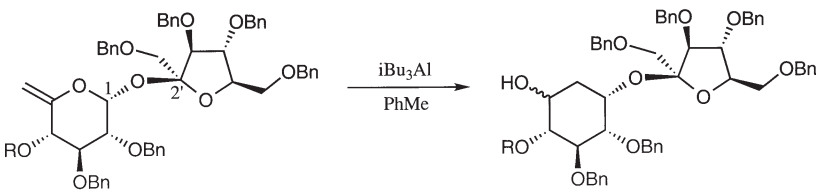
Application of the Triisobutylaluminum-Promoted Reductive Rearrangement to Sucrose-5-enes

BÉRENGÈRE DU ROIZEL, ANA M. P. HENRIQUES, ALAN J. PEARCE, AND PIERRE SINAŸ*
École Normale Supérieure, Département de Chimie, associé au CNRS, 24 rue Lhomond, 75231 Paris Cédex 05, France

(Received 2 August 2000 and in revised form 19 Nov 2000)

Abstract. Carbohydrate-based vinyl acetals (5-hex-enopyranosides) undergo reductive rearrangement with triisobutylaluminum (TIBAL) to afford highly functionalized cyclohexanes in which both the aglycon and anomeric stereochemistry are retained. Here, we report the first application of this process to the rearrangement of hex-5-enopyranosides of sucrose in which the interglycosidic oxygen atom of the vinyl acetal system links the anomeric centers of both monosaccharide units. The sucrose-derived 5-hex-enopyranoside **1** undergoes smooth reductive rearrangement with TIBAL to afford the (1→2′) ether-linked pseudo-disaccharide **2** in 34% yield. The rearrangement is accompanied by some loss of stereochemical integrity at C-2′ due to a competitive exo-cleavage of the interglycosidic (O-C2′) bond, hence diastereomers at C-2′ are also obtained in 12% yield. The 4-*O*-allyl-protected sucrose-5-ene **3** is similarly transformed into the corresponding (1→2′) ether-linked pseudo-disaccharide **4**, illustrating the compatibility of the allyl group with the TIBAL reaction conditions.



1 R=Bn
3 R=allyl

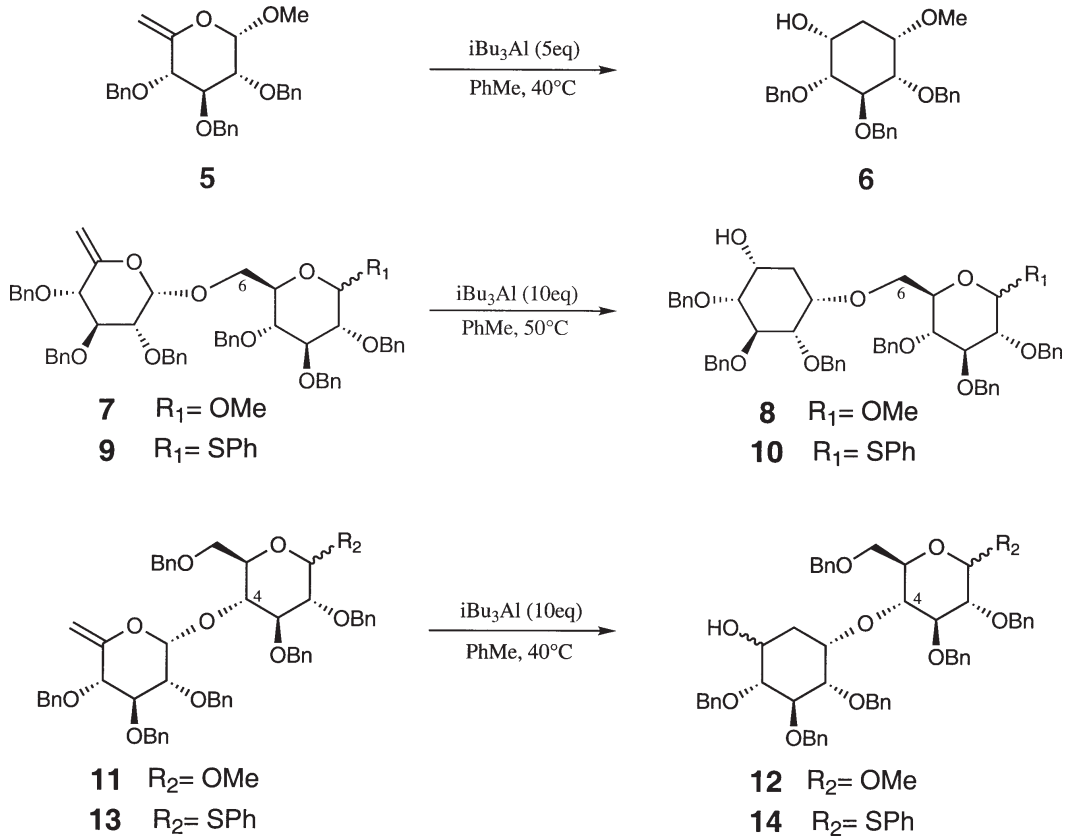
2 R=Bn
4 R=allyl

INTRODUCTION

The Lewis acid-promoted transformation of sugar-based vinyl acetals into carbocycles provides a direct approach to the synthesis of highly functionalized enantiomerically pure cyclohexanes.[1] We have developed an efficient methodology for the preparation of such cyclohexanes by the reductive rearrangement of carbohydrate-based vinyl acetals using triisobutylaluminum (TIBAL) as the Lewis acid.[2] Thus, 5-hex-enopyranosides such as **5** undergo reductive rearrangement with TIBAL to afford highly functionalized cyclohexanes such as **6**, in which both the aglycon and anomeric stereochemistry are retained (Scheme 1).

This versatile TIBAL-promoted rearrangement has also been applied to 5-hex-enopyranosides containing different aglycon moieties including *S*-, *Se*-, and *C*-aryl glycosides.[3] When applied to hex-5-enopyranosides **7**, **9** and **11**, **13** containing sugar aglycons, this led to transformation of the pyranose ring at the non-reducing end of the disaccharide into a carbocycle affording (1→6) and (1→4) ether-linked pseudo-disaccharides[4] **8**, **10** and **12**, **14**, respectively (Scheme 1), the latter of which was subsequently transformed into a 5′a-carbadisaccharide.[5] Furthermore, tandem[6] and cascade[7] variants of the

*Author to whom correspondence should be addressed. E-mail: pierre.sinay@ens.fr



Scheme 1. Typical examples of the TIBAL-promoted reductive rearrangement.

TIBAL-promoted rearrangement have been demonstrated for bis- and polyunsaturated systems, respectively.

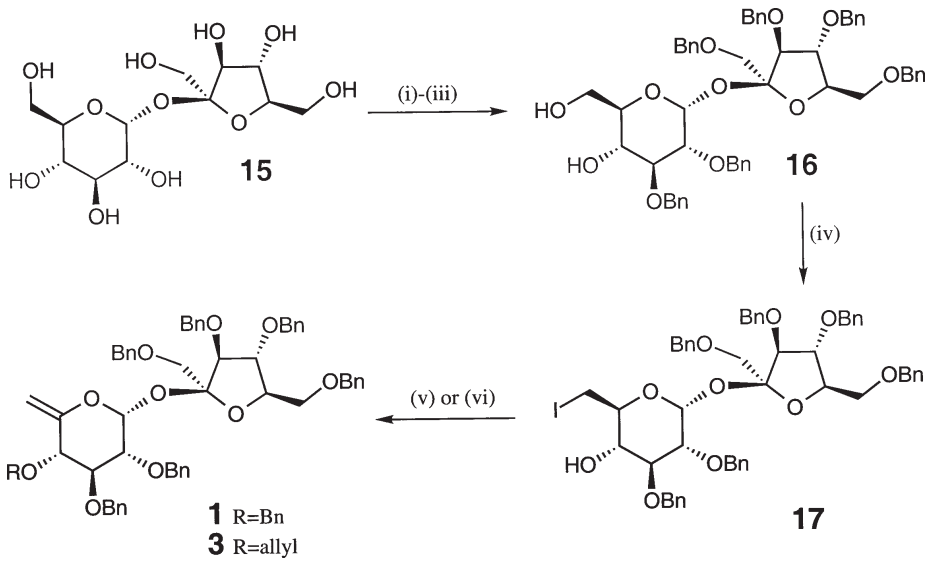
As part of our program to evaluate the wider scope and limitations of the TIBAL-promoted reductive rearrangement,[8] we herein report the first application of this process to the rearrangement of hex-5-enopyranosides (**1** and **3**) of sucrose, a non-reducing disaccharide. In contrast to previous systems, the interglycosidic oxygen atom of the vinyl acetal system links the anomeric centers of both monosaccharide units.

RESULTS AND DISCUSSION

Sucrose **15** was readily transformed into the sucrose-5-enes **1** and **3** using the synthesis summarized in Scheme 2. Acetonation of sucrose afforded 4,6-isopropylidene-sucrose,[9] which was benzylated using benzyl bromide and NaH in DMF, and subsequently hydrolyzed to afford the known 4,6-diol **16**.[10] Selective iodination of the primary alcohol of **16** was achieved using Garegg and Samuelsson's conditions[11] to afford iodide **17** in 93% yield. Iodide **17** underwent smooth benzylation-elimination with NaH in DMF containing benzyl bromide to afford the per-benzylated sucrose-5-ene **1** in 98% yield. The structure of **1** was confirmed by ^{13}C NMR spectroscopy, which showed clear signals for the exocyclic double bond (δ = 153.8, s, C-5 and 96.3, t, C-6). Similarly, iodide **17** underwent one-pot allylation-elimination with NaH in DMF containing allyl bromide to give the 4-*O*-allyl sucrose-5-ene **3** in 88% yield. The presence of the exocyclic double bond in **3** was confirmed by ^{13}C NMR spectroscopy (δ = 154.1, s, C-5 and 96.1, t, C-6).

Reaction of sucrose-5-ene **1** with excess TIBAL at 50 °C resulted in reductive rearrangement to afford the expected (1→2′) ether-linked pseudo-disaccharides **18** (20%) and **19** (14%) (Scheme 3).[a] Quite unexpectedly we isolated the corresponding epimers at C-2′, i.e., the (1→2′) ether-linked pseudo-disaccharides **20** (11%) and **21** (1%). The assignment of the anomeric configuration of the fructofuranoside linkage of the pseudo-disaccharides was based on the characteristic shifts of the C-2′ signals in the ^{13}C NMR spectra; C-2′ signals for α-

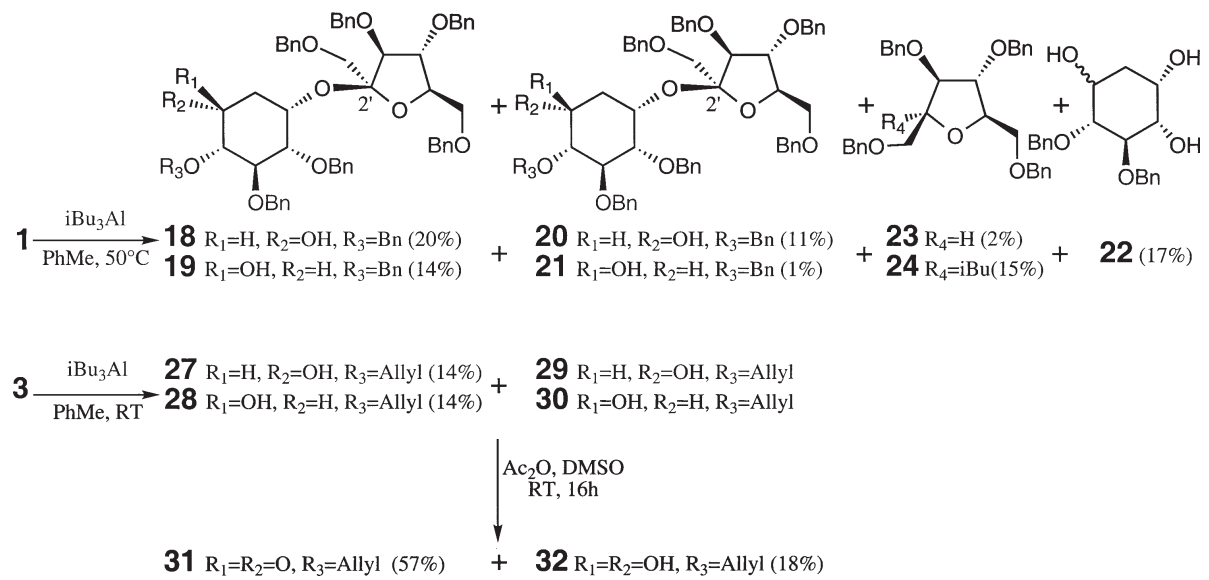
[a]High Resolution Mass Spectrometry was performed on this compound because there was not enough product to achieve elemental analysis. The difference observed (-8,8 ppm) is low enough to consider the sample "pure".



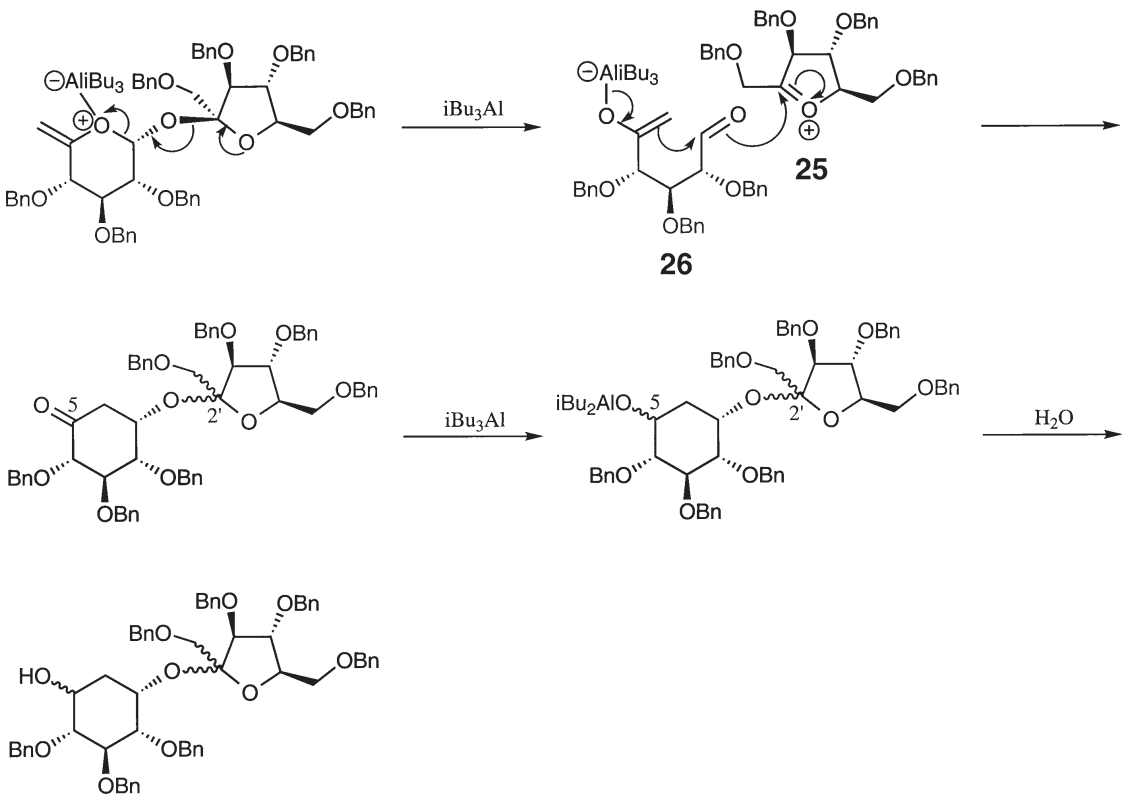
Scheme 2. Preparation of sucrose-5-ene substrates **1** and **3** for TIBAL-promoted rearrangement. *Reagents and Conditions:* (i) 2-methoxyprop-1-ene, cat PTSA, DMF, 70 °C, 2 h, 78%; (ii) NaH, BnBr, DMF, 56%; (iii) aq AcOH, acetone, 80 °C, 30 min, 83%; (iv) Ph_3P, I_2, Im, PhMe, 70 °C, 93%; (v) NaH, BnBr, DMF, RT, 98%; (vi) NaH, 1-bromoprop-2-ene, DMF, RT, 88%.

fructofuranosides occur at 107–108 ppm and at 103–104 ppm for β-fructofuranosides.[12]

We first suspected that formation of the α-fructofuranosides **20** and **21** might be due to a direct Lewis acid-promoted epimerization of **18** and **19** occurring after the rearrangement step. Although this has not specifically been demonstrated for **18** and **19**, no reaction was observed when octabenzyl sucrose[13] was treated with excess TIBAL at 50 °C for 4 days, and we thus reasoned that direct TIBAL-promoted epimerization at C-2′ was probably not occurring. We therefore concluded that cleavage of the C2′-O_{exo} bond must occur before or during the rearrangement step. This fact conforms with the formation of the three major side-products **22**, **23**,[14] and **24** (Scheme 3), resulting from the cleavage of the interglycosidic bond (C2′-O_{exo}). These products were identified by a combination of ^1H/^{13}C NMR and mass spectrometry although the stereo-



Scheme 3. TIBAL-promoted reductive rearrangement of sucrose-5-enes **1** and **3**.



Scheme 4. Proposed mechanism for the TIBAL-promoted reductive rearrangement of sucrose-5-ene **1**. The precise details of this mechanism are not known.

chemistry of **22** and **24** has not been vigorously established. Hence, we tentatively propose the following mechanism: coordination of the Lewis acid TIBAL to the endocyclic oxygen atom of the pyranose ring leads to cleavage of the C1-O_{endo} bond, which is accompanied by cleavage of the C2′-O_{exo} bond, leading to formation of the fructofuranosyl oxycarbenium intermediate **25** and aluminum enolate **26**. Carbocyclization of **26** and recombination with **25** lead to the formation of the isolated products after in situ reduction of the intermediate ketones with TIBAL. Thus, the recombination step accounts for the loss of stereochemical integrity observed at C-2′ (Scheme 4). This mechanism implies that carbocyclization of **26** leads to a single isomer at C-1, as previously observed for the regular rearrangement.[2] It should also be noted that formation of **18** and **19** can equally be accounted for by the regular rearrangement mechanism without invoking interglycosidic bond cleavage.

Reaction of 4-*O*-allyl-sucrose-5-ene **3** with excess TIBAL at RT also resulted in reductive rearrangement to afford the desired (1→2′) ether-linked pseudo-disaccharides **27**/**28** (28%) as a 1:1 mixture (Scheme 3), accompanied by the corresponding epimers at C-2′ **29** and **30**. This poor yield is due to the formation of side-products resulting from competitive interglycosidic bond cleavage and partial epimerization at C-2′, as observed in the previous case. However, the side-products were not isolated in this case. Although small quantities of pure **27** and **28** were isolated by flash chromatography of the mixture, the workup was significantly simplified by direct oxidation of the mixture with acetic anhydride in DMSO to afford a mixture of ketone **31** as a major diastereomer in 57% yield, together with 18% of the C-2′ epimer (α-furanose) as calculated by integration of proton 6-Ha: 2.87 (dd, 1 H, $J_{6a,6b}$ 15.0 Hz, $J_{5,6a}$ 5.0 Hz) for this minor diastereomer.

First, the compatibility of the allyl protecting group with the TIBAL-promoted reaction conditions[15] is significant, as previously we have only reported rearrangements of perbenzylated hex-5-enopyranosides. Second, oxidation to the ketone **31** is advantageous, given that the ketone function is ideal for homologation to a carbasugar.[5] In this context, access to the free 4-OH group after removal of the allyl group might also prove useful in controlling the stereochemistry at C-5.[16]

CONCLUSIONS

This work extends the scope of the TIBAL-induced rearrangement in carbohydrate chemistry:

1. This paper reports the first TIBAL-promoted reductive rearrangement of readily available sucrose-5-enes (**1** and **3**) to highly functionalized (1→2′) ether-linked pseudo-disaccharides (**18**, **19**, **27**, **28**).
2. The rearrangement is accompanied by some loss of stereochemical integrity at C-2′ due to cleavage of the interglycosidic (O–C2′) bond, leading to formation of diastereomers at C-2′. This arises from the unusual extended vinyl acetal system, in which the interglycosidic oxygen atom of the vinyl acetal system links the anomeric centers of both monosaccharide units.
3. The successful rearrangement of the 4-*O*-allyl protected sucrose-5-ene **3** demonstrates the compatibility of the allyl group with the TIBAL reaction conditions.
4. Ketone **31** provides a potential intermediate for homologation to 5a-carba-sucrose.

EXPERIMENTAL

General

Melting points: Büchi 510 apparatus and were uncorrected. IR: Nicolet Impact 400D. Optical rotations: Perkin Elmer 241 digital polarimeter. MS: Nermag R10-10 spectrometer, C.I. (ammonia). Elemental analyses: performed by Service d′Analyse de l'Université Pierre et Marie Curie, Paris. NMR: Brüker AM-400 (400 MHz and 100.6 MHz, for ^{1}H and ^{13}C, respectively), TMS as internal standard. All NMR assignments were supported by COSY and ^{1}H-^{13}C-correlation. TLC: silica gel 60 F_{254} (Merck) and detection by charring with concd H_2SO_4. Flash column chromatography: silica gel 60 (230–400 mesh, Merck).

1′,2,3,3′,4′,6′-Hepta-O-*benzyl-6-deoxy-6-iodo-sucrose (**17**).* Triphenylphosphane (0.50 g, 1.92 mmol), imidazole (0.26 g, 3.82 mmol), and iodine (0.49 g, 1.91 mmol) were added to a stirred solution of 1′,2,3,3′,4′,6′-hexa-*O*-benzyl-sucrose (**16**)[10] (1.27 g, 1.44 mmol) in anhydrous toluene (25 mL) at room temperature under argon. The mixture was heated at 70 °C for 2.5 h, when TLC (Et_2O/cyclohexane, 3:1) indicated no starting material (R_f 0.3) and a major product (R_f 0.8). The reaction mixture was cooled to room temperature, and saturated sodium thiosulfate (20 mL) was added. After 15 min, the aqueous layer was extracted with EtOAc (3 × 30 mL), and combined extracts were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 13–50% EtOAc in cyclohexane) to afford **17** (1.18 g, 93%), as a colorless oil. $[\alpha]_D^{22}$ +40 (*c* 1.0 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.42–7.33 (m, 30 H, arom. H), 5.99 (d, 1 H, $J_{1,2}$ 3.6 Hz, 1-H), 5.03 (d, *J* 11.3 Hz, 1 H, C*H*Ph), 4.76–4.62 (m, 7 H, 7 × C*H*Ph), 4.58–4.55 (m, 4 H, 3′-H, 3 × C*H*Ph), 4.47 (t, 1 H, $J_{3',4'=4',5'}$ 8.0 Hz, 4′-H), 4.36 (d, 1 H, *J* 11.3 Hz, C*H*Ph), 4.15 (ddd, 1 H, $J_{4',5'}$ 8.0 Hz, $J_{5',6'b}$ 5.0 Hz, $J_{5',6'a}$ 4.0 Hz, 5′-H), 3.84–3.82 (m, 2 H, 3-H, 6′-Ha), 3.81 (d, 1 H, $J_{1'a,1'b}$ 10.8 Hz, 1′-Ha), 3.74 (dd, 1 H, $J_{6'a,6'b}$ 10.6 Hz, $J_{5',6'b}$ 5.0, 6′-Hb), 3.66 (d, $J_{1'a,1'b}$ 10.8 Hz, 1′-Hb), 3.52 (dt, 1 H, $J_{4,5}$ 9.3 Hz, $J_{5,6a=5,6b}$ 3.0 Hz, 5-H), 3.46 (br t, 1 H, $J_{3,4=4,5}$ 9 Hz, 4-H), 3.42 (dd, 1 H, $J_{2,3}$ 9.6 Hz, $J_{1,2}$ 3.6 Hz, 2-H), 3.27 (dd, 1 H, $J_{6a,6b}$ 10.9 Hz, $J_{5,6a}$ 3.0 Hz, 6-Ha), 3.22 (dd, 1H, $J_{6a,6b}$ 10.9 Hz, $J_{5,6b}$ 3.0, 6-Hb), 2.30 (br s, 1 H, OH). ^{13}C NMR ($CDCl_3$): δ = 138.6, 138.1, 138.0, 137.9, 137.9, 137.8 (6 × s, C-arom. quat.), 128.5–127.4 (30 × d, Ph), 104.4 (C-2′), 89.1 (C-1), 83.7 (C-3′), 80.6 (C-4′), 80.4 (C-3), 79.5 (C-2), 79.1 (C-5′), 75.0 (t, *C*H_2Ph), 73.5 (C-4), 73.4, 73.2, 73.1, 72.6 (4 × t, *C*H_2Ph), 71.55 (C-1′), 71.5 (t, *C*H_2Ph), 70.1 (C-6′), 68.4 (C-5), 9.9 (C-6). MS (CI); *m*/*z* (%): 1010.8 (80) [MNH_4^+], 884.9 (100). $C_{54}H_{57}IO_{10}$ (992.9): calcd C 65.32, H 5.79; found C 65.31, H 5.89.

Hepta-O-*benzyl-2′*-O-*(6-deoxy-*α-D-*xylo-hex-5-enopyranosyl)*-β-D-*fructofuranoside (**1**).* Sodium hydride (2.4 g, 60.0 mmol, 60% in mineral oil) was added to a stirred solution of **17** (5.0 g, 5.0 mmol) in anhydrous DMF (100 mL) containing benzyl bromide (0.8 ml, 6.6 mmol) at room temperature. After 22 h, TLC (EtOAc/cyclohexane, 5:1) indicated no starting material (R_f 0.3) and product (R_f 0.4), and the reaction mixture was cooled to 0 °C and methanol (10 mL) was added dropwise. The solvent was removed in vacuo and the residue was partitioned between DCM (200 mL) and brine (200 mL). The aqueous layer was extracted with DCM (3 × 200 mL) and the combined organic layers were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 5–17% EtOAc in cyclohexane) to afford **1** (4.7 g, 98%), as a colorless oil. $[\alpha]_D^{22}$ +6 (*c* 1.0 in $CHCl_3$). ^{1}H NMR (CDCl3): δ = 7.47–7.33 (m, 35 H, arom. H), 5.86 (d, 1 H, $J_{1,2}$ 3.1 Hz, 1-H), 4.91–4.83 (m, 5 H, 6-Ha, 2 × CH_2Ph), 4.79–4.61 (m, 10 H, 6-Hb, 9 × C*H*Ph), 4.59–4.57 (br m, 1 H, 4′-H), 4.48 (d, 1 H, *J* 12.0 Hz, C*H*Ph), 4.31–4.26 (m, 2 H, 3′-H, 5′-H), 4.08–4.04 (m, 2 H, 3-H, 4-H), 3.90 (dt, 1 H, $J_{6'a,6'b}$ 10.1 Hz, $J_{4',6'a=5',6'a}$ 3 Hz, 6′-Ha), 3.83 (d, 1 H, $J_{1'a,1'b}$ 11.1 Hz, 1′-Ha), 3.79 (dt, 1 H, $J_{6'a,6'b}$ 10.1 Hz, $J_{4',6'b=5',6'b}$ 1.8 Hz, 6′-Hb), 3.67–3.64 (m, 2 H, 2-H, 1′-Hb). ^{13}C NMR ($CDCl_3$): δ = 153.8 (C-5), 138.6, 138.3, 138.15, 138.13, 138.1, 138.0, 137.8 (7 × s, C-arom. quat.), 128.4–127.5 (35 × d, Ph), 104.6 (C-2′), 96.3 (C-6), 91.4 (C-1), 83.8 (C-4′), 82.4 (C-3′), 80.2 (C-3), 79.8 (C-5′), 79.5 (C-4), 79.3 (C-2), 75.3, 74.0, 73.3, 73.2, 72.9, 72.6, 72.5 (7 × t, *C*H_2Ph), 71.7 (C-6′), 70.5 (C-1′). MS (CI); *m*/*z* (%): 972.6 (100) [MNH_4^+]. $C_{61}H_{62}O_{10}$ (955.2): calcd C 76.71, H 6.54; found C 76.60, H 6.72.

1′,3′,4′,6′-Tetra-O-*benzyl-2′*-O-*[1D-(1,2,4,5/3)-2,3,4-tri*-O-*benzyl-1,2,3,4,5-pentahydroxy-cyclohexyl]*-β-D-*fructofuranoside (**18**), 1′,3′,4′,6′-Tetra*-O-*benzyl-2′*-O-*[1D-(1,2,4,5/3)-2,3,4-tri*-O-*benzyl-1,2,3,4,5-pentahydroxy-cyclohexyl]*-α-D-*fructofuranoside (**20**), 1′,3′,4′,6′-tetra*-O-*benzyl-2′*-O-*[1D-(1,2,4/3,5)-2,3,4-tri*-O-*benzyl-1,2,3,4,5-pentahydroxy-cyclohexyl]*-α-D-*fructofuranoside (**21**), 1′,3′,4′,6′-tetra*-O-*benzyl-2′*-O-*[1D-(1,2,4/3,5)-2,3,4-tri*-O-*benzyl-1,2,3,4,5-pentahydroxy-cyclohexyl]*-β-D-

*fructofuranoside (**19**).* TIBAL (18.0 mL, 18.0 mmol, 1M in toluene) was added to a stirred solution of **1** (2.6 g, 2.7 mmol) in anhydrous toluene (90 mL) at room temperature under argon. The reaction mixture was heated at 50 °C and after 5 h further TIBAL (15.0 mL, 15.0 mmol, 1M in toluene) was added. After a further 2.5 h TLC (EtOAc/cyclohexane, 3:10) indicated no starting material (R_f 0.64) and four components (R_f 0.34, 0.28, 0.25, and 0.20) as part of a complex mixture. The mixture was cooled to 0 °C and icewater (50 mL) was added. The mixture was filtered into a separatory funnel, washing with EtOAc (50 mL), and the aqueous layer was extracted with EtOAc (2 × 100 mL). Combined extracts were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 10–50% EtOAc in cyclohexane) to afford by order of elution:

*(**18**) (512 mg, 20%), as a colorless oil.* $[\alpha]_D^{21}$ +24 (*c* 1.0 in $CHCl_3$). ^{1}H NMR (CDCl3): δ = 7.42–7.32 (m, 35 H, arom. H), 4.95–4.72 (m, 8 H, 8 × C*H*Ph), 4.68 (br m, 1 H, 1-H), 4.62 (m, 4 H, 4 × C*H*Ph), 4.49 (d, 1 H, $J_{3',4'}$ 7.5 Hz, 3′-H), 4.44 (d, 1 H, *J* 12.0 Hz, C*H*Ph), 4.29 (d, 1 H, *J* 12.3 Hz, C*H*Ph), 4.27 (dd, 1 H, $J_{4',5'}$ 8.3 Hz, $J_{3',4'}$ 7.5 Hz, 4′-H), 4.18 (t, 1 H, $J_{2,3=3,4}$ 9 Hz, 3-H), 4.14–4.08 (m, 2 H, H-5, H-5′), 3.79 (dd, 1 H, $J_{6'a,6'b}$ 10.7 Hz, $J_{5',6'a}$ 2.7 Hz, 6′-Ha), 3.68 (dd, 1 H, $J_{6'a,6'b}$ 10.7 Hz, $J_{5',6'b}$ 4.8 Hz, 6′-Hb), 3.68 (d, 1H, $J_{1'a,1'b}$ 10.7 Hz, 1′-Ha), 3.53 (d, 1 H, $J_{1'a,1'b}$ 10.7 Hz, 1′-Hb), 3.40 (dd, 1 H, $J_{3,4}$ 9 Hz, $J_{4,5}$ 3.3 Hz, 4-H), 3.36 (br d, 1 H, *J* 8.5 Hz, 2-H), 2.40 (dt, 1 H, $J_{6a,6b}$ 14.9 Hz, $J_{1,6a=5,6a}$ 3.9 Hz, 6-Ha), 1.27 (m, 1 H, $J_{6a,6b}$ 14.9 Hz, 6-Hb). ^{13}C NMR ($CDCl_3$): δ = 138.9, 138.8, 138.5, 138.0, 138.0, 137.8, 137.8, (7 × s, C-arom. quat.), 128.2–127.3 (35 × d, Ph), 103.4 (C-2′), 82.7 (C-3′+ C-4), 81.5 (C-2+ C-4′), 79.1 (C-3), 78.6 (C-5′), 75.5, 73.1, 73.0, 73.0, 72.7, 72.2 (6 × t, *C*H_2Ph), 71.8 (C-1′), 71.7 (t, *C*H_2Ph), 69.6 (C-1), 69.5 (C-6′), 67.8 (C-5), 32.1 (C-6′). MS (CI); *m*/*z* (%): 974.6 (100) [MNH_4^+]. $C_{61}H_{64}O_{10}$ (957.2): calcd C 76.55, H 6.74; found C 76.45, H 6.92.

*(**20**) (273 mg, 11%): as a colorless oil.* $[\alpha]_D^{22}$ +38 (*c* 0.8 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.42–7.26 (m, 35 H, arom. H), 4.90–4.40 (m, 16 H, 7 × CH_2Ph, 1-H, 5′-H), 4.24 (d, 1 H, $J_{3',4'}$ 3.5 Hz, 3′-H), 3.95 (dd, 1 H, $J_{4',5'}$ 6.4 Hz, $J_{3',4'}$ 3.5 Hz, 4′-H), 3.75 (d, 1H, $J_{1'a,1'b}$ 10.3 Hz, 1′-Ha), 3.64 (d, 1 H, $J_{1'a,1'b}$ 10.3 Hz, 1′-Hb), 3.50–3.33 (m, 3 H, 6′-H, 5-H), 2.34 (m, 1 H, $J_{6a,6b}$ 13.8 Hz, 6-Ha), 1.41 (m, 1 H, 6-Hb). ^{13}C NMR ($CDCl_3$): δ = 140.8, 138.7, 138.6, 138.1, 138.0, 137.9, 137.3, (7 × s, C-arom. quat.), 128.5–126.9 (35 × d, Ph), 108.4 (C-2′), 88.5 (C-3′), 83.3 (C-4′), 80.3 (C-5′), 73.5, 73.2, 72.8, 72.8, 72.1, 71.7 (6 × t, *C*H_2Ph), 69.7 (C-6′), 68.8 (C-1), 68.0 (C-1′), 67.7 (C-5), 65.1 (t, *C*H_2Ph), 31.8 (C-6). MS (CI); *m*/*z* (%): 974.9 (45) [MNH_4^+], 540.5 (80), 452.4 (100). $C_{61}H_{64}O_{10}$ (957.2): calcd C 76.55, H 6.74; found C 76.65, H 6.58.

*(**21**) (31 mg, 1%), as a colorless oil.* ^{1}H NMR ($CDCl_3$): δ = 7.39–7.26 (m, 35 H, arom. H), 5.04 (d, 1 H, *J* 11.2 Hz, C*H*Ph), 4.93 (d, 1 H, *J* 10.9 Hz, C*H*Ph), 4.86 (d, 1 H, *J* 12.1 Hz, C*H*Ph), 4.75–4.42 (m, 13 H, 11 × C*H*Ph, 1-H, 5′-H), 4.18 (d, 1 H, $J_{3',4'}$ 3.5 Hz, 3′-H), 4.15–4.09 (m, 1 H, 5-H), 4.03 (t, 1 H, $J_{2,3=3,4}$ 9 Hz, 3-H), 3.97 (dd, 1 H, $J_{4',5'}$ 6.4 Hz, $J_{3',4'}$ 3.5 Hz, 4′-H), 3.75 (d, $J_{1'a,1'b}$ 10.3 Hz, 1′-Ha), 3.69 (d, $J_{1'a,1'b}$ 10.3 Hz, 1′-Hb), 3.44–3.41 (m, 3 H, 2-H, 6′-H), 3.34 (t, 1 H, $J_{3,4=4,5}$ 9 Hz, 4-H), 2.31 (dt, $J_{6a,6b}$ 13.2 Hz, $J_{1,6a=5,6a}$ 4.4 Hz, 6-Ha), 2.19 (br s, 1 H, OH), 1.31 (m, 1 H, 6-Hb). ^{13}C NMR ($CDCl_3$): δ = 138.9, 138.8, 138.6, 138.2, 138.2, 138.2, 137.9 (7 × s, C-arom. quat.), 128.5–127.2 (35 × d, Ph), 108.1 (C-2′), 88.5 (C-3′), 86.6 (C-4), 83.0 (C-2), 81.4 (C-3), 79.9 (C-5′), 75.4, 75.4, 73.4, 73.2, 72.6, 72.0, 71.8 (7 × t, *C*H_2Ph), 69.9 (C-6′), 68.9 (C-5), 68.4 (C-1′), 65.6 (C-1), 29.7 (C-6). MS (CI); *m*/*z* (%): 974.7 (100) [MNH_4^+]. $C_{61}H_{64}O_{10}$: calcd 974.4843 found 974.4835 (–0.8 ppm) [MNH_4^+].

*(**19**) (358 mg, 14%) : as a colorless oil.* $[\alpha]_D^{21}$ +33 (*c* 1.0 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.42–7.30 (m, 35 H, arom. H), 5.02 (d, 1 H, *J* 11.5 Hz, C*H*Ph), 4.88-4.50 (m, 13 H, 12 × C*H*Ph, 1-H), 4.49 (d, 1 H, $J_{3',4'}$ 7.3 Hz, 3′-H), 4.43 (d, 1 H, *J* 12.0 Hz, C*H*Ph), 4.28 (dd, 1 H, $J_{4',5'}$ 7.8 Hz, $J_{3',4'}$ 7.3 Hz, 4′-H), 4.10 (ddd, 1 H, $J_{4',5'}$ 7.8 Hz, $J_{5',6'a}$ 4.7 Hz, $J_{5',6'b}$ 3.0 Hz, 5′-H), 4.05–3.99 (m, 1 H, 5-H), 3.94 (t, 1 H, $J_{2,3=3,4}$ 9 Hz, 3-H), 3.78 (dd, 1 H, $J_{6'a,6'b}$ 10.6 Hz, $J_{5',6'b}$ 3.0 Hz, 6′-Hb), 3.73 (d, 1 H, $J_{1'a,1'b}$ 10.8 Hz, 1′-Hb), 3.69 (d, 1 H, $J_{1'a,1'b}$ 10.8 Hz, 1′-Ha), 3.65 (dd, 1H, $J_{6'a,6'b}$ 10.6 Hz, $J_{5',6'a}$ 4.7 Hz, 6′-Ha), 3.34 (dd, 1 H, $J_{2,3}$ 9 Hz, $J_{1,2}$ 2.8 Hz, 2-H), 3.32 (t, 1 H, $J_{3,4=4,5}$ 9 Hz, 4-H), 2.51 (dt, 1 H, $J_{6a,6b}$ 13.4 Hz, $J_{1,6a=5,6a}$ 4.4 Hz, 6-Ha), 1.24 (br t, 1 H, *J* 12 Hz, 6-Hb). ^{13}C NMR ($CDCl_3$): δ = 138.8, 138.8, 138.6, 138.6, 138.2, 138.0, 137.9 (7 × s, C-arom. quat.), 128.5–127.3 (35 × d, Ph), 104.4 (C-2′), 86.5 (C-4), 83.5 (C-3′), 82.8 (C-2), 81.6 (C-3), 81.4 (C-4′), 78.5 (C-5′), 75.4, 75.3, 73.3, 73.1, 72.5, 72.2 (6 × t, *C*H_2Ph), 72.15 (C-1′), 71.8 (t, *C*H_2Ph), 69.8 (C-6′), 68.7 (C-5), 66.2 (C-1), 34.2 (C-6). MS (CI); *m*/*z* (%): 974.8 (100) [MNH_4^+]. $C_{61}H_{64}O_{10}$ (957.2): calcd C 76.55, H 6.74; found C 76.48, H 6.76.

The following side-products were also obtained:

*1D-(1,2,4/3)-3,4-Di-*O*-benzyl-1,2,3,4,5-pentahydroxy-cyclohexane (**22**) (158 mg, 17%), as a colorless oil.* ^{1}H NMR ($CDCl_3$): δ = 7.24–7.38 (m, 10H, Ph), 4.78, 4.89 (2 × d, 2H, *J* 11.2, CH_2Ph), 4.68 (s, 2H, CH_2Ph), 4.14 (m, 1H, C*H*OH), 3.98 (m, 1H, C*H*OH), 3.87 (t, 1H, $J_{3,4} = J_{2,3}$ 8.6, 3-H), 3.5 (m, 2 H, C*H*OH and O*H*), 3.43 (dd, 1 H, $J_{4,5}$ 2.9, $J_{3,4}$ 8.6, 4-H), 3.23 (br s, 1 H, O*H*), 2.96 (br s, 1H, O*H*), 2.21 (dt, 1 H, $J_{6a,6b}$ 15.1, 6-Hb), 1.53 (dt, 1 H, $J_{6a,6b}$ 15.1 Hz, 6-Ha). MS (FAB); *m*/*z* (%): 367.3 (100) [MNa^+].

*1,2,4,6-Tetra-*O*-benzyl-2-isobutyl-2,5-anhydro-*D*-glucitol (**24**) (376 mg, 15%), as a colorless oil.* ^{1}H NMR ($CDCl_3$): δ = 4.68, 4.65 (2 × d, 2H, *J* 11.5 Hz, CH_2Ph), 4.64–4.58 (m, 6H, 3 × CH_2Ph), 4.18 (m, 1H, 2-H), 4.15 (dd, $J_{2,3}$ 5.6 Hz, $J_{3,4}$ 3.6 Hz, 3-H), 4.01 (d, 1H, $J_{3,4}$ 3.6 Hz, 4-H), 3.70 (dd, 1H, $J_{1a,1b}$ 10.35 Hz, $J_{1b,2}$ 5.15 Hz, 1a-H), 3.69 (d, 1H, $J_{6a,6b}$ 9.25 Hz, 6a-H), 3.64 (d, 1H, $J_{6a,6b}$ 9.25 Hz, 6b-H), 3.63 (dd, 1H, $J_{1a,1b}$ 10.35 Hz, $J_{1a,2}$ 5.15 Hz, 1b-H), 1.9 (m, 1H, C*H*(CH_3)$_2$), 1.73 (d, 2H, *J* 5.9 Hz, CH_2CH(CH_3)$_2$), 1.05 (d, 3H, *J* 6.6 Hz, CH_3), 1.03 (d, 3H, *J* 6.6 Hz, CH_3) ^{13}C NMR 138.56, 138.35, 138.33, 138.12, (4 × C-arom. quat.), 128.36, 128.31, 128.24, 128.145, 127.85, 127.68, 127.65, 127.60, 127.58, 127.54, 127.49, 127.47, 127.44, 127.275, (20 × d, Ph), 87.76 (C4), 85.89 (C5), 85.52 (C2), 80.11 (C3), 73.29, 73.18, 72.26, 71.99 (4 × t, *C*H_2Ph), 71.21 (*C*H_2OBn), 71.05 (*C*H_2OBn), 42.10 (*C*H2CH(CH_3)$_2$), 24.60 (*C*H_3), 24.30 (*C*H_3), 23.78 (*C*H(CH_3)$_2$). MS (CI); *m*/*z* (%): 598.6 [MNH4+].

1,3,4,6-Tetra-O-*benzyl-2,5-anhydro*-D-*glucitol (23)*[14] *(28 mg, 2%), as a colorless oil. Tetra*-O-*benzyl-2′*-O-*(4*-O-*allyl-2,3-di*-O-*benzyl-6-deoxy*-α-D-*xylo-hex-5-enopyranosyl)*-β-D-*fructofuranoside (**3**)*: Sodium hydride (0.9 g, 22.5 mmol, 60% in mineral oil) was added to a stirred solution of **17** (4.4 g, 4.4 mmol) in anhydrous DMF (50 mL) containing allyl bromide (0.8 mL, 8.9 mmol) at room temperature. After 18 h, TLC (EtOAc/cyclohexane, 4:1) indicated no starting material (R_f 0.3) and product (R_f 0.4), and the reaction mixture was cooled to 0 °C and methanol (15 mL) was carefully added dropwise. The solvent was removed in vacuo and the residue was partitioned between DCM (200 mL) and water (200 mL). The organic layer was washed with brine (100 mL), dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (EtOAc/cyclohexane, 1:7) to afford **3** (3.5 g, 88%), as a colorless oil. $[\alpha]_D^{22}$ +18 (*c* 1.0 in $CHCl_3$). ^{1}H NMR (CDCl3): δ = 7.39–7.27 (m, 30 H, arom. H), 6.02 (ddt, 1 H, *J* 17.0 Hz, *J* 10.5 Hz, *J* 5.6 Hz, C*H* = CH_2), 5.79 (d, 1 H, $J_{1,2}$ 3.4 Hz, 1-H), 5.39 (ddt, 1 H, *J* 17.0 Hz, *J* 1.7 Hz, *J* 1.5 Hz, CH = C*H*H), 5.26 (ddt, 1 H, *J* 10.5 Hz, *J* 1.7 Hz, *J* 1.3 Hz, CH = CH*H*), 4.83 (s, 2 H, CH_2Ph), 4.77 (br s, 1 H, 6-Ha), 4.74–4.56 (m, 10 H, 9 × C*H*Ph, 6-Hb), 4.52 (m, 1 H, 4′-H), 4.42 (d, 1 H, *J* 12.0 Hz, C*H*Ph), 4.34-4.25 (m, 2 H, OCH_2CH), 4.26–4.21 (m, 2 H, 3′-H, 5′-H), 3.94 (t, 1 H, $J_{2,3=3,4}$ 9.2 Hz, 3-H), 3.88–3.81 (m, 2 H, 4-H, 6′-Ha), 3.78 (d, 1 H, $J_{1'a,1'b}$ 11.1 Hz, 1′-Ha), 3.75–3.72 (m, 1 H, 6′-Hb), 3.59 (d, 1 H, $J_{1'a,1'b}$ 11.1 Hz, 1′-Hb), 3.57 (dd, 1 H, $J_{2,3}$ 9.2 Hz, $J_{1,2}$ 3.4 Hz, 2-H). ^{13}C NMR ($CDCl_3$): δ= 154.1 (C-5), 138.6, 138.4, 138.2, 138.2, 138.2, 137.9 (6 × s, C-arom. quat.), 134.6 (*C*H = CH_2), 128.3–127.5 (30 × d, Ph), 117.1 (CH = *C*H_2), 104.6 (C-2′), 96.1 (C-6), 91.4 (C-1), 83.8 (C-4′), 82.5 (C-3′), 80.1 (C-3), 79.8 (C-5′), 79.2 (C-2), 79.1 (C-4), 75.3, 73.3, 73.2, 73.0 (4 × t, *C*H_2Ph), 73.0 (O*C*H_2CH), 72.6, 72.5 (2 × t, *C*H_2Ph), 71.8 (C-6′), 70.5 (C-1′). MS (CI); *m*/*z* (%): 922.5 (100) [MNH_4^+]. $C_{57}H_{60}O_{10}$ (905.1): calcd C 75.64, H 6.68; found C 75.68, H 6.68.

1′,3′,4′,6′-Tetra-O-*benzyl-2′*-O-*[1D-(1,2,4,5/3)-4*-O-*allyl-2,3-di*-O-*benzyl-1,2,3,4,5-pentahydroxy-cyclohexyl]*-β-D-*fructofuranoside (**27**) and 1′,3′,4′,6′-Tetra*-O-*benzyl-2′*-O-*[1D-(1,2,4/3,5)-4*-O-*allyl-2,3-di*-O-*benzyl-1,2,3,4,5-pentahydroxy-cyclohexyl]*-β-D-*fructofuranoside (**28**)*: TIBAL (67.4 ml, 67.4 mmol, 1M in toluene) was added to a stirred solution of **3** (6.1 g, 6.7 mmol) in anhydrous toluene (6 mL) at room temperature under argon. After 4 h TLC (EtOAc/cyclohexane, 3:7) indicated no starting material (R_f 0.7) and two major products (R_f 0.4 and 0.3) as part of a complex mixture. The mixture was cooled to 0 °C and icewater (250 mL) was added. The mixture was filtered (Celite) into a separatory funnel, washing with EtOAc (250 mL), and the aqueous layer was extracted with EtOAc (3 × 250 mL). Combined organic extracts were dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (eluent gradient, 9–30% EtOAc in cyclohexane) to afford **27**/**28** (1.7 g, 28% as a 1:1 mixture). Further flash chromatography (eluent gradient, 20–30% EtOAc in cyclohexane) of a small quantity of the mixture afforded first pure **27** as a colorless oil. $[\alpha]_D^{22}$ +15 (*c* 1.0 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.39–7.30 (m, 30 H, arom. H), 6.04 (ddt, 1 H, *J* 17.3 Hz, *J* 10.4 Hz, *J* 5.5 Hz, C*H* = CH_2), 5.35 (ddt, 1 H, *J* 17.3 Hz, *J* 1.6 Hz, *J* 1.7 Hz, CH = C*H*H), 5.21 (ddt, 1 H, *J* 10.3 Hz, *J* 1.7 Hz, *J* 1.0 Hz, CH = CH*H*), 4.87 (d, 1 H, *J* 10.7 Hz, C*H*Ph), 4.79 (d, 1 H, *J* 12.0 Hz, C*H*Ph), 4.78 (d, 1 H, *J* 10.7 Hz, C*H*Ph), 4.70 (s, 2 H, CH_2Ph), 4.67 (d, 1 H, *J* 11.6 Hz, C*H*Ph), 4.63 (br m, 1 H, 1-H), 4.57–4.50 (m, 4 H, 4 × C*H*Ph), 4.43 (d, 1 H, $J_{3',4'}$ 7.4 Hz, 3′-H), 4.39 (d, 1 H, *J* 12.0 Hz, C*H*Ph), 4.31–4.18 (m, 4 H, OCH_2CH, C*H*Ph, 4′-H), 4.09–4.02 (m, 3 H, 3-H, 5-H, 5′-H), 3.74 (dd, 1 H, $J_{6'a,6'b}$ 10.8 Hz, $J_{5',6'a}$ 2.7 Hz, 6′-Ha), 3.63 (d, 1H, $J_{1'a,1'b}$ 10.7 Hz, 1′-Ha), 3.62 (dd, 1 H, $J_{6'a,6'b}$ 10.8 Hz, $J_{5',6'b}$ 3.5 Hz, 6′-Hb), 3.47 (d, 1 H, $J_{1'a,1'b}$ 10.7 Hz, 1′-Hb), 3.32–3.28 (br m, 1 H, 2-H), 3.27 (dd, 1 H, $J_{3,4}$ 9.4 Hz, $J_{4,5}$ 3.4 Hz, 4-H), 2.35 (dt, 1 H, $J_{6a,6b}$ 15.0 Hz, $J_{1,6a=5,6a}$ 3.8 Hz, 6-Ha), 1.26 (br d, 1 H, *J* 15.0 Hz, 6-Hb). ^{13}C NMR ($CDCl_3$): δ= 139.0, 138.6, 138.0, 138.0, 137.9, 137.9, (6 × s, C-arom. quat.), 135.5 (*C*H = CH_2), 128.3–127.4 (30 × d, Ph), 116.8 (CH = *C*H_2), 103.4 (C-2′), 82.8 (C-3′+ C-4), 81.6 (C-2), 81.5 (C-4′), 79.1 (C-3), 78.7 (C-5′), 75.6, 73.2, 73.1, 73.1, 72.8, 72.2 (6 × t, *C*H_2Ph), 71.9 (C-1′), 71.3 (O*C*H_2CH), 69.7 (C-1), 69.6 (C-6′), 68.0 (C-5), 32.1 (C-6′). MS (CI); *m*/*z* (%): 924.6 (95) [MNH_4^+], 540.3 (95), 402.2 (100). $C_{57}H_{62}O_{10}$ (907.1): calcd C 75.47, H 6.89; found C 75.38, H 7.00. Further elution afforded **28** as a colorless oil. $[\alpha]_D^{22}$ +46 (*c* 1.0 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.39–7.29 (m, 30 H, arom. H), 6.00 (ddt, 1 H, *J* 17.1 Hz, *J* 10.5 Hz, *J* 5.8 Hz, C*H* = CH_2), 5.34 (ddt, 1 H, *J* 17.1 Hz, *J* 1.5 Hz, *J* 1.8 Hz, CH = C*H*H), 5.22 (ddt, 1 H, *J* 10.2 Hz, *J* 1.8 Hz, *J* 1.0 Hz, CH = CH*H*), 4.82–4.50 (m, 12 H, 11 × C*H*Ph, 1-H), 4.48–4.44 (m, 1 H, OC*H*HCH), 4.46 (d, 1 H, $J_{3',4'}$ 7.3 Hz, 3′-H), 4.41 (d, 1 H, *J* 12.0 Hz, C*H*Ph), 4.25 (dd, 1 H, $J_{4',5'}$ 7.9 Hz, $J_{3',4'}$ 7.3 Hz, 4′-H), 4.26–4.19 (m, 1 H, OCH*H*CH), 4.07 (ddd, 1 H, $J_{4',5'}$ 7.9 Hz, $J_{5',6'b}$ 4.8 Hz, $J_{5',6'a}$ 3.0 Hz, 5′-H), 4.00-3.93 (m, 1 H, 5-H), 3.84 (dd, 1 H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 9.2 Hz, 3-H), 3.76 (dd, 1 H, $J_{6'a,6'b}$ 10.6 Hz, $J_{5',6'a}$ 3.0 Hz, 6′-Ha), 3.71-3.62 (m, 3 H, 1′-H, 6′-Hb), 3.27 (dd, 1 H, $J_{2,3}$ 9.7 Hz, $J_{1,2}$ 3.2 Hz, 2-H), 3.16 (t, 1 H, $J_{3,4=4,5}$ 9.2 Hz, 4-H), 2.49 (dt, 1 H, $J_{6a,6b}$ 13.5 Hz, $J_{1,6a=5,6a}$ 4.5 Hz, 6-Ha), 2.10 (br d, 1 H, *J* 1.5 Hz OH), 1.20 (ddd, $J_{6a,6b}$ 13.5 Hz, $J_{5,6b}$ 11.8 Hz, $J_{1,6b}$ 1.9 Hz, 6-Hb). ^{13}C NMR ($CDCl_3$): δ= 138.8, 138.7, 138.6, 138.2, 138.0, 138.0 (6 × s, C-arom. quat.), 135.5 (*C*H = CH_2), 128.4–127.3 (30 × d, Ph), 116.8 (CH = *C*H_2), 104.4 (C-2′), 86.2 (C-4), 83.5 (C-3′), 82.7 (C-2), 81.5 (C-3), 81.4 (C-4′), 78.5 (C-5′), 75.4 (t, *C*H_2Ph), 74.1 (O*C*H_2CH), 73.3, 73.2, 72.5, 72.2 (4 × t, *C*H_2Ph), 72.2 (C-1′), 71.8 (t, *C*H_2Ph), 69.8 (C-6′), 68.7 (C-5), 66.2 (C-1), 34.1 (C-6′). MS (CI); *m*/*z* (%): 924.6 (100) [MNH_4^+]. $C_{57}H_{62}O_{10}$ (907.1): calcd C 75.47, H 6.89; found C 75.34, H 6.92.

1′,3′,4′,6′-Tetra-O-*benzyl-2′*-O-*[1D-(1,2,4/3)-4*-O-*allyl-2,3-di*-O-*benzyl-1,2,3,4-tetrahydroxy-cyclohex-5-onyl]*-β-D-*fructofuranoside (**31**)*: Acetic anhydride (27.1 mL, 0.3 mol) was added to a stirred solution of **27**/**28** (2.7 g, 3.0 mmol as a 1:1 mixture) in anhydrous DMSO (135 mL) at room temperature under argon. The reaction mixture was stirred for 16 h. TLC (EtOAc/cyclohexane, 3:7) indicated no starting material (R_f 0.4) and formation of product (R_f 0.5). The reaction mixture was diluted with EtOAc (1.5 L) and then washed with water (400 mL), brine (400 mL), dried ($MgSO_4$), filtered, and

the solvent was removed in vacuo. The residue was purified by flash chromatography (20% EtOAc in cyclohexane) to afford **31** (2.0 g, 57%), as a colorless oil. $[\alpha]_D^{22}$ +24 (*c* 1.0 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.38–7.29 (m, 30 H, arom. H), 6.01 (ddt, 1 H, *J* 17.3 Hz, *J* 10.5 Hz, *J* 5.7 Hz, C*H* = CH_2), 5.36 (ddt, 1 H, *J* 17.3 Hz, *J* 1.5 Hz, *J* 1.6 Hz, CH = C*H*H), 5.24 (ddt, 1 H, *J* 9.3 Hz, *J* 1.5 Hz, *J* 1.1 Hz, CH = CH*H*), 4.81–4.56 (m, 10 H, 9 × C*H*Ph, 1-H), 4.54 (s, 2 H, CH_2Ph), 4.44 (d, 1 H, *J* 11.9 Hz, C*H*Ph), 4.43 (d, 1 H, $J_{3',4'}$ 7.1 Hz, 3′-H), 4.42-4.38 (m, 1 H, OC*H*HCH), 4.18–4.05 (m, 3 H, 4′-H, 5′-H, OCH*H*CH), 4.00 (t, 1 H, $J_{2,3\,=\,3,4}$ 8 Hz, 3-H), 3.95 (d, 1 H, $J_{3,4}$ 8 Hz, 4-H), 3.73–3.68 (m, 3 H, 2-H, 6′-H), 3.67 (d, 1H, $J_{1'a,1'b}$ 10.7 Hz, 1′-Ha), 3.63 (d, 1 H, $J_{1'a,1'b}$ 10.7 Hz, 1′-Hb), 2.97 (dd, 1 H, $J_{6a,6b}$ 15.0 Hz, $J_{5,6a}$ 5.2 Hz, 6-Ha), 2.30 (dd, $J_{6a,6b}$ 15.0 Hz, $J_{5,6b}$ 3.4 Hz, 6-Hb). ^{13}C NMR ($CDCl_3$): δ = 204.3 (C-5), 138.5, 138.4, 138.4, 138.1, 138.0, 137.9 (6 × s, C-arom. quat.), 134.5 (*C*H = CH_2), 128.3–127.4 (30 × d, Ph), 117.5 (CH = *C*H_2), 104.8 (C-2′), 85.4 (C-4), 83.5 (C-3′), 81.9 (C-4′), 81.6 (C-3), 81.0 (C-2), 78.5 (C-5′), 75.1, 73.4, 73.0 (3 × t, *C*H_2Ph), 72.6 (O*C*H_2CH), 72.5, 72.5 (2 × t, *C*H_2Ph), 72.3 (C-1′), 71.9 (t, *C*H_2Ph), 70.1 (C-6′), 66.9 (C-1), 42.6 (C-6). MS (CI); *m*/*z* (%): 922.7 (30) [MNH_4^+], 326.2 (100). $C_{57}H_{60}O_{10}$ (905.1): calcd C 75.64, H 6.68; found C 75.65, H 6.78.

Acknowledgment. We thank the European Community for a TMR Marie Curie Research Training Grant (#ERBFMBICT-983225) to A.J.P.

REFERENCES AND NOTES

(1) (a) Ferrier, R.J.; Middleton, S. *Chem. Rev*. **1993**, *93*, 2779–2831. (b) Dalko, P.I.; Sinaÿ, P. *Angew. Chem., Int. Ed. Engl*. **1999**, *38*, 773–777.

(2) Das, S.K.; Mallet, J.-M.; Sinaÿ, P. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 493–496.

(3) Sollogoub, M.; Mallet, J.-M.; Sinaÿ, P. *Angew. Chem., Int. Ed. Engl*. **2000**, *39*, 362–364.

(4) Pearce, A.J.; Sollogoub, M.; Mallet, J.-M.; Sinaÿ, P. *Eur. J. Org. Chem.* **1999**, 2103–2117.

(5) Sollogoub, M.; Pearce, A.J.; Hérault, A.; Sinaÿ, P. *Tetrahedron: Asymmetry* **2000**, *11*, 283–294.

(6) Pearce, A.J.; Mallet, J.-M.; Sinaÿ, P. *Heterocycles* **2000**, *52*, 819–826.

(7) Pearce, A.J.; Chevalier, R.; Mallet, J.-M.; Sinaÿ, P. *Eur. J. Org. Chem.* **2000**, 2203–2206.

(8) We have recently demonstrated that acyclic non-carbohydrate-based substituted vinyl ethers also undergo TIBAL-promoted reductive rearrangement; see du Roizel, B.; Sollogoub, M.; Pearce, A.J.; Sinaÿ, P. *Chem. Commun*. **2000**, 1507–1508.

(9) Fanton, E.; Gelas, J.; Horton, D.; Karl, H.; Khan, R.; Lee, C.-K.; Patel, G. *J. Org. Chem.* **1981**, *46*, 4057–4060.

(10) (a) Hough, L.; Kabir, A.K.M.S.; Richardson, A.C. *Carbohydr. Res*. **1984**, *125*, 247–252. (b) Chiu, A.K.B.; Hough, L.; Richardson, A.C.; Toufeili, I.A.; Dziedzic, S.Z., *Carbohydr. Res*. **1987**, *162*, 316–322.

(11) Garegg, P.; Samuelsson, B. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2866–2869.

(12) (a) Krog-Jensen, C.; Oscarson, S. *J. Org. Chem.* **1996**, *61*, 1234–1238. (b) Angyal, S.J.; Bethell, G.S. *Aust. J. Chem*. **1976**, *29*, 1249.

(13) Kaesbeck, L.; Kessler, H. *Liebigs Ann. Org. Bioorg. Chem.* **1997**, *1*, 169–174.

(14) Charette, A.B.; Côté, B. *J. Org. Chem.* **1993**, *58*, 933–936.

(15) Sollogoub, M.; Hérault, A.; Sinaÿ, P. Unpublished results.

(16) Rochepeau-Jobron, L.; Jacquinet, J.-C. *Carbohydr. Res*. **1997**, *303*, 395–406.