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# Redox glycosidation: the use of Nozaki–Takai methylenylation in a highly stereoselective synthesis of sucrose

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## ABSTRACT

Sequential reaction of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**7**) with butyllithium and 2-[2,3,5-tri-*O*-benzyl-4-*O*-(*tert*-butyldiphenylsilyl)-D-arabinonoyl]thio-3-nitropyridine (**6**) at −78° gave 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl 2,3,5-tri-*O*-benzyl-4-*O*-(*tert*-butyldiphenylsilyl)-D-arabinonate (**8**; 71%, $\alpha:\beta > 50:1$). Ester carbonyl methylenylation, desilylation, and iodoetherification in the presence of silica gave 3,4,6-tri-*O*-benzyl-1-deoxy-1-iodo-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-β-D-fructofuranoside (**15**; 44%, $\alpha:\beta > 50:1$). This neopentylic iodide 15 was converted into sucrose (**1**; 80%) by free-radical substitution using TEMPO (**24**) followed by sodium–ammonia reduction, acetylation, and Zemplén methanolysis.

## INTRODUCTION

Recently, we reported the development of a new strategy for the elaboration of glycosides. In the process, various sugar alcohols were converted into disaccharides via the formation of aldonic esters, Tebbe methylenylation, and subsequent iodoetherification [1,*]. Alternatively, we reported that aldonic esters may also be converted into glycosides via thionation, reductive *S*-methylation and cyclization [2]. These redox glycosidation methods provide alternative to the classical syntheses of disaccharides by applications of the Koenigs–Knorr reaction and related alkylative processes [3]. Herein we provide full experimental details on the use of redox

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* Redox glycosidation has been used by Sinaÿ[1] for the synthesis of two Kdo disaccharides, and Briner and Vasella[1] have discussed alternative nonclassical approaches to glycosides.

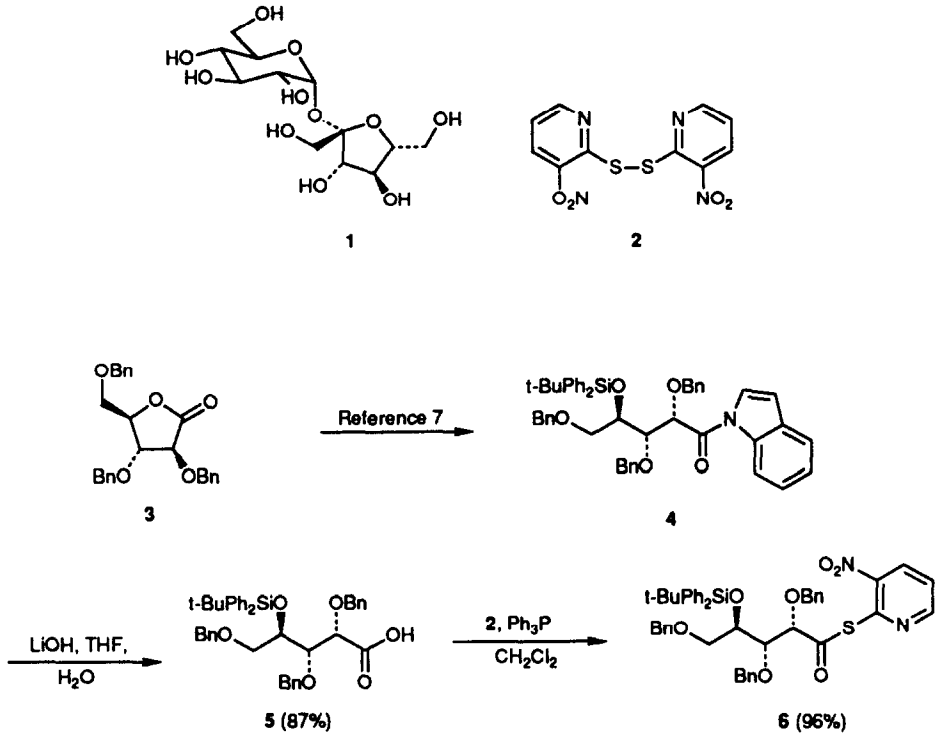
glycosidation methods for the synthesis of sucrose [4] (**1**). This molecule is an excellent target to demonstrate the validity of any new glycosidation methodology since it is a notoriously difficult substance to prepare stereoselectively in high yield. In 1953, Lemieux and Huber reported the first total synthesis of sucrose (**1**) using, as a key step, the reaction of Brigl's anhydride * with 1,3,4,6-tetra-*O*-acetyl-D-fructofuranose [5]. This synthesis was a triumph which has never significantly been improved upon [6]. Redox glycosidation methods have recently proven to be useful for the elaboration of sucrose (**1**) with excellent diastereoselectivities at both anomeric centers.

*Preparation and methylenylation of the α-glucopyranosyl ester* **8**.—We sought to convert 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**7**) into sucrose (**1**) via α-selective esterification, carbonyl methylenylation, and iodoetherification. D-Arabinonic acid was converted, via the lactone **3**, into the acyl indole [7] **4**. In an improvement on the literature procedure [7], this reactive amide **4** was hydrolyzed using lithium hydroxide in aqueous THF to give the corresponding carboxylic acid **5** (87%). Subsequent reaction with disulfide **2** and triphenylphosphine [8] gave the active ester **6** (96%) which was used directly to esterify alcohol **7**. The exact conditions employed for the esterification reaction need further comment. Several years prior to our work, Pfeffer and coworkers had reported a curious method [9] for the preparation of either the α- and β- hexadecanoic esters of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**7**). In THF at −30 to −40°, the lithium alkoxide derived from alcohol **7** gave predominantly the α-ester on reaction was hexadecanoyl chloride. In contrast, alkoxide esterification in benzene at 62° gave predominantly the corresponding β-ester. In an adaption of this process, alcohol **7** was reacted sequentially with butyllithium and thiolester **6**. At −40°, this gave both the α- and β-esters **8** and **10** (94%, $\alpha:\beta = 9:1$). However, prolonged reaction at −78° gave the α-ester **8** (71%) with excellent diastereoselectivity ($\alpha:\beta > 50:1$). The two anomeric esters were easily distinguished by comparison of their $^1$H-NMR spectra. [$^1$H-NMR $\delta$ **8** 6.49 (d, 1 H, *J* 3.2 Hz), **10** 5.79 (d, 1 H, *J* 7.6 Hz)]. For the origin of the α-anomeric stereoselectivity in this process, it is most reasonable to assume that, under the transesterification reaction conditions, the α- and β-alkoxides interconvert [9,**]. We favor a differential aggregation hypothesis to explain the esterification stereoselectivities. It is reasonable to speculate that the α-alkoxide exists predominantly as the dimeric entity **11**. In contrast, the less sterically congested β-alkoxide should be most tetrameric (**12**) at low temperatures [11]. In consequence, the α-alkoxide should be in fact more nucleophilic †. At higher temperatures the tetrameric β-alkoxide **12** should be in equilibrium with the more nucleophilic β-dimer. Thus,

* See Danishefsky et al.[5] for recent applications of Brigl anhydrides in the synthesis of glycosides.

** Schmidt and coworkers[10] have used anomeric alkoxide alkylation for the synthesis of several glycosides.

† For comparison, dimeric enolates are more reactive[11] than tetramers; for a review on aggregation of lithium salts, see ref. 11.

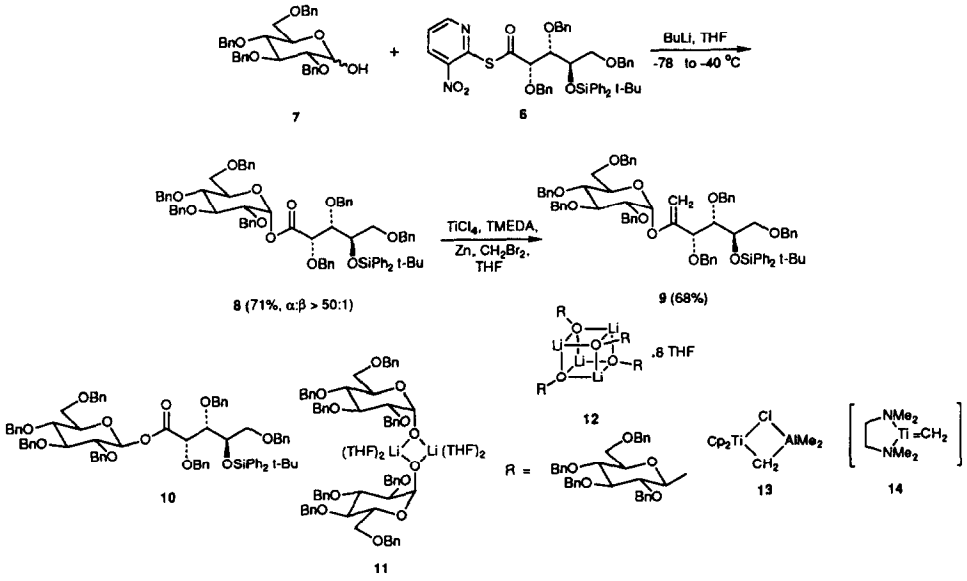



Scheme 1.

the $\alpha:\beta$ esterification ratio should diminish at higher temperatures and this was indeed observed. It is clear that, whatever the exact mechanistic reasons, alkoxide esterification using activated esters is highly $\alpha$-selective with both glucopyranose and mannopyranose systems [1,2,8].

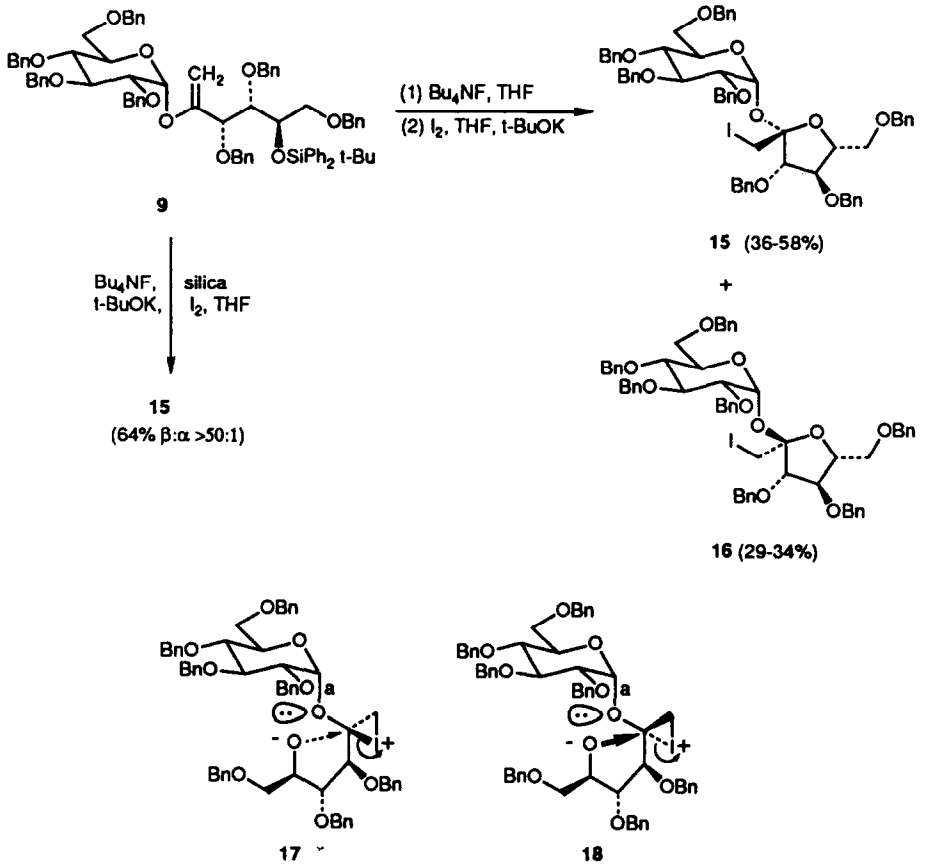
The conversion of ester **8** into the anomeric vinyl ether **9** proved particularly troublesome. Attempted methylenylation using the Tebbe reagent [12] **13**, either generated in situ or as the recrystallized solid, were unsuccessful and only unreacted ester **8** was recovered unchanged, even though we have widely applied reagent **13** for such methylenylation reactions [1]. In contrast, ester **8** was smoothly methylenylated using the Nozaki–Takai method [13]. Thus, reaction of **8** with zinc, dibromomethane, titanium tetrachloride, and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) gave the alkene **9**. Presumably, this process involves the intermediacy of carbene **14** or an equivalent metallocyclobutane and such a species should be less Lewis acidic than **13**.

*Iodoetherification of the vinyl ether* **9** *and completion of the synthesis of sucrose* (**1**).—The vinyl ether **9** was converted into the 1-deoxy-1-iodofructofuranoside **15** using two distinct procedures. Reaction of **9** with tetrabutylammonium fluoride resulted in desilylation to provide, on chromatography, the corresponding alcohol. This was cyclized by reaction with iodine and potassium *tert*-butoxide to produce




Scheme 2.

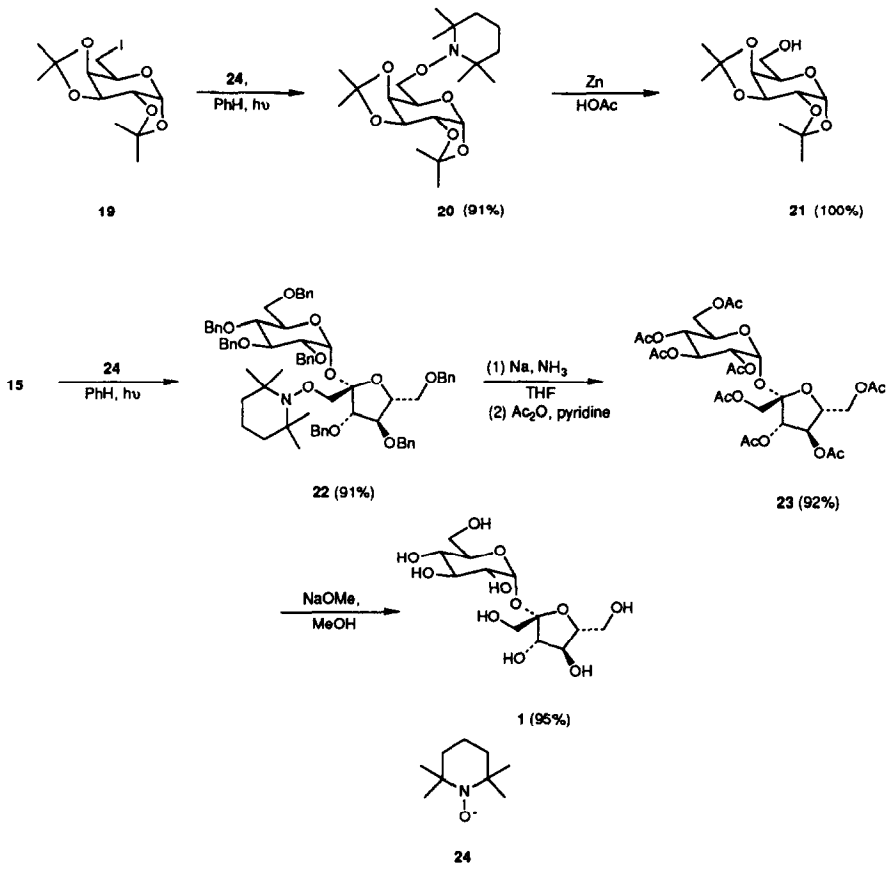
the two iodides **15** and **16**. The fructofuranose stereochemistry in each of these two substances was determined from the $^{13}$C-NMR spectra [14] and from their relative $[\alpha]_D$ values [15]. Thus, the $\beta$ anomer **15** showed the lower optical rotation {$[\alpha]_D$ $+40°$ ($c$ 1.0, $CHCl_3$)} and higher-field resonance for the furanose anomeric carbon in the $^{13}$C-NMR spectrum ($\delta$ 103.0), whereas the $\alpha$ anomer **16** showed a higher optical rotation {$[\alpha]_D$ $+77°$ ($c$ 0.6, $CHCl_3$)} and a lower-field carbon resonance ($\delta$ 109.2). It is clear from these results that iodoetherification gave the required sucrose stereoisomer **15** as the major component. However, the stereochemical bias was only very modest (1.1–1.9:1). In contrast to this diastereoselectivity, direct reaction of the silyl ether **9** with tetrabutylammonium fluoride on silica, iodine, and potassium *tert*-butoxide gave only the desired iodide **15** (64%, $\beta:\alpha$ $>50:1$). It is most remarkable that iodoetherification was essentially stereospecific in the presence of silica. In a blank experiment, the $\alpha$-iodide **16** was found to be stable to the reaction conditions. Thus diastereoselectivity in the silica-modified process was certainly the result of kinetic control rather than because of selective decomposition of the unwanted isomer **16**. Presumably, cyclization of **9** is subject to stereoelectronic control and through the minimization of steric congestion between the iodine and pyranose ring and between the benzyloxymethyl group and the pyranose anomeric oxygen atom. Thus, it is reasonable to propose that **17** and **18** constitute, for steric reasons, lower-energy transition states than the two conformations corresponding to **17** and **18** by 180° rotation about bond *a*. Additionally, both **17** and **18** should be stabilized by the C-1 oxygen lone-pair of glucopyranose being antiperiplanar to the tertiary C–I bond. Transition state **17**




Scheme 3.

should be disfavored relative to **18** because of unfavorable steric interactions between iodine and the C-3 benzyloxy group and between the benzyloxymethyl group and the anomeric oxygen. Additionally, both of these steric terms would be exaggerated by coordination of benzyloxy group by Lewis acidic sites on the silica surface. Whatever the exact origin of stereocontrol, it is clear that the silica-modified method, a most fortuitous discovery, is particularly useful in the assembly of sucrose (**1**). It is possible that silica-modified iodoetherification reactions of related molecules may show enhanced stereoselectivities.

At this stage, iodide **15** had been assembled in 31% overall yield from **6** and **7** with excellent ($> 50:1$) stereoselectivity at each anomeric center. Completion of the synthesis required only the nucleophilic substitution of the iodo group and deprotection. Unfortunately, this process proved to be most difficult. The iodide **15** is neopentylic, doubly $\beta$-oxygenated, and particularly sterically congested since it is present on an axial substituent. All of these factors are reinforced to diminish reactivity towards $S_N2$ displacement (see ref. 16 for prior examples). Unfortu-




Scheme 4.

nately, we were unable to displace iodide **15** by any oxygen-centered nucleophile. Even under forcing conditions using crown ether-solubilized salts at high pressures [17], the desired displacement reaction was not observed. Thus, we explored radical-substitution chemistry. Initially, we examined the radical substitution of the model galactopyranosyl iodide [18] **19**. Irradiation of **19** in the presence of TEMPO (**24**) smoothly and cleanly provided the corresponding hydroxylamine **20** (88%). Prior to our work, Bergmann reported the use of mixtures of **24** and tributylstannane as reagents to convert alkyl iodides into such hydroxylamine derivatives [19]. Additionally, Pattenden has shown that **24** is an excellent reagent for trapping alkyl radicals generated from cobaloximines [20]. Zinc reduction of the hydroxylamine derivative **20** smoothly provided the primary alcohol [18] **21** in quantitative yield.

Reaction of iodide **15** with **24** gave the corresponding hydroxylamine derivative **22**. This radical-substitution reaction worked equally well with or without tributylstannane. Finally, dissolving-metal reduction of **22** gave sucrose (**1**), isolated as its

octaacetate **23**, Zemplén methanolysis of which provided the target sucrose (**1**). Both sucrose (**1**) and its octaacetate **23** (available from Aldrich) were identical [TLC, mp, $[\alpha]_D$, IR, 400-MHz $^1$H-NMR, 101-MHz $^{13}$C-NMR, FAB HRMS] with samples of authentic material [5].

These results demonstrate that redox glycosidation is indeed a valid strategy for the elaboration of sucrose (**1**), which was prepared in 25% overall yield from **6** and **7** with $> 50:1$ stereoselectivity at each anomeric center. Both the stereoselective esterification and silica-modified iodoetherification reactions [21] should be of general utility. Additionally, the radical substitution of an iodide by an oxygen group should find further applications. Recently, Nakamura et al. have described an alternative method for the radical substitution of alkyl iodides using tributylstannane and oxygen [22].

## EXPERIMENTAL

*General methods.*—All reactions were carried out under dry $N_2$ at room temperature unless otherwise stated. Low reaction-temperatures are recorded as bath temperatures. Melting points were determined on a Reichert hot stage apparatus and are uncorrected. Optical rotations were all recorded at room temperature. Microanalyses were determined at Galbraith Laboratories, Knoxville, TN, or by G.D. Searle and Co., Skokie, IL.

Column chromatography was carried out on E. Merck Silica Gel 60, 230–400 mesh ASTM, and analytical thin-layer chromatography (TLC) was performed on E. Merck precoated Silica Gel 60 $F_{254}$ plates. Hexanes refer to the redistilled ACS reagent with boiling range 35–60°. The following solvents were purified by distillation: hexanes, EtOAc, $Et_2O$, $CH_2Cl_2$ (from $CaH_2$, $N_2$), $Et_2O$ (from $Ph_2CO$–Na, $N_2$), THF (from $Ph_2CO$–Na, $N_2$), TMEDA (from $CaH_2$, $N_2$), and PhH (from Na, $N_2$). Organic extracts were dried over $Na_2SO_4$ or $MgSO_4$, filtered, and rotary-evaporated at $\leq 50°$; involatile oils were further evaporated at $< 2$ torr. Samples for combustion analysis were purified by rechromatography with rotary evaporation ($< 40°$) of the appropriate fraction and further evaporation ($< 0.1$ torr) for $\geq 12$ h, or for solid compounds by recrystallization. 1-[2,3,5-Tri-*O*-benzyl-4-*O*-(*tert*-butyldiphenylsilyl)-D-arabinoyl]indole (**4**) was prepared on a 23.5-g scale following literature methods [7]. Reactions using TEMPO (**24**) were carried out in ambient lighting.

*[2,3,5-Tri-*O*-benzyl-4-*O*-(tert-butyldiphenylsilyl)-D-arabinonic acid* (**5**).—To a solution of the indole **4** (23.0 g) in THF (1.6 L) was added a solution of LiOH (7.0 g) in $H_2O$ (120 mL) and the mixture was heated under reflux overnight. The solution was poured into $H_2O$ (2.2 L) and acidified to pH 4 by careful addition of orthophosphoric acid. The mixture was extracted with EtOAc ($4 \times 600$ mL) and the combined extracts were dried ($Na_2SO_4$) and evaporated. The residue was chromatographed (eluant 4:1 $Et_2O$–hexanes) to afford the acid **5** (17.45 g, 87%) as a white crystalline solid: mp 116° ($Et_2O$–hexanes): (lit. [7] mp 116°).

*2-[2,3,5-tri-O-benzyl-4-O-(*tert*-butyldiphenylsilyl)-D-arabinonoyl]thio-3-nitropyridine* (**6**).—To a solution of **5** (10.0 g) in $CH_2Cl_2$ (25 mL) at room temperature was added 3,3′-dinitro-2,2′-dipyridyl disulfide (**2**) (5.5 g) and $PPh_3$ (4.65 g). After 6 h, the suspension was filtered through celite and evaporated to afford a brownish-yellow oil. Chromatography on silica (eluant 3:7 $Et_2O$–hexanes) gave **6** (11.6 g, 96%) as a yellow oil which was used directly for esterification: $^1$H-NMR ($CDCl_3$): $\delta$ 8.81 (dd, 1 H, *J* 1.1, 4.7 Hz), 8.29 (dd, 1 H, *J* 1.1, 8.1 Hz), 7.67 (d, 2 H, *J* 7.6 Hz), 7.63 (d, 2 H, *J* 7.6 Hz), 7.48 (dd, 1 H, *J* 4.8, 8.2 Hz), 7.39–7.29 (m, 2 H), 7.27–7.14 (m, 19 H), 4.85 (d, 1 H, *J* 10.9 Hz), 4.63 (d, 1 H, *J* 10.6 Hz), 4.53 (bs, 1 H), 4.47 (d, 1 H, *J* 10.6 Hz), 4.39 (d, 1 H, *J* 10.7 Hz), 4.18 (s, 2 H), 4.09 (app dd, 2 H, *J* 9.8, 11.6 Hz), 3.54 (s, 2 H), and 1.05 (s, 9 H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ 199.8, 152.7, 149.5, 147.1, 138.1, 137.9, 136.6, 135.9, 135.8, 133.9, 133.3, 133.0, 129.7, 129.5, 128.4, 128.29, 128.25, 128.14, 128.11, 128.07, 127.98, 127.86, 127.7, 127.5, 127.32, 127.26, 123.9, 84.7, 81.1, 77.22, 77.18, 74.9, 74.73, 74.70, 72.51, 72.48, 72.3, 70.6, 27.1, and 19.3.

*2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl 2,3,5-tri-O-benzyl-4-O-(*tert*-butyldiphenylsilyl)-D-arabinonate* (**8**).—(*A*) Disulfide **2** (1.10 g) and $Ph_3P$ (0.93 g) were added to a solution of **5** (2.0 g) in dry $CH_2Cl_2$ (5 mL) under $N_2$ at room temperature and the slurry was stirred for 4 h. The solids were filtered off and the resultant thioester **6** purified by chromatography (eluant 3:2 $Et_2O$–hexanes). BuLi in hexanes (1.6 M, 1.9 mL) was added to a solution of **7** (1.28 g) in dry THF (5 mL) at −78° under $N_2$. After 10 min, a solution of the crude **6** in dry THF (3 mL) was added and stirring continued for 48 h at −78° and then for 92 h at −40°. The mixture was quenched by addition to satd $NH_4Cl$ solution (50 mL) and the ester was extracted with $Et_2O$. Drying ($Na_2SO_4$) of the extract followed by evaporation and chromatography (eluant 3:2 $Et_2O$–hexanes) gave esters **8** and **10** (2.65 g, 94%) as a 9:1 mixture of $\alpha$:$\beta$ anomers. The $\alpha$ anomer **8** showed $[\alpha]_D$ + 41.5° (*c* 1.5, $CHCl_3$); IR ($CCl_4$) 3066, 3032, 2930, 2860, 1774, 1453, 1360, 1108, and 785 $cm^{-1}$; $^1$H-NMR ($CDCl_3$): $\delta$ 7.69 (d, 2 H, *J* 7.2 Hz), 7.60 (d, 2 H, *J* 6.8 Hz), 7.47–7.05 (m, 41 H), 6.49 (d, 1 H, *J* 3.2 Hz), 4.83 (d, 1 H, *J* 11.2 Hz), 4.76 (d, 1 H, *J* 10.8 Hz), 4.67 (d, 1 H, *J* 11.6 Hz), 4.65–4.54 (m, 4 H), 4.52–4.44 (m, 3 H), 4.42 (d, 1 H, *J* 10.8 Hz), 4.31 (d, 1 H, *J* 12.4 Hz), 4.29–4.19 (m, 2 H), 4.18 (d, 1 H, *J* 11.2 Hz), 4.08 (d, 1 H, *J* 11.6 Hz), 3.99 (d, 1 H, *J* 11.6 Hz), 3.87–3.65 (m, 4 H), 3.51–3.48 (m, 2 H), 3.43 (dd, 1 H, *J* 2.4, 10.8 Hz), 3.16 (dd, 1 H, *J* 1.8, 10.8 Hz), and 1.04 (s, 9 H); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ 170.8, 138.6, 138.5, 138.4, 138.3, 137.8, 137.6, 135.9, 134.0, 133.5, 129.6, 129.41, 128.37, 128.3, 128.22, 128.17, 128.12, 128.06, 128.0, 127.92, 127.87, 127.82, 127.76, 127.67, 127.61, 127.56, 127.51, 127.44, 127.39, 127.3, 127.2, 127.1, 91.0, 81.8, 81.4, 78.5, 78.3, 76.6, 75.5, 74.8, 74.1, 73.4, 73.1, 72.5, 72.3, 70.9, 67.4, 27.1, and 19.4; FABMS *m/z* 1197 ($M + H^+$), 1089, 912, 856, 768, 765, 708, 687, 673, 657, 629, 617, 597, 289, and 263.

*Anal.* Calcd for $C_{76}H_{80}O_{11}Si$: C, 76.23; H, 6.73. Found: C, 76.21; H, 6.92.

The $\beta$ anomer **10** showed inter alia $^1$H-NMR ($CDCl_3$) $\delta$ 5.79 (d, 1 H, *J* 7.6 Hz) and this signal was used to estimate the diastereoselectivity of esterification.

(*B*) A solution of 2,3,4,6-tetra-*O*-benzyl-D-glucose (**7**, 2.6 g) in anhyd THF (10.3 mL) at −78° was treated with butyllithium (1.6 M in hexanes, 3.9 mL). The yellow solution was kept for 45 min and then a solution of the thioester **6** (5.0 g) in anhyd THF (10.3 mL) was slowly added. The mixture was sealed under $N_2$ and kept for 2 weeks at −78° before being poured into satd aq $NH_4Cl$ (80 mL). The mixture was extracted with $Et_2O$ (4 × 100 mL), and the extract was dried ($Na_2SO_4$), and evaporated to afford the crude ester (5.0 g). Chromatography (eluant 3:7 $Et_2O$–hexanes) gave the ester (5.0 g). Chromatography (eluant 3:7 $Et_2O$–hexanes) gave the ester **8** (4.08 g, 71%) as a > 50:1 mixture of $\alpha:\beta$ anomers ($^1$H-NMR).

*5(*R*)-(*tert*-Butyldiphenylsilyloxy-3(*S*),4(*S*),6-tribenzyloxy-2-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyloxy)-1-hexene* (**9**).—To anhyd THF (15 mL) at 0° was added $TiCl_4$ in $CH_2Cl_2$ (1.0 M, 14 mL). The yellow solution was warmed to 25° and treated with TMEDA (4.0 mL). After 15 min, activated Zn dust (2.0 g) was added portionwise and the suspension stirred for 30 min at room temperature. Dibromomethane (0.65 mL) was added followed by a solution of the ester **8** (2.0 g) in THF (6 mL). The suspension was stirred for 48 h at room temperature before being cooled to 0° and quenched with satd aq $K_2CO_3$. Filtration through Celite followed by chromatography (eluant 1:3 $Et_2O$–hexanes) afforded the pure α-anomeric vinyl ether **9** (1.36 g, 68%) as a yellow oil: $[\alpha]_D$ +33° (*c* 1.56, $CHCl_3$); IR ($CCl_4$) 2929, 2855, 1636, 1497, 1454, 1363, 1104, 737, and 697 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, 2 H, *J* 7.4 Hz), 7.66 (d, 2 H, *J* 7.4 Hz), 7.36–7.11 (m, 39 H), 7.03–6.96 (m, 2 H), 5.39 (d, 1 H, *J* 3.6 Hz), 4.96 (d, 1 H, *J* 10.8 Hz), 4.88 (d, 1 H, *J* 10.8 Hz), 4.78 (d, 1 H, *J* 10.8 Hz), 4.73–4.55 (m, 8 H), 4.50 (d, 1 H, *J* 10.8 Hz), 4.45 (d, 1 H, *J* 12.4 Hz), 4.29–4.24 (m, 1 H), 4.19 (d, 1 H, *J* 11.6 Hz), 4.17 (d, 1 H, *J* 3.6 Hz), 414–4.05 (m, 2 H), 4.06 (d, 1 H, *J* 11.6 Hz), 4.01 (d, 1 H, *J* 12.0 Hz), 3.78–3.52 (m, 7 H), and 1.05 (s, 9 H); $^{13}$C-NMR (101 MHz, $CDCl_3$): δ 157.1, 139.0, 138.7, 138.4, 138.2, 138.1, 137.8, 136.1, 135.8, 134.6, 133.7, 129.5, 129.3, 128.4, 128.3, 128.1, 128.04, 127.96, 127.92, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.23, 127.20, 127.0, 95.1, 89.4, 82.2, 81.7, 79.3, 79.0, 77.2, 75.7, 75.1, 75.0, 73.5, 73.0, 72.5, 71.7, 71.6, 71.0, 68.3, 27.2, and 19.5; FABMS *m/z* 1195 ($M + H^+$), 872, 723, 646, 565, 91. Anal. calcd for $C_{77}H_{82}O_{10}Si$: C, 77.36; H, 6.91. Found: C, 77.15; H, 7.04.

*3,4,6-Tri-*O*-benzyl-1-deoxy-1-iodo-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-β-D-fructofuranoside* (**15**) *and 3,4,6-tri-*O*-benzyl-1-deoxy-1-iodo-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α-D-fructofuranoside* (**16**).—(*A*) A solution of the vinyl ether **9** (1.25 g) in anhyd THF (12 mL) was treated with $Bu_4NF$ in THF (1.0 M, 15 mL). The mixture was stirred for 40 h and then the solvent was evaporated and the residue chromatographed (eluant 2:3 $Et_2O$–hexanes). The resultant alcohol was dissolved in anhyd THF (10 mL) and treated with Bu$^t$OK (350 mg) and $I_2$ (920 mg). The mixture was stirred for 12 h and then quenched with satd aq $Na_2S_2O_3$ (50 mL). The mixture was extracted with $Et_2O$ (4 × 50 mL), and the extract was dried ($Na_2SO_4$) and evaporated. Chromatography (eluant 2:3 $Et_2O$–hexanes) of the residue gave **15** and **16** (789 mg, 70%) as a 1.1:1 mixture of epimers. The

epimers were separated by further chromatography (eluant 1:4 $Et_2O$–hexanes) to afford the $\beta$ anomer **15** (400 mg, 35%) and the $\alpha$ anomer **16** (380 mg, 34%) both as colorless syrups. The $\beta$ anomer **15** showed $[\alpha]_D$ +40° (*c* 1.0, $CHCl_3$); IR ($CCl_4$) 3031, 2919, 2863, 1496, 1453, 1362, 1171, 1094, 977, and 787 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$); $\delta$ 7.35–7.12 (m, 35 H), 5.73 (d, 1 H, *J* 3.6 Hz), 4.88 (d, 1 H, *J* 11.2 Hz), 4.82 (d, 1 H, *J* 10.8 Hz), 4.76 (d, 1 H, *J* 11.2 Hz), 4.73 (d, 1 H, *J* 10.8 Hz), 4.68 (d, 1 H, *J* 7.6 Hz), 4.65 (d, 1 H, *J* 7.6 Hz), 4.57–4.58 (m, 4 H), 4.48 (d, 1 H, *J* 12 Hz), 4.46 (d, 1 H *J* 10.8 Hz), 4.42 (b s, 2 H), 4.37 (d, 1 H, *J* 12.0 Hz), 4.17–4.06 (m, 3 H), 3.93 (app t, 1 H, *J* 9.6 Hz), 3.71 (dd, 1 H, *J* 6.0, 10.2 Hz), 3.66-3.60 (m, 2 H), 3.58 (dd, 1 H, *J* 3.6, 10.8 Hz), 3.54 (d, 1 H, *J* 11.6 Hz), 3.50 (dd, 1 H, *J* 3.2, 9.6 Hz), 3.446 (d, 1 H, *J* 11.2 Hz), and 3.438 (d, 1 H, *J* 11.6 Hz); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ 138.8, 138.5, 138.2, 138.1, 138.02, 137.96, 137.8, 128.4, 128.33, 128.29, 128.03, 127.92, 127.87, 127.85, 127.8, 127.72, 127.68, 127.6, 127.5, 103.0, 90.8, 85.4, 82.9, 81.9, 80.6, 79.8, 77.6, 75.5, 74.9, 73.4, 73.3, 73.2, 72.8, 72.6, 71.4, 70.8, 68.5, 9.8; FABMS *m/z* 1083 ($M + H^+$), 1066, 1048, 975, 958, 941, 867, 847, 829, 812, 543, 435, 415, 341, 325, 307.

*Anal.* Calcd for $C_{61}H_{63}IO_{10}$: C, 67.65; H, 5.86. Found: C, 67.28; H, 5.96.

The $\alpha$ anomer **16** showed $[\alpha]_D$ +77° (*c* 0.6, $CHCl_3$); IR ($CCl_4$) 3031, 2925, 2863, 1496, 1453, 1362, 1208, 1101, 989, and 786 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 7.38–7.08 (m, 35 H), 5.50 (d, 1 H, *J* 3.6 Hz), 4.82 (d, 1 H, *J* 10.8 Hz), 4.81 (d, 1 H, *J* 10.4 Hz), 4.75 (d, 1 H, *J* 11.6 Hz), 4.73–4.69 (m, 3 H), 4.67 (d, 1 H, *J* 11.2 Hz), 4.61 (d, 1 H, *J* 10.8 Hz), 4.53 (d, 1 H, *J* 11.2 Hz), 4.46–4.39 (m, 5 H), 4.35 (d, 1 H, *J* 12.0 Hz), 4.26 (dt, 1 H, *J* 10.0, 1.2 Hz), 4.09 (d, 1 H *J* 1.2 Hz), 4.04 (dd, 1 H, *J* 9.2, 9.4 Hz), 3.88 (dd, 1 H, *J* 1.4, 4.8 Hz), 3.86–3.81 (m, 2 H), 3.80 (d, 1 H, *J* 9.2 Hz), 3.58 (dd, 1 H, *J* 3.6, 10.0 Hz), 3.56 (d, 1 H, *J* 10.4 Hz), 3.50 (d, 1 H, *J* 10.8 Hz), and 3.42 (d, 2 H, *J* 5.2 Hz); $^{13}$C-NMR (101 MHz, $CDCl_3$): $\delta$ 139.0, 138.5, 138.3, 138.23, 138.19, 138.1, 137.6, 128.35, 128.27, 128.2, 128.1, 128.04, 127.97, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 109.2, 90.6, 88.2, 83.6, 83.1, 81.8, 80.1, 77.5, 77.2, 75.4, 75.1, 73.6, 73.3, 72.5, 71.7, 71.5, 70.3, 68.3, and 4.3; FABMS *m/z* 1083 ($M + H^+$), 545, 544, 540, 451, 435, 416, 391, 341, 325, 307, 289, 271.

*Anal.* Calcd for $C_{61}H_{63}IO_{10}$: C, 67.65; H, 5.86. Found: C, 67.52; H, 6.03.

(*B*) In another experiment iodoetherification of **9** (1.25 g) gave **15** (650 mg, 57%) and **16** (330 mg, 29%).

(*C*) $Bu_4NF$ on silica (450 mg) was added to a solution of the vinyl ether **9** (200 mg) in anhyd THF (5 mL). The mixture was stirred for 24 h and then $Bu^tOK$ (200 mg) and $I_2$ (350 mg) were added. The suspension was stirred for 4 days and then quenched with sat aq $Na_2S_2O_3$ (30 mL). The mixture was extracted with $Et_2O$ (4 × 50 mL), and the extract was dried ($Na_2SO_4$), and evaporated. The residue was chromatographed (eluant $Et_2O$–hexanes) to afford the disaccharide **15** (116 mg, 64%). The product was identical with the iodide **15** obtained in the previous procedure.

*Determination of the stability of 3,4,6-tri-O-benzyl-1-deoxy-1-iodo-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-α-D-fructofuranoside* (**16**).—Tetrabutylammonium

fluoride on silica (22 mg) was added to a solution of iodide **16** (10 mg) in anhyd THF (0.25 mL). The mixture was stirred for 24 h and then Bu$^t$OK (10 mg) and $I_2$ (17.5 mg) were added. The suspension was stirred for 4 days and then quenched with satd aq $Na_2S_2O_3$ (10 mL). The mixture was extracted with $Et_2O$ (4 × 20 mL), and the extract was dried ($Na_2SO_4$), and evaporated. The residue was chromatographed (eluant 2:3 $Et_2O$–hexanes) to afford the unreacted disaccharide **16** (9 mg, 90%).

*1,2 : 3,4-Di-O-isopropylidene-6-O-(2,2,6,6-tetramethyl-1-piperidinyl)-α-D-galactopyranose* (**20**).—To a solution of iodide **19** (200 mg) in benzene (30 mL) was added TEMPO (**24**) (106 mg). When the orange color disappeared (20 min), the solvent was evaporated. The residue was chromatographed on silica (eluant 1:1 $Et_2O$–hexanes) to afford **20** (196 mg, 91%) as a clear oil: $[\alpha]_D$ −61° (*c* 0.5, $CHCl_3$); IR (film) 1460, 1370, 1265, 1205, 1080, 1000, and 890 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): δ 5.53 (d, 1 H, *J* 4.8 Hz), 4.60 (dd, 1 H, *J* 2.4, 8.0 Hz), 4.30 (dd, 1 H, *J* 2.0, 4.8 Hz), 4.27 (d, 1 H, *J* 9.2 Hz), 4.05–3.88 (m, 3 H), 1.57 (s, 3 H), 1.44 (s on m, 9 H), 1.35 (s, 3 H), 1.34 (s, 3 H), 1.19 (s, 6 H), and 1.10 (s, 6 H); $^{13}$C-NMR (101 MHz, $CDCl_3$): δ 109.0, 108.4, 96.3, 75.3, 71.5, 70.8, 70.6, 66.2, 59.8 (b), 39.6, 32.9 (b), 26.04, 25.93, 25.0, 24.4, 19.9, and 17.1; EI-MS *m/z* 399 ($M^+$), 384, 326, 156, 127, 83, 69, 55; EI-HRMS calcd for $C_{21}H_{37}NO_6$: ($M^+$), 399.2621; found ($M^+$), 399.2636.

*Anal.* Calcd for $C_{21}H_{37}NO_6$: C, 63.13; H, 9.33; N, 3.50. Found: C, 62.91; H, 9.53; N, 3.39.

*1,2 : 3,4-Di-O-isopropylidene-α-D-galactopyranose* (**21**).—The hydroxylamine **20** (20 mg) was added to a suspension of activated Zn (20 mg) in 10% AcOH (5 mL) at room temperature. After 16 h, the mixture was filtered and the filtrate was extracted with EtOAc (3 × 20 mL). The extracts were dried ($MgSO_4$), evaporated and the residue purified by chromatography to afford **21** (13 mg, 100%) as a colorless oil identical ($^1$H- and $^{13}$C-NMR) with authentic material [18].

*(2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl) 3,4,6-tri-O-benzyl-1-(2,2,6,6-tetramethyl-1-piperidinyl)-β-D-fructofuranoside* (**22**).—(*A*) A solution of iodide **15** (20 mg) in benzene (5 mL) was treated with TEMPO (**24**) (9.4 mg) and $Bu_3SnH$ (0.02 mL). The orange solution was stirred for 2 h at room temperature and then the solution was concentrated in vacuo. The resultant oil was dissolved in $Et_2O$, washed with aq KF, dried ($MgSO_4$) and the solvent evaporated in vacuo. The residue was chromatographed (eluant 1:9 $Et_2O$–hexanes) to afford **22** (18 mg, 88%) as a pale-yellow oil: $[\alpha]_D$ +38° (*c* 0.6, $CHCl_3$); IR ($CHCl_3$) 2936, 2928, 2861, 1261, 1075, and 1025 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.35–7.10 (m, 35 H), 5.72 (d, 1 H, *J* 3.6 Hz), 4.88 (d, 1 H, *J* 10.6 Hz), 4.82 (d, 1 H, *J* 10.7 Hz), 4.80 (d, 1 H, *J* 10.9 Hz), 4.70 (d, 1 H, *J* 10.7 Hz), 4.64 (d, 1 H, *J* 10.7 Hz), 4.62 (d, 2 H, *J* 11.1 Hz), 4.55 (d, 2 H, *J* 11.8 Hz), 4.52–4.43 (m, 5 H), 4.31 (d, 1 H, *J* 12.2 Hz), 4.25 (app t, 1 H, *J* 8.2 Hz), 4.10–4.04 (m, 2 H), 4.02–3.98 (m, 1 H), 3.94–3.89 (m, 2 H), 3.74–3.59 (m, 3 H), 3.45 (dd, 1 H, *J* 3.6, 9.7 Hz), 3.39 (b dd, *J* 2.7, 10.8 Hz), 3.26 (b d, *J* 10.7 Hz), 1.43–1.40 (m, 4 H), 1.35–1.20 (m, 2 H), 1.25 (s, 6 H), and 1.12 (s, 6

H); $^{13}$C-NMR (101 MHz, $CDCl_3$): δ 138.8, 138.7, 138.5, 138.2, 138.1, 137.9, 128.5, 128.4, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 103.3, 89.1, 84.1, 81.8, 81.4, 79.6, 78.6, 76.5, 75.3, 74.5, 73.1, 72.9, 72.5, 72.0, 70.8, 70.3, 68.1, 60.0, 59.7, 39.6, 39.4, 33.3, 32.2, 29.5, 20.3, 20.1, 16.9, and 16.8; FABMS *m/z* 1113 ($M + H^+$), 1098, 740, 573, 415; FAB–HRMS calcd for $C_{70}H_{81}NO_{11}$: ($M + H^+$), 1112.5888; found: ($M + H^+$), 1112.5800. Iodide **15** (1.91 g) in benzene (100 mL) was treated with TEMPO (**24**) (900 mg). The solution was stirred at room temperature under $N_2$ until the orange color disappeared (~ 2 h). The solvent was removed in vacuo and the residue chromatographed (eluant 1 : 9 $Et_2O$–hexanes) to afford **22** (1.79 g, 91%). The product was identical with the hydroxylamine obtained in the previous procedure.

*(2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl 1,3,4,6-tetra-O-acetyl-β-D-fructofuranoside* (**23**).—The TEMPO adduct **22** (1.75 g) in anhyd THF (50 mL) was added to a solution of Na (5 g) in liquid ammonia (200 mL) at −78°. The temperature was maintained for 4 h at −78° and then allowed to warm to −33° before being quenched with satd aq $NH_4Cl$ (200 mL). The mixture was evaporated to dryness, and anhyd pyridine (250 mL), followed by $Ac_2O$ (100 mL) were added. The mixture was stirred for 6 h at 0° and then extracted with EtOAc (3 × 300 mL). The extract was washed with aq $CuSO_4$ (2 × 200 mL), dried ($MgSO_4$), and evaporated. Chromatography (eluant 1 : 9 EtOH–EtOAc) gave the known octaacetate [5] **23** (980 mg, 92%) as a white, crystalline solid: mp 86–87.5° (EtOAc–hexanes) (lit. [5] 89–90°); $[\alpha]_D$ +60°, +58.1° (*c* 0.82, 0.84, $CHCl_3$) ([lit. [5] $[\alpha]_D$ +60° (*c* 1.0 $CHCl_3$)]; IR ($CCl_4$) 3015, 1760, 1440, 1380, 1210, and 1040 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$): δ 5.71 (d, 1 H, *J* 3.8 Hz), 5.49–5.42 (m, 2 H), 5.37 (app t, 1 H, *J* 6.0 Hz), 5.08 (app t, 1 H, *J* 10.4 Hz), 4.87 (dd, 1 H, *J* 3.6, 10.4 Hz), 4.38–4.12 (m, 8 H), 2.20 (s, 3 H), 2.139 (s, 3 H), 2.136 (s, 3 H), 2.133 (s, 3 H), 2.129 (s, 3 H), 2.12 (s, 3 H), 2.07 (s, 3 H), and 2.04 (s, 3 H); $^{13}$C-NMR (101 MHz, $CDCl_3$): δ 170.2, 170.1, 169.7, 169.6, 169.5, 169.3, 169.1, 103.7, 89.6, 78.8, 75.4, 74.7, 69.9, 69.3, 68.2, 67.9, 63.3, 62.5, 61.4, 20.3, and 20.2; FABMS *m/z* 701 ($M + Na^+$), 679 ($M + H^+$), 659, 641, 619, 331, 271, 211, 169, 109; HRMS calcd for $C_{28}H_{38}O_{19}$: ($M + Na^+$), 701.1905; found: ($M + Na^+$), 701.1887.

*Sucrose* (**1**).—A solution of the synthetic sucrose octaacetate (**23**, 635 mg) in anhyd MeOH (250 mL) was treated with NaOMe in dry MeOH (1 M; 1.0 mL). After 1 h, Amberlite IR-120 ($H^+$, 1 g) was added. The suspension was stirred for 10 min before being filtered and evaporated to leave **1** (305 mg, 95%) as a white foam. Recrystallization from water gave synthetic sucrose **1**: mp 184–186°, ($H_2O$) (lit. [5] mp 187°); $[\alpha]_D$ +66° (*c* 0.6, $H_2O$) {lit. [5] $[\alpha]_D^{25}$ +66.7° (*c* 1.0, $H_2O$)}; IR (KBr) 3620, 3480, 3440, 3000, 2820, 1460, 1410, 1140, 1070, 930, and 870 $cm^{-1}$; $^1$H-NMR (400 MHz, $D_2O$): δ 5.45 (d, 1 H, *J* 3.9 Hz), 4.25 (d, 1 H, *J* 8.7 Hz), 4.10 (app t, 1 H, *J* 8.7 Hz), 3.92–3.80 (m, 7 H), 3.73 (s, 2 H), 3.60 (dd, 1 H, *J* 3.9, 10.0 Hz), 3.50 (app t, 1 H, *J* 9.2 Hz) (lit. [23] $^1$H-NMR spectrum); $^{13}$C-NMR (101 MHz, $D_2O$); δ 103.2, 91.7, 80.9, 75.9, 73.5, 72.1, 71.9, 70.6, 68.7, 61.9, 60.8, 59.6 (lit. [24] $^{13}$C-NMR spectrum); FABMS *m/z* 365 ($M + Na^+$), 343 ($M + H^+$), 327, 295, 282, 255, 237, 214, 197, 181.

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