley, *J. Chem. Soc.*, **1965**, 1419.

5 a) S. Koto, K. Asami, M. Hirooka, K. Nagura, M. Takizawa, S. Yamamoto, N. Okamoto, M. Sato, H. Tajima, T. Yoshida, N. Nonaka, T. Sato, S. Zen, K. Yago, and F. Tomonaga, *Bull. Chem. Soc. Jpn.*, **72**, 765 (1999). b) S. Koto, A. Kusunoki, and M. Hirooka, *Bull. Chem. Soc. Jpn.*, **73**, 967 (2000). c) M. Hirooka, Y. Mori, A. Sasaki, S. Koto, Y. Shinoda, and A. Morinaga, *Bull. Chem. Soc. Jpn.*, **74**, 1679 (2001).

6 a) S. Koto, N. Morishima, T. Yoshida, M. Uchino, and S. Zen, *Bull. Chem. Soc. Jpn.*, **56**, 1171 (1983). b) Y. E. Tsvetkov, P. I. Kitov, L. V. Backinowsky, and N. K. Kochetkov, *J. Carbohydr. Chem.*, **15**, 1027 (1996). c) N. Morishima and Y. Mori, *Chem. Pharm. Bull.*, **47**, 1481 (1999).

7 S. Koto, N. Morishima, Y. Mori, H. Tanaka, S. Hayahi, Y. Iwai, and S. Zen, *Bull. Chem. Soc. Jpn.*, **60**, 2301 (1987).

8 a) B. Lindberg, *Adv. Carbohydr. Chem. Biochem.*, **48**, 279 (1990). b) D. A. Johnson and H.-W. Liu, "Comprehensive Natural Products Chemistry," ed by D. Barton, K. Nakanishi, and O. Meth-Cohn, ed by B. M. Pinto, Elsevier, Amsterdam (1999), Vol. 3, p. 311. c) Y. A. Knirel, A. S. Shashkov, B. A. Dmitriev, N. K. Kochetkov, N. V. Kasyanchuk, and I. Y. Zhakharova, *Bioorg. Khim.*, **6**, 1851 (1980). d) A. R. W. Smith, S. E. Zamze, S. M. Munro, K. J. Carter, and R. C. Hignett, *Eur. J. Biochem.*, **149**, 73 (1985). e) A. S. Shashkov, Y. A. Knirel, N. V. Tanatar, and N. K. Kochetkov, *Carbohydr. Res.*, **146**, 346 (1986). f) S. Yokota, S. Kaya, S. Sawada, T. Kawamura, Y. Araki, and E. Ito, *Eur. J. Biochem.*, **167**, 203 (1987). g) T. L. Arsenault, D. B. MacLean, W. Zou, and W. A. Szarek, *Can. J. Chem.*, **72**, 1376 (1994). h) S. Cérantola and H. Montrozier, *Eur. J. Biochem.*, **246**, 360 (1997). i) S. N. Senchenkova, A. S. Shashkov, M. L.Kecskés, B. C. Ahohuendo, Y. A. Knirel, and K. Rudolph, *Carbohydr. Res.*, **329**, 831 (2000). j) E. L. Zdorovenko, V. V. Ovod, G. V. Zatonsky, A. S. Shashkov, N. A. Kocharova, and Y. A. Knirel, *Carbohydr. Res.*, **330**, 505 (2001). k) S. N. Senchenkova, X. Huang, P. Laux, Y. A. Knirel, A. S. Shashkov, and K. Rudolph, *Carbohydr. Res.*, **337**, 1723 (2002)

9 a) Y. E. Tsvetkov, L. V. Backinowsky, and N. K. Kochetkov, *Carbohydr. Res.*, **193**, 75 (1989). b) W. Zou, A. K. Sen, W. A. Szarek, and D. B. MacLean, *Can. J. Chem.*, **71**, 2194 (1993).

10 a) U. Mamat, U. Seydel, D. Grimmecke, O. Holst, and E. T. Rietschel, "Comprehensive Natural Products Chemistry," ed by D. Barton, K. Nakanishi, and O. Meth-Cohn, ed by B. M. Pinto, Elsevier, Amsterdam (1999), Vol. 3, p. 179. b) C. G. Hellerqvist, B. Lindberg, S. Svensson, T. Holme, and A. A. Lindberg, *Acta Chem. Scand.*, **23**, 1588 (1969). c) C. G. Hellerqvist, J. Hoffman, B. Lindberg, Å. Pilotti, and A. A. Lindberg, *Acta Chem. Scand.*, **25**, 1512 (1971). d) A. Weintraub, A. A. Lindberg, P. Lipniunas, and B. Nilsson, *Glycoconjugate J.*, **5**, 207 (1988).

11 a) H. B. Borén, P. Garegg, and N.-H. Wallin, *Acta Chem. Scand.*, **26**, 1082 (1972). b) G. Ekborg, P. J. Garegg, and B. Gotthammar, *Acta Chem. Scand.*, **B29**, 765 (1975). c) N. K. Kochetkov, V. I. Targov, N. N. Malysheva, and A. S. Shashkov, *Tetrahedron*, **36**, 1099 (1980). d) T. Iversen and D. R. Bundle, *Carbohydr. Res.*, **103**, 29 (1982). e) M. A. Probert, J. Zhang, and D. R. Bundle, *Carbohydr. Res.*, **296**, 149 (1996). f) J. Zhang, A. Otter, D. R. Bundle, *Bioorg. Med. Chem.*, **4**, 1989 (1996).

12 a) Jpn. Kokai Tokkyo Koho, JP 59 36690 (84 36690); *Chem. Abstr.*, **102**, 7029z (1985). b) PCT Int. Appl., WO 00 52020; *Chem. Abstr.*, **133**, 208122p (2000). c) T. Ogawa and H. Yamamoto, *Carbohydr. Res.*, **137**, 79 (1985).

13 a) T. Ogawa, S. Nakabayashi, and T. Kitajima, *Carbohydr. Res.*, **114**, 225 (1983). b) H. Paulsen, J. P. Lorentzen, and W. Kutscher, *Carbohydr. Res.*, **136**, 153 (1985).

14 a) T. Ogawa and T. Nukada, *Carbohydr. Res.*, **136**, 135 (1985). b) O. Srivastava and O. Hindsgaul, *Can. J. Chem.*, **64**, 2324 (1986). c) H. Paulsen and B. Helpap, *Carbohydr. Res.*, **216**, 289 (1991). d) R. D. Marwood, A. M. Riley, D. J. Jenkins, and B. V. L. Potter, *J. Chem. Soc., Perkin Trans. 1*, **2000**, 1935.

15 a) D. Dubreuil, J. Cleophax, and A. Loupy, *Carbohydr. Res.*, **252**, 149 (1994). b) J. Stanek, Jr., "Carbohydrate Chemistry," Topics in Current Chemistry, ed by J. Thiem, Springer-Verlag, Berlin, Heidelberg (1990), Vol. 154, p. 209. c) S. Koto, K. Takenaka, N. Morishima, A. Sugimoto, and S. Zen, *Bull. Chem. Soc. Jpn.*, **57**, 3603 (1984).

16 a) A. Lipták, P. Fügedi, and P. Nánási, *Carbohydr. Res.*, **65**, 209 (1978). b) J. S. Brimacombe and L. C. N. Tucker, *Carbohydr. Res.*, **5**, 36 (1967). c) B. Danieli, F. Peri, G. Roda, G. Carrea, and S. Riva, *Tetrahedron*, **55**, 2045 (1999).

17 K. Bock and C. Pedersen, *J. Chem. Soc., Perkin Trans. 2*, **1974**, 293.

18 a) V. Pozsgay, P. Nánási, and A. Neszmélyi, *J. Chem. Soc., Chem. Commun.*, **1979**, 828. b) V. Pozsgay, P. Nánási, and A. Neszmélyi, *Carbohydr. Res.*, **90**, 215 (1981).

19 a) A. A. Lindberg and L. L. Minor, "Methods in

Microbiology," ed by T. Bergan, Academic Press, New York (1984), Vol. 15, p. 1. b) V. Pozsgay, *Adv. Carbohydr. Chem. Biochem.*, **56**, 153 (2000).

20 a) D. H. R. Barton, J. A. Ferreira, and J. C. Jaszberenyi, "Preparative Carbohydrate Chemistry," ed by S. Hanessian, Marcel Dekker, Inc., New York (1997), p. 151. b) J. Manuel, G. Fernandez, and C. O. Mellet, *Sulfur Rep.*, **19**, 61 (1996). c) V. Pozsgay and A. Neszmélyi, *Carbohydr. Res.*, **85**, 143 (1980). d) H. N. Yu, P. Zhang, C.-C. Ling, and D. R. Bundle, *Tetrahedron: Asymmetry*, **11**, 465 (2000). e) R. H. Bell, D. Horton, D. M. Williams, and E. Winter-Mihaly, *Carbohydr. Res.*, **58**, 109 (1977).

21 a) K. Sato and A. Yoshitomo, *Chem. Lett.*, **1995**, 39. b) K. Zegelaar-Jaarsveld, S. C. van der Plas, G. A. van der Marel, and J. H. van Boom, *J. Carbohydr. Chem.*, **15**, 665 (1996). c) K. Sato, A. Yoshitomo, and Y. Takai, *Bull. Chem. Soc. Jpn.*, **70**, 885 (1997). d) V. Pozsgay and A. Neszmélyi, *Tetrahedron Lett.*, **21**, 211 (1980).

22 D. P. Larson and C. H. Heathcock, *J. Org. Chem.*, **62**, 8406 (1997).

23 a) J. M. J. Fléchet and H. H. Baer, *Carbohydr. Res.*, **42**, 369 (1975). b) H. Paulsen, W. Kutschker, and O. Lockoff, *Chem. Ber.*, **114**, 3233 (1981). c) S. Koto, N. Morishima, K. Takenaka, K. Kanemitsu, N. Shimoura, M. Kawase, S. Kojiro, T. Nakamura, T. Kawase, and S. Zen, *Bull. Chem. Soc. Jpn.*, **62**, 3549 (1989).

24 a) B. M. Pinto, M. M. W. Buiting, and K. B. Reimer, *J. Org. Chem.*, **55**, 2177 (1990). b) P. Westheim, P. E. de Haan, M. J. Dees, and J. H. van Boom, *Carbohydr. Res.*, **180**, 195 (1988). c) J. Zhang, J. Mao, H. Chen, and M. Cai, *Tetrahedron: Asymmetry*, **5**, 2283 (1994). d) E. Bousquet, M. Khitri, L. Ley, F. Nicotra, L. Panza, and G. Russo, *Carbohydr. Res.*, **311**, 171 (1988).

25 S. Koto, N. Morishima, H. Sato, Y. Sato, and S. Zen, *Bull. Chem. Soc. Jpn.*, **58**, 120 (1985).

26 Y. Fang, F. Kong, and Q. Wong, *J. Carbohydr. Chem.*, **6**, 169 (1987).