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Chemical behavior of benzylidene acetal groups bridging the contiguous glucose residues in malto-oligosaccharide derivatives

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ABSTRACT

Treatment of phenyl α-maltoside with an excess of α,α-dimethoxytoluene in the presence of (+)-10-camphorsulfonic acid, followed by partial hydrolysis to remove unstable acyclic acetal substituents, gave phenyl 3,2′:4′,6′-di-*O*-benzylidene-α-maltoside (**1**). Thus, one of the benzylidene groups formed an eight-membered cyclic acetal ring bridging the two monosaccharide components. This acetal function was stable under conventional acylation and alkylation conditions, but was selectively hydrolyzed by 80% acetic acid at room temperature. Treatment of a per-*O*-benzoyl derivative of **1** with *N*-bromosuccinimide–barium carbonate afforded phenyl 2,6,3′,4′-tetra-*O*-benzoyl-6′-bromo-6′-deoxy-α-maltoside in 80% yield. Reductive ring opening of the tri-*O*-benzyl derivative of **1** with lithium aluminum hydride–aluminum chloride gave a 2,3,6,3′,4′-penta-*O*-benzyl derivative, while reduction with sodium cyanoborohydride–hydrogen chloride or borane trimethylamine complex–aluminum chloride afforded a 2,3,6,3′,6′-penta-*O*-benzyl derivative in good yield. Similar regioselectivity was observed in the reductive cleavage of a 1,6-anhydro-3′,2″:4″,6″-di-*O*-benzylidene-β-maltotriose derivative.

INTRODUCTION

As reported in the previous paper[1], we found that an eight-membered interglycosidic benzylidene acetal was readily formed in addition to the usual six-membered cyclic acetal when 1,6-anhydro-β-maltotriose was subjected to Evans benzylidenation[2] by the acetal exchange reaction using an excess α,α-dimethoxytoluene followed by partial hydrolysis of unstable intermediates. Although a few examples of interglycosidic cyclic acetals of disaccharides had been reported[3], the compounds were generally formed in poor yield and with low regioselectivity. As our interglycosidic benzylidene acetal was obtained in moderately good yield, detailed examination of its chemical behavior seemed quite significant from the view point of broadening the methodology for the regioselective protection of oligosaccharides.

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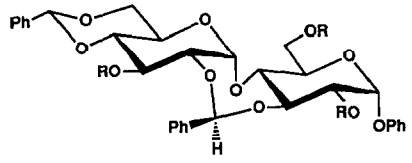
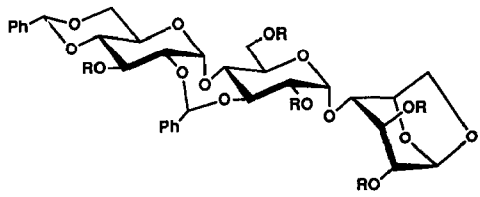
We now describe the preparation of 3,2′:4′,6′-di-*O*-benzylidene derivatives of maltosides (**1** and **8**) as a system similar to but of smaller size than the 1,6-anhydro-3′,2″:4″,6″-di-*O*-benzylidene-β-maltotriose (**5**) previously reported. In addition, we discuss the behavior of the interglycosidic benzylidene group in derivatives of **1** and **5** under various conditions for selective ring-opening, etc.

RESULTS AND DISCUSSION

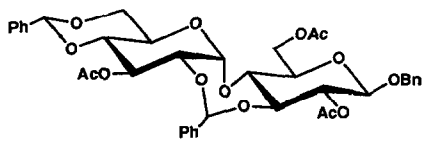
Phenyl α-maltoside was treated in *N*,*N*-dimethylformamide (DMF) at 60°C under diminished pressure with 3.3 mol equiv of α,α-dimethoxytoluene in the presence of (+)-10-camphorsulfonic acid and subsequently the reaction products were caused to undergo selective hydrolysis of their unstable acyclic acetal groups by careful addition of water at 0°C, with monitoring by TLC. The 3,2′:4′,6′-di-*O*-benzylidene derivative **1** was then isolated in 69% yield. Interpretation of the ^{1}HNMR spectrum of **1** met difficulties due to overlapping signals, but the spectrum of acetylated **1** (**2**) could be fully analyzed (see Tables I and II). The vicinal coupling constants of the ring protons of **2** revealed that both pyranose rings adopt the typical $^4C_1$ conformation. The signals due to H-2, H-3′, and H-6a appeared at low magnetic fields (δ 5.08, 5.54, and 4.47, respectively), revealing the acetylated positions in **2**. Furthermore, the configuration of the methine carbon of the 3,2′-*O*-benzylidene group was elucidated as *R* by measurement of a nuclear Overhauser enhancement[4]. Thus, irradiation of the methine proton at δ 6.01 generated a 14% enhancement of the α-oriented H-3 at δ 4.76, but no enhance-



1: R = H
2: R = Ac
3: R = Bz
4: R = Bn



5: R = H
6: R = Ac
7: R = Bn



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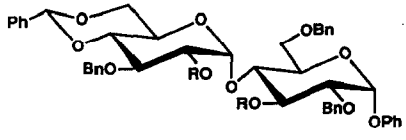


9: R = H
10: R = Ac

TABLE I

^{1}HNMR data for partially acetylated maltose and maltotriose derivatives [a]

Proton	Chemical shifts and multiplicities [b]							
	2	**8**	**10**	**13**	**15**	**16**	**17**	**19**
H-1	5.71 d	4.52 d	5.47 d	5.64 d	5.70 d	5.48 s	5.48 s	5.49 s
H-2	5.08 dd	5.14 dd	3.6 m	3.71 dd	3.71 dd	3.38 s	3.39 m	3.39 s
H-3	4.76 t	4.16 t	5.74 t	4.16 t	4.16 t	3.68 s	3.69 s	3.72 s
H-4	3.75 t	3.7 m [c]	4.16 t	4.01 t	4.02 t	3.59 s	3.59 s	3.61 s
H-5	4.2 m [c]	3.7 m [c]	3.99 dt	3.9 m [c]	3.9 m [c]	4.75 d	4.75 d	4.72 d
H-6a	4.47 dd	4.47 dd	3.86 dd	3.82 dd	3.86 dd	3.90 d	[c]	3.93 d
H-6b	4.2 m [c]	4.36 d	3.6 m [c]	3.61 dd	3.63 dd	3.60 dd	[c]	[c]
H-1′	5.45 d	5.38 d	5.38 d	5.42 d	5.42 d	4.94 d	4.93 d	4.96 d
H-2′	3.5 m	3.53 dd	4.86 dd	4.95 dd	4.97 dd	3.51 dd	3.53 dd	3.55 dd
H-3′	5.54 t	5.48 t	3.94 t	3.96 dd	3.9 m	4.07 t	4.09 t	4.09 t
H-4′	3.43 t	3.42 t	3.6 m [c]	3.56 t	5.10 t	3.8 m [c]	3.9 m [c]	[c]
H-5′	3.89 dt	3.87 dt	3.6 m [c]	3.87 dt	3.9 m [c]	4.1 m [c]	4.12 m [c]	4.1 m [c]
H-6′a	4.2 m [c]	4.25 dd	4.10 dd	4.1 m [c]	3.37 dd	3.72 m	[c]	3.79 dd
H-6′b	3.5 m [c]	3.53 dd	3.80 dd	4.1 m [c]	3.31 dd	3.72 m	[c]	3.6 m [c]
H-1″						5.63 d	5.65 d	5.74 d
H-2″						4.96 dd	4.96 dd	5.00 dd
H-3″						3.92 t	3.85 t	3.95 t
H-4″						3.54 t	5.07 t	3.6 m [c]
H-5″						3.8 m [c]	3.91 m	3.84 dt
H-6″a						4.12 m	[c]	4.12 dd
H-6″b						4.12 m	3.34 dd	3.6 m [c]

[a] Spectra were measured for solutions in $CDCl_3$, using Me_4Si as the internal standard. [b] Other peaks: **2**, 5.39 (s, 1 H, C*H*Ph) and 6.01 (s, 1 H, C*H*Ph); **8**, 1.92, 2.12, and 2.13 (3 s, 9 H, 2 OAc), 4.64 and 4.90 (2 d, 2 H, CH_2Ph), 5.39 (s, 1 H, C*H*Ph), and 5.82 (s, 1 H, C*H*Ph); **10**, 5.54 (s, 1 H, C*H*Ph); **13**, 4.50 (s, 2 H, CH_2Ph), 4.53, 4.58, 4.68, 4.72, 4.75, 4.81, 4.82, and 5.06 (8 d, 8 H, 4 CH_2Ph); **15**, 4.47 (s, 2 H, CH_2Ph), 4.30, 4.41, 4.57, 4.59, 4.66, 4.69, 4.77, and 5.05 (8 d, 8 H, 4 CH_2Ph); **16**, 1.86 (s, 3 H, OAc), 1.97 (s, 3 H, OAc), 4.64, 4.72, 4.80, and 4.81 (4 d, 4 H, 2 CH_2Ph); **17**, 1.85 (s, 3 H, OAc), 1.88 (s, 3 H, OAc), 4.35 and 4.42 (2 d, 2 H, CH_2Ph); **19**, 1.95 (s, 3 H, OAc), 4.49 (s, 2 H, CH_2Ph), 4.67 and 4.89 (2 d, 2 H, 2 CH_2Ph), and 5.54 (s, 1 H, C*H*Ph). [c] Not analyzed, due to overlapping signals.

ment of the signal of β-oriented H-2′ at $\delta \sim 3.5$. In a similar way, treatment of benzyl β-maltoside with α,α-dimethoxytoluene followed by partial hydrolysis and acetylation gave benzyl 2,6,3′-tri-*O*-acetyl-3,2′:4′,6′-di-*O*-benzylidene-β-maltoside (**8**) in 51% yield.

In addition to smooth per-*O*-acetylation, **1** could undergo per-*O*-benzoylation and per-*O*-bezylation with such conventional reagents as benzoyl chloride–pyridine and benzyl bromide–sodium hydride–DMF, giving the 2,6,3′-tri-*O*-benzoyl (**3**) and 2,6,3′-tri-*O*-benzyl derivative (**4**) respectively. Compound **5**, generated from the corresponding per-*O*-acetate (**6**) by the Zemplén procedure, was also per-*O*-benzylated in a similar way to give **7**. Using **4** as a model substrate, the labilities of the two benzylidene groups to acid were compared. Thus, **4** was treated with 80% aqueous acetic acid at room temperature to give an 83% yield of the 4′,6′ monobenzylidene derivative **9**, which was converted into the 3,2′-diacetate **10** for structure elucidation. These results indicated that the interglycosidic benzylidene

TABLE II

Further ^{1}HNMR data for partially acetylated maltose and maltotriose derivatives

Coupling	Coupling constants (Hz)							
	2	**8**	**10**	**13**	**15**	**16**	**17**	**18**
$J_{1,2}$	3.7	8.9	3.7	3.7	3.8	< 2	< 2	< 2
$J_{2,3}$	9.3	10.0	9.3	9.5	10.1	< 2	< 2	< 2
$J_{3,4}$	9.4	10.0	9.3	9.5	10.1	< 2	< 2	< 2
$J_{4,5}$	9.5	10.0	9.5	9.7	9.8	< 2	< 2	< 2
$J_{5,6a}$	5.5	5.1	3.0	3.9	4.0	5.5	6.5	5.2
$J_{5,6b}$	[a]	< 2	[a]	1.7	1.8	< 2	< 2	< 2
$J_{6a,6b}$	10.8	11.9	11.5	11.2	11.3	7.0	[a]	[a]
$J_{1',2'}$	4.3	4.6	4.2	3.7	3.7	3.7	3.6	3.0
$J_{2',3'}$	9.5	9.6	9.7	9.4	10.1	9.3	9.3	9.5
$J_{3',4'}$	9.5	9.6	9.7	9.4	10.1	9.3	9.3	9.4
$J_{4',5'}$	9.5	9.9	9.5	10.1	9.6	9.8	[a]	[a]
$J_{5',6'a}$	4.9	5.1	4.9	2.9	3.4	[a]	[a]	4.0
$J_{5',6'b}$	9.7	10.4	4.6	10.0	4.6	[a]	[a]	[a]
$J_{6'a,6'b}$	[a]	10.2	9.8	[a]	10.7	[a]	[a]	10.3
$J_{1'',2''}$						4.0	4.0	4.0
$J_{2'',3''}$						10.1	10.0	9.7
$J_{3'',4''}$						10.1	9.6	9.9
$J_{4'',5''}$						10.3	9.6	9.9
$J_{5'',6''a}$						[a]	[a]	4.4
$J_{5'',6''b}$						[a]	4.6	9.9
$J_{6''a,6''b}$						[a]	10.5	[a]

[a] Not analyzed, due to overlapping signals.

acetal is more readily hydrolyzed under acidic conditions than the 4′,6′ benzylidene acetal having a six-membered ring, probably because of higher strain in the eight-membered ring[5].

Our interest was next directed toward examining how the interglycosidic acetal groups would react in oxidative ring-opening reactions. Treatment of **3** with *N*-bromosuccinimide–barium carbonate in carbon tetrachloride–1,1,2,2-tetrachloroethane[6] for 4 h under reflux gave crystalline phenyl 2,6,3′,4′-tetra-*O*-benzoyl-6′-bromo-6′-deoxy-α-maltoside (**11**) in 80% yield. The observed simple removal of the interglycosidic benzylidene group under those conditions was very unexpected, because the 4′,6′-*O*-benzylidene group underwent the usual brominative ring opening. The cleavage of the 3,2′-*O*-benzylidene group presumably involved complexation of a bromonium species with an acetal oxygen as in the iodine-promoted deacetalation reported by Szarek and co-workers[7].

The reductive cleavages of the interglycosidic benzylidene acetals were also quite interesting. Examinations were carried out using three reagent systems, namely, lithium aluminum hydride–aluminum chloride[8], sodium cyanoborohydride–hydrogen chloride[9], and borane trimethylamine complex–aluminum chloride[10], with the results summarized in Table III. Treatment of **4** with lithium aluminum hydride–aluminum chloride in 8:5 diethyl ether–dichloromethane un-

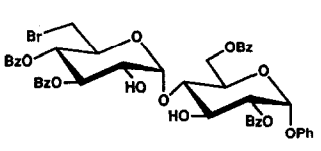
TABLE III

Reductive ring opening reactions of di-*O*-benzylidene derivatives of maltose (**4**) and maltotriose (**7**)

Starting material	Reagent	Conditions	Product (yield %)	
			2′,6′-(2″,6″-) $(OH)_2$	2′,4′-(2″,4″-) $(OH)_2$
4	$LiAlH_4$–$AlCl_3$	Et_2O–CH_2Cl_2, reflux, 3 h	**12** (74%)	
4	$NaBH_3CN$–HCl	Oxolane, 0°C, 1 h		**14** (65%)
4	$BH_3 \cdot NMe_3$–$AlCl_3$	Oxolane, r.t., 2 d		**14** (75%)
7	$LiAlH_4$–$AlCl_3$	Et_2O–CH_2Cl_2, reflux, 2 h	**16** [a] (82%)	
7	$NaBH_3CN$-HCl	Oxolane, 0°C, 2 h		**17** [a] (58%)
7	$BH_3 \cdot NMe_3$–$AlCl_3$	Oxolane, r.t., 4 d		**17** [a] (80%)

[a] Diacetate of the actual reductive-cleavage product.

der reflux for 3 h (Entry 1) gave phenyl 2,3,6,3′,4′-penta-*O*-benzyl-α-maltoside (**12**), which was characterized as the 2′,6′-diacetate (**13**). In the ^1H NMR spectrum of **13** (see Tables I and II), a one-proton doublet of doublets assignable to H-2′ and a two-proton multiplet assignable to H-6a,6b were observed at δ 4.95 and δ ~4.1, respectively, supporting the assigned structure. Similar treatment of **7** with lithium aluminum hydride–aluminum chloride and subsequent *O*-acetylation afforded the 2″,6″-di-*O*-acetyl-2,3,2′,3′,6′,3″,4″-hepta-*O*-benzyl derivative (**16**) in 82% overall yield. On the other hand, reduction of **4** and **7** with sodium cyanoborohydride–hydrogen chloride or borane trimethylamine complex–aluminum chloride followed by acetylation predominantly afforded phenyl 2′,4′-di-*O*-acetyl-2,3,6,3′,6′-penta-*O*-benzyl-α-maltoside (**15**) and 2″,4″-di-*O*-acetyl-1,6-anhydro-2,3,2′,3′,6′,3″,6″-hepta-*O*-benzyl-β-maltotriose (**17**), respectively. Both products carried acetyl groups



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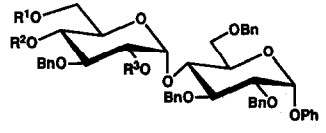
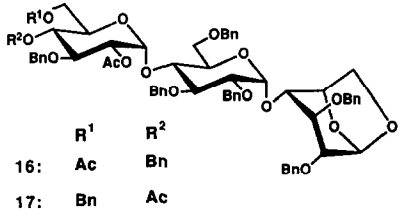
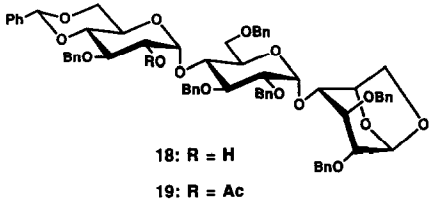


	R¹	R²	R³
12:	H	Bn	H
13:	Ac	Bn	Ac
14:	Bn	H	H
15:	Bn	Ac	Ac

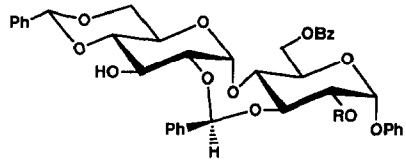


	R¹	R²
16:	Ac	Bn
17:	Bn	Ac



18: R = H

19: R = Ac



20: R = H

21: R = Bz

at O-2 and O-4 of their nonreducing ends. Furthermore, it was observed that the interglycosidic benzylidene acetal group of **7** could undergo selective reduction with borane trimethylamine complex–aluminum chloride, leaving the 4″,6″-*O*-benzylidene group unaffected. The starting material was consumed after 4 h at room temperature, and the 2,3,2′,3′,6′,3″-hexa-*O*-benzyl-4″,6″-*O*-benzylidene derivative (**18**) was obtained as a major product. It was converted into the 2″-*O*-acetyl derivative (**19**) for structure elucidation. The regioselectivities observed in all reductive ring openings of the benzylidene acetal groups at the 4′,6′ or 4″,6″ positions were the same as previously reported for the monosaccharide system; i.e., the benzyl group generated by reduction with lithium aluminum hydride–aluminum chloride[8] is at O-4, whereas reductions with sodium cyanoborohydride–hydrogen chloride[9] and with borane trimethylamine complex–aluminum chloride[10] in oxolane provide 6-benzyl ethers. In contrast, the interglycosidic benzylidene acetals always gave a 3(3′)-benzyl ether with HO-2′ (HO-2″) unsubstituted irrespective of the reagents employed. This regioselectivity might be explainable by thinking of the electron-withdrawing effect of an anomeric center.

As expected from well-known generalizations on the relative reactivities of hydroxyl groups[11], the free hydroxyls of **1** showed the reactivity order OH-6 > OH-2 > OH-3′. Thus, treatment of **1** with 1.1 and 2.1 mol equiv of benzoyl chloride in pyridine gave the 6-*O*-benzoyl derivative (**20**) and the 2,6-dibenzoate (**21**) in 61 and 49% yields, respectively.

Combining the ability to generate benzyl or benzoyl groups at specific positions with their simple function as temporarily protected intermediates, a set of benzylidene acetals of oligosaccharide molecules like **1**, **5**, and **8** will be able to provide a variety of building blocks for synthetic glycotechnology.

EXPERIMENTAL

General methods.—Melting points were determined in capillaries with an Ishii melting-point apparatus and are uncorrected. Optical rotations were determined with a Perkin–Elmer Model 241MC polarimeter. IR spectra were recorded with a Shimadzu IR-27 spectrophotometer, for potassium bromide disks or on KRS

(thallium bromide–iodide) for thin films. ^{1}H NMR spectra were recorded at 400 or 500 MHz with JEOL JNM-GX 400 or JNM-GX 500 spectrometers for solutions in $CDCl_3$, using Me_4Si as the internal standard. Molecular sieves were activated at 180–200°C under diminished pressure for 5–8 h. Reactions were monitored by TLC on precoated plates of Silica Gel $60F_{254}$ (layer thickness, 0.25 mm; E. Merck, Darmstadt, Germany). Column chromatography was performed on Silica Gel 60 (70-230 mesh; E. Merck). Solvent extracts were dried over anhyd Na_2SO_4 unless otherwise specified, and solutions were concentrated under diminished pressure below 40°C. Analytical samples were dried at 60–65°C over P_2O_5 for 5–6 h in vacuo.

Phenyl 3,2′:4′,6′-di-O-benzylidene-α-maltoside (**1**).—Phenyl α-maltoside[12] (418 mg, 1 mmol) and α,α-dimethoxytoluene (0.5 mL, 3.3 mmol) were dissolved in dry DMF (20 mL) and the acidity of the solution was adjusted to a reading of 3 with wet pH paper by addition of (+)-10-camphorsulfonic acid (80 mg). The solution was stirred under diminished pressure (~ 2.6 kPa) at 60°C for 5 h and cooled in an ice bath; TLC with 1:1 benzene–EtOAc showed three major product spots (R_f 0.54, 0.72, and 0.82). Water (0.5 mL) was added to the solution, and the mixture was stirred at 0°C for 20 min. TLC with 1:1 benzene–EtOAc now showed the presence of a single major product (R_f 0.54). The mixture was diluted with $CHCl_3$, and successively washed with water, aq $NaHCO_3$, and brine, dried, and concentrated. The residual syrup was chromatographed on a column of silica gel with 60:20:1 toluene–EtOAc–pyridine to give **1** (412 mg, 69%) as an amorphous solid; $[\alpha]_D^{21.5}$ +114° (*c* 0.46, $CHCl_3$); ^{1}H NMR: δ 3.34 (dd, 1 H, *J* 7.1, 9.5 Hz, H-4), 3.41 (dd, 1 H, *J* 3.9, 8.8 Hz, H-2′), 3.95 (dt, 1 H, *J* 1.5, 10.0 Hz, H-5), 4.08 (t, 1 H, *J* 7.1 Hz, H-3′), 5.43 (s, 1 H, C*H*Ph), 5.48 (d, 1 H, *J* 4.2 Hz, H-1), 5.57 (d, 1 H, *J* 3.9 Hz, H-1), and 6.11 (s, 1 H, C*H*Ph). Anal. Calcd for $C_{32}H_{34}O_{11} \cdot 0.75\ H_2O$: C, 63.20; H, 5.88. Found: C, 63.14; H. 5.95.

Phenyl 2,6,3′-tri-O-acetyl-3,2′:4′,6′-di-O-benzylidene-α-maltoside (**2**).—A solution of **1** (50 mg, 0.08 mmol) in dry pyridine (2 mL) and Ac_2O (1 mL) was stirred at room temperature for 1 day, quenched with MeOH (1 mL), concentrated under diminished pressure. The concentrate was then subjected to several additions and evaporations of pyridine. The residual syrup was chromatographed on a silica gel column with 200:4:1 toluene–EtOAc–pyridine to give **2** (60 mg, quantitative); $[\alpha]_D^{20.5}$ +82.5° (*c* 0.16, $CHCl_3$); for ^{1}H NMR data see Tables I and II. Anal. Calcd for $C_{38}H_{40}O_{14}$: C, 63.33; H, 5.59. Found: C, 63.08; H, 5.57.

Phenyl 2,6,3′-tri-O-benzoyl-3,2′:4′6′-di-O--benzylidene-α-maltoside (**3**).—To a solution of **1** (119 mg, 0.2 mmol) in dry pyridine (2 mL) was added benzoyl chloride (0.16 mL, 1.4 mmol) at −15°C. The solution was stirred at room temperature overnight, poured into ice–water, and extracted with $CHCl_3$. The extract was successively washed with cold M HCl, aq $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on a silica gel column with 99:1 toluene–EtOAc as the eluent, giving **3** (187 mg, quantitative) as a white powder; $[\alpha]_D^{22}$ +55.7° (*c* 0.49, $CHCl_3$); ν_{max} (film) 3450 (OH) and 1700 cm^{-1}

(C=O); ^{1}H NMR: δ 3.59 (t, 1 H, J 10.3 Hz, H-6'b), 3.62 (t, 1 H, J 9.8 Hz, H-4'), 3.68 (dd, 1 H, J 4.3, 9.2 Hz, H-2'), 3.93 (t, 1 H, J 9.2 Hz, H-4), 4.03 (dt, 1 H, J 5.2, 9.8 Hz, H-5'), 4.31 (dd, 1 H, J 5.19, 10.4 Hz, H-6'a), 4.52–4.49 (m, 1 H, H-5), 4.64 (dd, 1 H, J 1.8, 11.9 Hz, H-6b), 4.74 (dd, 1 H, J 6.7, 12.2 Hz, H-6a), 5.06 (dd, 1 H, J 8.8, 10.1 Hz, H-3), 5.39 (dd, 1 H, J 3.7, 10.3 Hz, H-2), 5.42 (s, 1 H, C*H*Ph), 5.54 (d, 1 H, J 4.3 Hz, H-1'), 5.87 (t, 1 H, J 9.5 Hz, H-3'), 5.88 (d, 1 H, J 3.7 Hz, H-1), and 6.04 (s, 1 H, C*H*Ph). Anal. Calcd for $C_{53}H_{46}O_{14}$: C, 70.19; H, 5.11. Found: C, 70.11; H, 5.14.

Phenyl 2,6,3'-tri-O-benzyl-3,2':4',6'-di-O-benzylidene-α-maltoside (**4**).—To a solution of **1** (2.9 g, 5 mmol) in dry DMF (50 mL) was added NaH (60% oil dispersion; 2 g, 50 mmol) portionwise at 0°C, and the suspension was stirred at 0°C for 2 h. Benzyl bromide (6 mL, 50 mmol) was added dropwise with stirring at 0°C. The mixture was stirred at room temperature overnight, quenched with MeOH (5 mL), and partitioned between Et_2O and water. The organic phase was successively washed with brine, cold M HCl, $NaHCO_3$, and brine, dried over anhyd K_2CO_3, and concentrated. The residue was chromatographed on a silica gel column with 38:2:1 benzene–EtOAc–pyridine as the eluent to give syrupy **4** (3.62 g, 83%), $[\alpha]_D^{22}$ +46° (c 0.57, $CHCl_3$); ^{1}H NMR: δ 4.49 (d, 1 H, J 12.5 Hz, 1/2 CH_2Ph), 4.56 (d, 1 H, J 12.5 Hz, 1/2 CH_2Ph), 4.65 (d, 1 H, J 12.4 Hz, 1/2 CH_2Ph), 4.71 (d, 1 H, J 12.2 Hz, 1/2 CH_2Ph), 4.91 (s, 2 H, C*H*Ph), 5.47 (s, 1 H, C*H*Ph), 5.48 (d, 1 H, J 3.3 Hz, H-1), 5.51 (d, 1 H, J 3.7 Hz, H-1), and 6.18 (s, 1 H, C*H*Ph). Anal. Calcd for $C_{53}H_{52}O_{11}$: C, 73.59; H, 6.06. Found: C, 73.56; H, 6.06.

1,6-Anhydro-2,3,2',6',3''-penta-O-benzyl-3',2'':4''6''-di-O-benzylidene-β-maltotriose (**7**).—To a suspension of 2,3,2',6',3''-penta-*O*-acetyl-1,6-anhydro-3'-2'':4'',6''-di-*O*-benzylidene-β-maltotriose[1] (**6**; 1.92 g, 2.2 mmol) in MeOH (30 mL) was added 5.2 M methanolic NaOMe (0.1 mL). The mixture was stirred at room temperature overnight, and concentrated, and toluene was added and evaporated several times. To a solution of the residue in DMF (30 mL) was then added NaH (60% oil dispersion; 1.2 g, 30 mmol) at 0°C, and the mixture was stirred at 0°C for 1 h. Benzyl bromide (5 mL, 42 mmol) was added to the mixture. The suspension was stirred at room temperature for 14 h, quenched by the successive addition of MeOH (5 mL) and concd aq NH_4OH (2 mL), further stirred for 1 day, and partitioned between $CHCl_3$ and water. The organic layer was successively washed with water, cold M HCl, aq $NaHCO_3$, and brine, dried over anhyd K_2CO_3, and concentrated. The residual syrup was chromatographed on a column of silica gel with 49:1 toluene–EtOAc as the eluent to give **7** (2.23 g, 82%); $[\alpha]_D^{23}$ −13° (c 0.22, $CHCl_3$); ^{1}H NMR: δ 3.39 (bs, 1 H, H-2), 4.76 (d, 1 H, J 4.9 Hz, H-5), 4.90 (s, 2 H, CH_2Ph), 5.03 (d, 1 H, J 11.7 Hz, 1/2 CH_2Ph), 5.04 (d, 1 H, J 3.7 Hz, H-1'), 5.47 (s, 1 H, C*H*Ph), 5.48 (s, 1 H, H-1), 5.70 (d, 1 H, J 3.9 Hz, H-1''), and 6.11 (s, 1 H, C*H*Ph). Anal. Calcd for $C_{67}H_{68}O_{15}$: C, 72.29; H, 6.16. Found: C, 72.21; H, 6.22.

Benzyl 2,6,3'-tri-O-acetyl-3,2':4',6'-O-benzylidene-β-maltoside (**8**).—Benzyl β-maltoside[13] (432 mg, 1 mmol) and α,α-dimethoxytoluene (0.6 mL, 3.9 mmol) were dissolved in dry DMF (20 mL) and the acidity of the solution was adjusted a

reading of ~ 3 with wet pH paper by addition of (+)-10-camphorsulfonic acid (100 mg). The solution was stirred under diminished pressure (~ 2.6 kPa) at 60°C for 3 h and cooled in an ice bath; TLC with 2:1 benzene–EtOAc showed three major product spots (R_f 0.59, 0.74, and 0.84). Water (0.5 mL) was added to the solution, and the mixture was stirred at 0°C for 2 h and then at room temperature for 20 min. TLC with the same solvent showed the presence of a single major product (R_f 0.59). The mixture was partitioned between aq $NaHCO_3$ and $CHCl_3$, and the organic layer was successively washed with aq $NaHCO_3$, and brine, dried over anhyd K_2CO_3, and concentrated. The residue was dissolved in pyridine (30 mL) and Ac_2O (10 mL). The solution was stirred at 60°C for 4 h, and concentrated under reduced pressure, and pyridine was added and evaporated several times. The residual syrup was chromatographed on a column of silica gel with 19:1 → 9:1 benzene–EtOAc to give **8** (375 mg, 51%); $[\alpha]_D^{25}$ −35° (*c* 0.28, $CHCl_3$); for ^{1}H NMR data see Tables I and II. Anal. Calcd for $C_{39}H_{42}O_{14}$: C, 63.75; H, 5.76. Found: C, 63.39; H, 5.92.

*Phenyl 2,6,3′-tri-*O*-benzyl-4′,6′-*O*-benzylidene-α-maltoside* (**9**).—To a solution of **4** (100 mg, 0.12 mmol) in acetic acid (2 mL) was added water (0.5 mL) in portions at room temperature. The solution was stirred at room temperature for 4 h, and partitioned between $CHCl_3$ and water. The organic layer was successively washed with water, aq $NaHCO_3$, and brine, dried over K_2CO_3, and concentrated. Chromatography of the residual syrup on a silica gel column with 9:1 toluene–EtOAc as the eluent gave **9** (75 mg, 83%) as a white powder; $[\alpha]_D^{20}$ +21.4° (*c* 0.11, $CHCl_3$); ^{1}H NMR δ 5.19 (d, 1 H, *J* 3.7 Hz, H-1′), 5.46 (d, 1 H, *J* 3.4 Hz, H-1), and 5.54 (s, 1 H, C*H*Ph). Anal. Calcd for $C_{46}H_{48}O_{11} \cdot 0.5H_2O$: C, 70.30; H, 6.28. Found: C, 70.37; H, 6.33.

*Phenyl 3,2′-di-*O*-acetyl-2,6,3′-tri-*O*-benzyl-4′,6′-*O*-benzylidene-α-maltoside* (**10**).—Compound **9** (38 mg, 0.05 mmol) was acetylated with dry pyridine (2 mL) and (0.5 mL) as described for the preparation of **2**. Column chromatography with 19:1 toluene–EtOAc as the eluant, gave **10** (35 mg, 83%); $[\alpha]_D^{20}$ +113° (*c* 0.30, $CHCl_3$); for ^{1}H NMR data see Tables I and II. Anal. Calcd for $C_{50}H_{52}O_{13}$: C, 69.75; H, 6.09. Found: C, 69.83, H, 6.04.

*Phenyl 2,6,3′,4′-tetra-*O*-benzoyl-6′-bromo-6′-deoxy-α-maltoside* (**11**).—To a suspension of **3** (453 mg, 0.5 mmol) and $BaCO_3$ (250 mg, 1.27 mmol) in refluxing CCl_4 (4.5 mL) and 1,1,2,2-tetrachloroethane (0.5 mL) was added *N*-bromosuccinimide (220 mg, 1.24 mmol) with stirring. The mixture was stirred under reflux for 4 h, cooled, poured into aq sodium thiosulfate, and extracted with $CHCl_3$. The extract was washed with aq sodium thiosulfate and brine, dried over $MgSO_4$, and concentrated. Chromatographic purification on a silica gel column with 9:1 toluene–EtOAc as the eluent gave **11** (361 mg, 80%), which was crystallized from benzene–hexane; mp 162–164°C; $[\alpha]_D^{24}$ +120° (*c* 0.31, $CHCl_3$); ν_{max} (KBr) 3400 (OH) and 1715 cm^{-1} (C=O); ^{1}H NMR: δ 3.44 (dd, 1 H, *J* 6.6, 11.6 Hz, H-6′a), 3.60 (dd, 1 H, *J* 2.4, 11.6 Hz, H-6′b), 3.93 (dd, 1 H, *J* 3.7, 9.2 Hz, H-2′), 4.11 (dd, 1 H, *J* 8.9, 10.1 Hz, H-4), 4.40 (dt, 1 H, *J* 3.6, 6.4 Hz, H-5′), 4.44 (dt, 1 H, *J* 3.7, 10.1 Hz,

H-5), 4.66–4.71 (m, 3 H, H-3,6a,6b), 5.41 (dd, 1 H, *J* 3.7, 10.1 Hz, H-2), 5.45 (t, 1 H, *J* 9.7 Hz, H-4), 5.49 (d, 1 H, *J* 3.7 Hz, H-1), 6.06 (d, 1 H, *J* 3.6 Hz, H-1′), and 6.11 (t, 1 H, *J* 9.5 Hz, H-3′). Anal. Calcd for $C_{46}H_{41}O_{14}Br$: C, 61.55; H, 4.60; Br, 8.90. Found: C, 61.34; H, 4.42; Br, 8.52.

Phenyl 2,3,6,3′,4′-penta-O-benzyl-α-maltoside (**12**).—To a solution of **4** (300 mg, 0.35 mmol) in 1:1 dry Et_2O–CH_2Cl_2 (10 mL) was added $LiAlH_4$ (100 mg, 2.6 mmol) in portionwise at 0°C. The solution was heated under reflux and $AlCl_3$ (300 mg, 2.3 mmol) in dry Et_2O (3 mL) was then added dropwise. The mixture was stirred under reflux for 3 h, quenched by the successive addition of EtOAc (1 mL) and water (1 mL), and partitioned between $CHCl_3$ and water. The organic layer was washed three times with aq satd potassium sodium tartarate, dried, and concentrated. Chromatographic purification of the residual syrup with 9:1 toluene–EtOAc as the eluent gave **12** (224 mg, 74%); $[\alpha]_D^{20}$ +121° (*c* 0.58, $CHCl_3$); ^{1}H NMR: δ 4.19 (t, 1 H, *J* 9.5 Hz, H-3 or 3′), 3.99 (t, 1 H, *J* 9.5 Hz, H-3 or 3′), 4.43 (d, 1 H, *J* 12.0 Hz, 1/2 C*H*$_2$Ph), 4.53–4.70 (m, 6 H, 3 × C*H*$_2$Ph), 4.84 (d, 1 H, *J* 10.7 Hz, 1/2 C*H*$_2$Ph), 4.85 (d, 1 H, *J* 12.6 Hz, 1/2 C*H*$_2$Ph), 5.09 (d, 1H, *J* 3.4 Hz, H-1′), 5.26 (d, 1 H, *J* 11.5 Hz, 1/2 C*H*$_2$Ph), and 5.47 (d, 1 H, *J* 3.4 Hz, H-1). Anal. Calcd for $C_{53}H_{56}O_{11}$: C, 73.25; H, 6.50. Found: C, 72.92; H, 6.55.

Phenyl 2′,6′-di-O-acetyl-2,3,6,3′,4′-penta-O-benzyl-α-maltoside (**13**).—Compound **12** (125 mg, 0.14 mmol) was acetylated with pyridine (2 mL) and Ac_2O (0.5 mL) as described for the preparation of **2**. Column chromatography of the product with 97:3 toluene–EtOAc as the eluent gave **13** (125 mg, 91%); $[\alpha]_D^{20}$ +99° (*c* 0.22, $CHCl_3$); for ^{1}H NMR data see Tables I and II. Anal. Calcd for $C_{57}H_{60}O_{13}$: C, 71.83; H, 6.35. Found: C, 71.57; H, 6.35.

Phenyl 2,3,6,3′,6′-penta-O-benzyl-α-maltoside (**14**).—*By reductive cleavage with by $NaBH_3CN$–HCl.* To a suspension of **4** (300 mg, 0.35 mmol), powdered 3A molecular sieves (600 mg), and $NaBH_3CN$ (600 mg, 9.5 mmol) in dry oxolane (20 mL) stirred at 0°C was added dropwise a satd solution of HCl in Et_2O (~2 mL). The suspension was stirred at 0°C for 1 h, filtered through a Celite pad, and washed with $CHCl_3$. The combined filtrate and washings was successively washed with aq $NaHCO_3$ and brine, dried, and concentrated. The residual syrup was chromatographed on a column of silica gel with 19:1 toluene–EtOAc as the eluent to give syrupy **14** (196 mg, 658%); $[\alpha]_D^{22}$ +64.7° (*c* 0.43, $CHCl_3$); ^{1}H NMR: δ 3.99 (t, 1 H *J* 9.8 Hz, H-3 or 3′), 4.23 (t, 1 H, *J* 9.5 Hz, H-3 or 3′), 4.43 (d, 1 H, *J* 11.6 Hz, 1/2 C*H*$_2$Ph), 4.44 (d, 1 H, *J* 12.1 Hz, 1/2 C*H*$_2$Ph), 4.50 (d, 2 H, *J* 11.9 Hz, C*H*$_2$Ph), 4.51 (d, 1 H, *J* 11.6 Hz, 1/2 C*H*$_2$Ph), 4.60 (d, 1 H, *J* 11.9 Hz, 1/2 C*H*$_2$Ph), 4.67 (d, 1 H, *J* 11.9 Hz, 1/2 C*H*$_2$Ph), 4.77 (d, 1 H, *J* 11.3 Hz, 1/2 C*H*$_2$Ph), 4.87 (d, 1 H, *J* 11.3 Hz, 1/2 C*H*$_2$Ph), 5.19 (d, 1 H, *J* 3.7 Hz, H-1), 5.25 (d, 1 H, *J* 11.3 Hz, 1/2 C*H*$_2$Ph), and 5.46 (d, 1 H, *J* 3.4 Hz, H-1). Anal. Calcd for $C_{53}H_{56}O_{11}$: C, 73.25; H, 6.50. Found: C, 72.93; H, 6.56.

By reductive cleavage with $BH_3 \cdot NMe_3$–$AlCl_3$. To a suspension of **4** (300 mg, 0.35 mmol), 4A powdered molecular sieves (2 g), and $BH_3 \cdot NMe_3$ complex (145 mg, 2.0 mmol) in dry oxolane (15 mL) was added $AlCl_3$ (280 mg, 2.1 mmol). The mixture

was stirred at room temperature for 2 days and filtered, and the residue was washed with $CHCl_3$. The combined filtrate and washings was worked up as described above to give **14** (226 mg, 75%).

Phenyl 2',4'-di-O-acetyl-2,3,6,3',6'-penta-O-benzyl-α-maltoside (**15**).—Compound **14** (35 mg, 0.04 mmol) was acetylated with pyridine (2 mL) and Ac_2O (0.5 mL) as described for the preparation of 2. Silica gel column chromatography with 19:1 toluene–EtOAc as the eluent gave **15** (32 mg, 83%); $[\alpha]_D^{24}$ +87° (*c* 0.22, $CHCl_3$); for ^{1}H NMR data see Tables I and II. Anal. Calcd for $C_{57}H_{60}O_{13}$: C, 71.83; H, 6.35. Found: C, 71.70; H, 6.41.

2",6"-Di-O-acetyl-1,6-anhydro-2,3,2',3',6',3",4"-hepta-O-benzyl-β-maltotriose (**16**).—To a solution of **7** (160 mg, 0.14 mmol) in 1:1 dry Et_2O–CH_2Cl_2 (20 mL) was added $LiAlH_4$ (50 mg, 1.3 mmol) at room temperature. The mixture was stirred and heated to reflux temperature, and $AlCl_3$ (140 mg, 1.05 mmol) in dry Et_2O (4 mL) was added. The suspension was stirred under reflux for 2 h, quenched by successive additions of EtOAc (0.5 mL) and water (1 mL), stirred overnight, and partitioned between water and $CHCl_3$. The organic layer was successively washed with concd aq potassium sodium tartrate (3 times) and brine, dried over anhyd Na_2SO_4, and evaporated to dryness. The residual syrup was acetylated with pyridine (5 mL) and Ac_2O (2 mL) as described for the preparation of **2**, and the product was chromatographed on a silica gel column with 15:1 toluene–EtOAc as the eluent to give **16** (141 mg, 82%); $[\alpha]_D^{24}$ +40° (*c* 0.29, $CHCl_3$); for ^{1}H NMR data see Tables I and II. Anal. Calcd for $C_{71}H_{76}O_{17}$: C, 70.98; H, 6.38. Found: C, 70.72; H, 6.36.

2",4"-Di-O-acetyl-1,6-anhydro-2,3,2',3',6',3",6"-hepta-O-benzyl-β-maltotriose (**17**).—*By reductive cleavage with $NaBH_3CN$–HCl.* To a suspension of **7** (160 mg, 0.14 mmol), powdered 3A molecular sieves (300 mg), and $NaBH_3CN$ (100 mg, 1.6 mmol) in dry oxolane (10 mL), stirred at 0°C, was added dropwise a satd solution of HCl in dry Et_2O (~ 0.5 mL). The mixture was stirred at 0°C for 2 h and filtered through a Celite pad, and the residue was washed with $CHCl_3$. The combined filtrate and washings was successively washed with M HCl, aq $NaHCO_3$, and brine, dried, and concentrated. The residual syrup was then acetylated with pyridine (5 mL) and Ac_2O (2 mL) as described for the preparation of **2**. Column chromatography on silica gel with 19:1 toluene–EtOAc as the eluent gave **17** (96 mg, 58%); $[\alpha]_D^{24}$ +41° (*c* 0.18, $CHCl_3$); for ^{1}H NMR data see Tables I and II. Anal. Calcd for $C_{71}H_{76}O_{17} \cdot 0.5H_2O$: C, 70.46; H, 6.41. Found: C, 70.49; H, 6.33.

By reductive cleavage with $BH_3 \cdot NMe_3$–$AlCl_3$. To a suspension of **7** (160 mg, 0.14 mmol), powdered 4A molecular sieves (3 g), and $BH_3 \cdot NMe_3$ complex (73 mg, 1 mmol) in dry oxolane (20 mL) was added $AlCl_3$ (140 mg, 1.05 mmol) with stirring at room temperature. The mixture was stirred for 1 day and filtered through a Celite pad, and the residue was washed with $CHCl_3$. The combined filtrate and washings was successively washed with aq $NaHCO_3$ and brine, dried, and concentrated. The residual syrup on acetylation with pyridine (5 mL) and Ac_2O (2 mL) as

described for the preparation of **2**, followed by silica gel column chromatography, gave **17** (129 mg, 80%).

1,6-Anhydro-4",6"-O-Benzylidene-2,3,2',3',6',3"-hexa-O-benzyl-β-maltotriose (**18**).—A mixture of **7** (250 mg, 0.23 mmol), $BH_3 \cdot NMe_3$ complex (131 mg, 1.8 mmol), and 4A molecular sieves (3 g) in dry oxolane (25 mL) was stirred at room temperature for 30 min, and then $AlCl_3$ (240 mg, 1.8 mmol) was added to the suspension. The mixture was stirred at room temperature for 4 h, when TLC with 9:1 benzene–EtOAc showed the disappearance of **7**. The suspension was filtered through a Celite pad and the residue was washed with $CHCl_3$. The combined filtrate and washings was treated with Dowex 50W-X8 (H^+ form), filtered, and concentrated. The residual syrup was chromatographed on a silica gel column with 15:1 toluene–EtOAc as the eluent to give **18** (143 mg, 58%); $[\alpha]_D^{24}$ +21° (*c* 0.34, $CHCl_3$); ^{1}H NMR: δ 4.98 (d, 1 H, *J* 3.1 Hz, H-1'), 5.47 (s, 1 H, H-1), 5.65 (d, 1 H, *J* 4.0 Hz, H-1"), and 5.88 (s, 1 H, C*H*Ph). Anal. Calcd for $C_{67}H_{70}O_{15}$: C, 72.16; H, 6.33. Found: C, 72.26; H, 6.39.

2"-O-Acetyl-1,6-anhydro-4",6"-O-benzylidene-2,3,2',3',6',3"-hexa-O-benzyl-β-maltotriose (**19**).—Compound **18** (78 mg, 0.7 mmol) was acetylated with pyridine (1 mL) and Ac_2O (0.5 mL) in the same manner as described for the preparation of **2**. Column chromatography on silica gel with 19:1 toluene–EtOAc as the eluent gave **19** (75 mg, 91%); $[\alpha]_D^{24}$ +33° (*c* 0.23, $CHCl_3$); for ^{1}H NMR data see Tables I and II. Anal. Calcd for $C_{69}H_{72}O_{16}$: C, 71.61; H, 6.27. Found: C, 71.57; H, 6.27.

Phenyl 6-O-benzoyl-3,2':4',6'-di-O-benzylidene-α-maltoside (**20**).—To a solution of **1** (595 mg, 1 mmol) in dry pyridine (3 mL) was added benzoyl chloride (0.13 mL, 1.1 mmol) at −15°C. The solution was stirred at the same temperature overnight, then poured into ice–water, and the mixture was extracted with $CHCl_3$. The extract was successively washed with cold M HCl, aq $NaHCO_3$, and brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on a silica gel column with 9:1 toluene–EtOAc as the eluent, giving **20** (447 mg, 64%) as a white powder; $[\alpha]_D^{22}$ +94.4° (*c* 0.50, $CHCl_3$); ν_{max} (film) 3450 (OH) and 1715 cm^{-1} (C=O); ^{1}H NMR: δ 3.34 (t, 1 H, *J* 9.5 Hz, H-4'), 3.43 (dd, 1 H, *J* 3.9, 8.8 Hz, H-2'), 3.52 (t, 1 H, *J* 10.2 Hz, H-6'b), 3.69 (t, 1 H, *J* 9.2 Hz, H-4), 3.82 (dt, 1 H, *J* 4.9, 10.1 Hz, H-5'), 3.92 (m, 1 H, H-2), 4.09 (t, 1 H, *J* 9.0 Hz, H-3'), 4.24 (dd, 1 H, *J* 5.1, 10.2 Hz, H-6'a), 4.30–4.33 (m, 1 H, H-5), 4.49 (t, 1 H, *J* 9.3 Hz, H-3), 4.55–4.63 (m, 2 H, H-6), 5.42 (s, 1 H, C*H*Ph), 5.47 (d, 1 H, *J* 3.9 Hz, H-1'), 5.60 (d, 1 H, *J* 3.9 Hz, H-1), and 6.14 (s, 1 H, C*H*Ph). Anal. Calcd for $C_{39}H_{38}O_{12} \cdot 0.5\ H_2O$: C, 66.19; H, 5.55. Found: C, 65.99; H, 5.49.

Phenyl 2,6-di-O-benzoyl-3,2':4',6'-di-O-benzylidene-α-maltoside (**21**).—To a solution of **1** (595 mg, 1 mmol) in dry pyridine (5 mL) was added benzoyl chloride (0.24 mL, 2.07 mmol) at −15°C. The mixture was stirred at the same temperature overnight, quenched with water (10 mL), and partitioned between $CHCl_3$ and water. The organic layer was successively washed with cold M HCl, aq $NaHCO_3$, and brine, dried, and concentrated. The residue was chromatographed on a column of silica gel with 196:4:1 toluene–EtOAc–pyridine as the eluent to give **3**

(53 mg, 6%), a 2:3 mixture of 2,6- (**21**) and 3′,6-dibenzoate [^{1}H NMR δ 5.40 (s, 0.6 H, C*H*Ph), 5.52 (d, 0.6 H, *J* 4.3 Hz, H-1), 5.65 (d, 0.6 H, *J* 3.7 Hz, H-1), 5.79 (t, 0.6 H, *J* 9.2 Hz, H-3′), and 6.03 (s, 0.6 H, C*H*Ph)] (79 mg, 9%), and pure **21** (393 mg, 49%); $[\alpha]_D^{21.5}$ +81.3° (*c* 0.55, $CHCl_3$); ν_{max} 1715 (C=O) and 3475 cm^{-1} (OH); ^{1}H NMR: δ 3.39 (t, 1 H, *J* 9.5 Hz, H-4′), 3.51 (dd, 1 H, *J* 3.7, 8.8 Hz, H-2′), 3.54 (t, 1 H, *J* 10.5 Hz, H-6′b), 3.87 (dt, 1 H, *J* 5.4, 9.8 Hz, H-5′), 3.90 (t, 1 H, *J* 9.0 Hz, H-4), 4.16 (t, 1 H, *J* 9.3 Hz, H-3′), 4.26 (dd, 1 H, *J* 5.1 10.5 Hz, H-6′a), 4.43–4.47 (m, 1 H, H-5), 4.62–4.70 (m, 2 H, H-6), 4.98 (t, 1 H, *J* 10.3 Hz, H-3), 5.39 (d, 1 H, *J* 3.7, 10.5 Hz, H-2), 5.45 (s, 1 H, C*H*Ph), 5.49 (d, 1 H, *J* 3.9 Hz, H-1′), 5.87 (d, 1 H, *J* 3.7 Hz, H-1), and 6.13 (s, 1 H, C*H*Ph). Anal. Calcd for $C_{46}H_{42}O_{13}$: C, 68.82; H, 5.27. Found: C, 68.96; H, 5.36.

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