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Synthesis of α,α-, α,β-, and β,β-(dimaltoside)s of ethane-1,2-diol, propane-1,3-diol, and butane-1,4-diol: A proposal for an initial adhesion mode

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Abstract

Nine dimaltoside derivatives of ethane-1,2-diol, propane-1,3-diol, and butane-1,4-diol having the α,α, α,β, and β,β anomeric configurations at the linkage sites have been synthesized. Suitably protected maltosyl halides or a 1-(phenylthio) derivative were condensed with the foregoing diols and the resulting monomaltosyl derivatives were further condensed with the maltosyl donors to give, after deprotection, the title compounds. Their structures were fully characterized by NMR spectroscopy. Interactions between the three α,α-(dimaltoside)s and cinnamyl alcohol are briefly discussed.

Keywords: Maltoside; Dimaltoside; Ethane-1,2-diol; Propane-1,3-diol; Butane-1,4-diol; Adhesion

1. Introduction

Non-covalent interactions between two carbohydrates, between a carbohydrate and a protein, and similar molecular combinations, as exemplified by enzyme–substrate interactions and many other kinds of molecular recognition processes, such as adhesions [1], antigen–antibody interactions [2], and receptor binding [3], are significant research targets in biological chemistry. However, even if the structures of these complexes are clarified by X-ray crystallography, NMR spectroscopy, or other modern techniques, it does not necessarily mean that the attractive (or repulsive) forces operating between the two parts of the complex are fully manifested. Even in a simple disaccharide, or a combination of a carbohydrate and an amino acid in water, the final conformation of the carbohydrates may be determined by diverse forces working between any set of functional groups, including those of water. These forces may originate from hydrogen bonding [4], from dipolar and CH/π interactions [5], from hydrophobic-group aggregation (for example, in water), and others.

To commence a basic study on the problem of molecular recognition processes involving sugars, which could be useful for a general understanding of the adhesion phenomenon, we initiated examination of the difference in chemical shift in the ^{1}H NMR spectra of various newly-prepared

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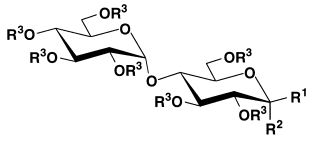
(dimaltoside)s described here in D_2O, both in the presence and absence of a second compound. It was hoped that the added compound might interact variably with the (dimaltoside)s depending on their structures. To make the conformations of the (dimaltoside)s flexible under minimal external force, two maltoses were linked, head to head, via a small alkylene chain $[(CH_2)_n; n = 2–4]$. These (dimaltoside)s might chelate a foreign (or a guest) compound between the two averaged planes of a dimaltoside molecule, by bending the bond angles of the chain, when the foreign compound matches the dimaltoside well. In this paper we describe mainly the synthesis of these (dimaltoside)s, and touch briefly on the interaction between some of them with cinnamyl alcohol.

2. Results and discussion

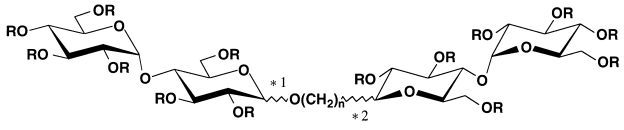
Synthesis.—1,2-Di(*O*-maltosyl)ethanediol (**31**) with two β-anomeric configurations was first prepared. Initially, per-*O*-acetylmaltosyl bromide (**1**) [6] was treated with a 0.5-molar proportion of ethane-1,2-diol under rigorously anhydrous Königs–Knorr conditions in CH_2Cl_2 in order to obtain the dimaltoside derivative **21** in one step. However, the yield of the desired compound was poor, and a two-step synthesis was attempted. Treatment of **1** with a 5-molar excess of ethane-1,2-diol gave the monomaltoside derivative **10** in 73% yield, together with **21** (6.4%). No formation of α-anomeric products was observed. Successive reaction of **10** with **1** gave **21** in good yield. Zemplén deacetylation gave the final product **31**. In a similar way, 1,3- and 1,4-di(*O*-β-maltosyl)alkanediols **34** and **37** were prepared by condensation of **1** with propane-1,3-diol or butane-1,4-diol, with successive coupling of the resulting monomaltosides (**11** and **12**) with **1** to give the peracetyl (dimaltoside)s (**25** and **28**). These were deacetylated to give the final products **34** and **37**. Structures of **10–12**, **21**, **25**, **28**, **31**, **34**, and **37** were confirmed by their ^1H and ^{13}C NMR spectra (Tables 1–3).

(Dimaltoside)s having the α-anomeric configurations were next prepared. For this purpose per-*O*-benzylmaltosyl bromide (**7**) was considered suitable as the glycosylating agent. To obtain this, 4-methoxyphenylmethyl maltoside (**3**) was examined as a starting material, because the methoxybenzyl group was expected to be readily cleaved [7] from the per(*O*-benzyl)ated products. Initially, maltose was heated with an excess of neat 4-methoxyphenylmethanol in the presence of *p*-toluenesulfonic acid (modified Fischer condensation), whereupon, however, only bis(4-methoxyphenylmethyl) ether was produced. Accordingly, per-*O*-acetylmaltosyl bromide [6] (**1**) was treated with 4-methoxyphenylmethanol in benzene in the



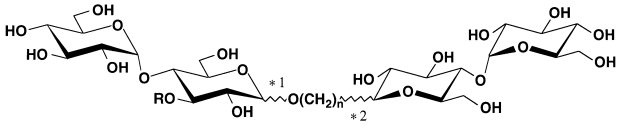
	R^1	R^2	R^3
1	H	Br	Ac
2	$OCH_2C_6H_4OCH_3(p)$	H	Ac
3	$OCH_2C_6H_4OCH_3(p)$	H	H
4	$OCH_2C_6H_4OCH_3(p)$	H	Bn
5	H, OH		Bn
6	H	Cl	Bn
7	H, Br		Bn
8	OAc	H	Bn
9	H	SC_6H_5	Bn
10	$O(CH_2)_2OH$	H	Ac
11	$O(CH_2)_3OH$	H	Ac
12	$O(CH_2)_4OH$	H	Ac
13	H	$O(CH_2)OH$	Bn
14	$O(CH_2)_2OH$	H	Bn
15	H	$O(CH_2)_2OTBDMS$	Bn
16	$O(CH_2)_2OTBDMS$	H	Bn
17	H	$O(CH_2)_3OH$	Bn
18	$O(CH_2)_3OH$	H	Bn
19	H	$O(CH_2)_4OH$	Bn
20	$O(CH_2)_4OH$	H	Bn

Chart 1.



	n	R	*1	*2
21	2	Ac	β-D	β-D
22	2	Bn	α-D	α-D
23	2	Bn	α-D	β-D
24	2	Bn, Ac	α-D	β-D
25	3	Ac	β-D	β-D
26	3	Bn	α-D	α-D
27	3	Bn	α-D	β-D
28	4	Ac	β-D	β-D
29	4	Bn	α-D	α-D
30	4	Bn	α-D	β-D

Chart 2.



	n	*1	*2
31	2	β-D	β-D
32	2	α-D	α-D
33	2	α-D	β-D
34	3	β-D	β-D
35	3	α-D	α-D
36	3	α-D	β-D
37	4	β-D	β-D
38	4	α-D	α-D
39	4	α-D	β-D

Chart 3.

presence of Ag_2CO_3–I_2 (modified Königs–Knorr conditions [8]) and the resulting 4-methoxybenzyl glycoside **2** (90%) was deacetylated to give **3**, which was then benzylated ($PhCH_2Br$–NaH) to give the per-*O*-benzylglycoside **4**. Removal of the 4-methoxybenzyl group was successfully carried out by merely heating **4** in an acidic medium, without use of DDQ [9], $Ce(NH_4)_2(NO_3)_6$ (CAN) [7,10], or NIS, to yield the free sugar **5**. When either DDQ or CAN was used, the yield of **5** turned out to be poor. To obtain the corresponding bromide **7**, compound **5**, after acetylation (to give the 1-acetate **8**), was treated with $TiBr_4$; however, the resulting 1-bromide was unstable and decomposed rapidly during the next condensation reaction without contributing as the glycosyl donor. Therefore, **5** was treated with $SOCl_2$ in CH_2Cl_2 in the presence of catalytic amount of DMF [11], whereupon the stable 1-chloride **6** [12] was obtained in high yield.

Condensation of **6** with ethane-1,2-diol (a 10-molar excess for **6** was used) was performed under Königs–Knorr conditions in CH_2Cl_2; however, this gave a mixture of α- (**13**) and β-monomaltoside (**14**) in a ratio of 1:6.3 (88% overall yield). Changing the catalyst from $Hg(CN)_2$ to HgI_2–I_2 or CF_3SO_3Ag–*s*-collidine [13] slightly improved the

Table 1
^{1}H NMR chemical shifts[a] (δ, ppm, in $CDCl_3$) of *O*-acetylated β-linked maltosides (**10, 11**, and **12**) and β,β-linked (dimaltoside)s (**21, 25**, and **28**)

	10	**11**	**12**	**21**	**25**	**28**
H-1	4.58	4.54	4.53	4.57	4.48	4.50
H-2	4.85	4.82	4.81	4.80	4.80	4.80
H-3	5.27	5.25	5.25	5.25	5.25	5.25
H-4	3.98	3.99	3.99	3.99	3.98	3.99
H-5	3.74	3.68	3.68	3.68	3.67	3.67
H-6a	4.19	4.22	4.22	4.22	4.22	4.22
H-6b	4.54	4.53	4.51	4.52	4.48	4.48
H-1′	5.40	5.41	5.41	5.41	5.40	5.41
H-2′	4.86	4.86	4.86	4.86	4.86	4.86
H-3′	5.35	5.36	5.36	5.36	5.36	5.36
H-4′	5.04	5.05	5.05	5.05	5.05	5.05
H-5′	3.97	3.97	3.97	3.97	3.97	3.97
H-6′a	4.05	4.06	4.05	4.05	4.05	4.05
H-6′b	4.25	4.25	4.25	4.25	4.25	4.25
H-1″a	3.83	3.67	3.55	3.74	3.57	3.47
H-1″b	3.83	3.98	3.89	3.88	3.83	3.84
H-2″a	3.71	1.80	1.68	3.74	1.83	1.56
H-2″b	3.71	1.80	1.68	3.88	1.83	1.62
H-3″a		3.71	1.61		3.57	1.56
H-3″b		3.71	1.61		3.83	1.62
H-4″a			3.63			3.47
H-4″b			3.63			3.84
OH	2.40	1.91	1.71			
CH_3CO	2.00	2.00	2.00 (9H)	2.00 (6H)	2.00 (6H)	2.00 (9H)
	2.01	2.01	2.02	2.02 (6H)	2.02	2.02
	2.02 (6H)	2.02	2.04	2.04	2.03	2.04
	2.04	2.03	2.10	2.10	2.04	2.10
	2.10	2.04	2.14	2.15	2.10	2.14
	2.15	2.10			2.14	
		2.15				

[a] Confirmed by ^{1}H–^{1}H COSY and, if necessary, by further HMQC.

Table 2
^{1}H NMR chemical shifts[a] (δ, ppm, in D_2O) of β,β-(**31, 34**, and **37**), α,α-(**32, 35**, and **38**), and α, β-linked dimaltosides (**33, 36**, and **39**)

	31	**34**	**37**	**32**	**35**	**38**	**33**		**36**		**39**	
							α[b]	β[b]	α[b]	β[b]	α[b]	β[b]
H-1	4.56	4.49	4.52	4.99	4.95	4.93	4.98	4.55	4.94	4.48	4.93	4.48
H-2	3.36	3.31	3.34	3.62	3.61	3.60	3.60	3.34	3.60	3.31	3.60	3.31
H-3	3.79	3.78	3.82	4.00	4.00	3.98	4.01	3.79	3.98	3.78	3.98	3.79
H-4	3.66	3.63	3.67	3.65	3.66	3.65	3.64	3.65	3.63		3.64	3.65
H-5	3.62	3.60	3.63	3.87	3.80	3.80	3.88	3.61	3.81	3.62	3.80	3.66
H-6a	3.81	3.78	3.81	3.82	3.86	3.82	3.77[c]	3.79[c]	3.77[d]	3.81[d]	3.78[e]	3.81[e]
H-6b	3.97	3.94	3.98	3.89	3.90	3.89	3.88	3.95	3.88	3.94	3.88	3.94
H-1′	5.42	5.40	5.44	5.40	5.42	5.41	5.41		5.39	5.40	5.40	5.41
H-2′	3.60	3.59	3.63	3.59	3.60	3.59	3.58		3.59		3.60	
H-3′	3.71	3.69	3.73	3.72	3.71	3.70	3.69	3.70	3.68	3.69	3.69	3.70
H-4′	3.44	3.42	3.46	3.43	3.42	3.43	3.42		3.42	3.43	3.43	
H-5′	3.74	3.72	3.76	3.73	3.74	3.73	3.74		3.73		3.74	
H-6′a	3.78	3.77	3.81	3.78	3.79	3.78	3.77		3.78		3.77	
H-6′b	3.88	3.86	3.90	3.87	3.88	3.87	3.87		3.87		3.87	
H-1″a	3.92	3.80	3.76	3.77	3.68	3.57	3.76		3.65		3.58	
H-1″b	4.13	4.02	4.00	3.95	3.85	3.77	3.94		3.85		3.77	
H-2″a	3.92	1.97	1.76	3.77	2.01	1.70	3.92		1.98		1.72	
H-2″b	4.13	1.97	1.76	3.95	2.01	1.79	4.11		1.98		1.75	
H-3″a		3.80	1.76		3.68	1.70			3.87		1.72	
H-3″b		4.02	1.76		3.85	1.79			4.05		1.75	
H-4″a			3.76			3.57					3.72	
H-4″b			4.00			3.77					4.97	

[a] Confirmed by ^{1}H–^{1}H COSY and, if necessary, by further HMQC.
[b] α and β mean α- and β-linked maltoside portions, respectively.
[c,d,e] Interconvertible, respectively.

ratios for the α anomer (1:3.3, 73% and 1:0.8, 78%, respectively). To enhance the yield of the α anomer, synthesis of the 1-phenylthio derivative (**9**) of **5** was attempted. Treatment of the 1-acetate **8** with $PhSSiMe_3$ by a conventional method [14] gave the 1-thio-α-glycoside **9**, whose structure was confirmed by its proton–carbon correlated spectrum (HMQC) (see Experimental section). Condensation of **9** with ethane-1,2-diol gave the α anomer **13** predominantly [α (**13**): β (**14**) = 1:0.36, 91%]. A trial to obtain a better yield of the α anomer by treating **9** and half-protected 2-(*t*-butyldimethylsilyl)ethanol was unsuccessful [α (**15**): β (**16**) = 1:0.5, overall yield 78%]. Condensation using the imidate method [15] by utilizing the 1-trichloroacetimidate of **5** failed to give products in good yields.

Table 3
^{13}C NMR chemical shifts[a] (δ, ppm, in D_2O) of β,β-linked (dimaltoside)s (**31, 34**, and **37**)

	31	**34**	**37**
C-1	103.06	103.02	102.87
C-2	73.86	73.87	73.89
C-3	77.00	77.05	77.11
C-4	77.65	77.75	77.73
C-5	75.44	75.42	75.42
C-6	61.59	61.64	61.64
C-1′	100.45	100.46	100.44
C-2′	72.52	72.60	72.52
C-3′	73.70	73.75	73.71
C-4′	70.21	70.21	70.21
C-5′	73.56	73.57	73.56
C-6′	61.36	61.37	61.37
C-1″	69.87	67.93	70.94
C-2″	69.87	29.97	26.18
C-3″		67.93	26.18
C-4″			70.94

[a] Confirmed by ^{1}H–^{1}H COSY and, if necessary, by further HMQC.

Preparations of benzylated monomaltosides of propane-1,3-diol and butane-1,4-diol were next tried using both 1-chloride **6** (with CF_3SO_3Ag–*s*-collidine) and **9**. The results were for propane-1,3-diol, α (**17**): β (**18**) = 1:0.58 (81%) and 1:0.36 (75%), respectively; and for butane-1,4-diol, α (**19**): β (**20**) = 1:0.78 (90%) and 1:0.53 (78%), respectively, indicating that **9** gave better yields for the α anomers, although the overall yields were somewhat diminished.

Next, maltosylation of the benzylated monomaltosides **13, 17**, and **19** was performed similarly by using the foregoing two reagents (**6** and **9**). The

results were for **13**, α (**22**): β (**23**) = 1:0.33 (56%) and 1:0.47 (64%); for **17**, α (**26**): β (**27**) = 1:0.5 (69%) and 1:1 (74%); and for **19**, α (**29**): β (**30**) = 1:0.72 (79%) and 1:0.9 (65%). This result indicates that, in these second condensations, **6** was superior to **9** in production of the α anomer. As the pair of α and β anomers had close mobilities, respectively, they were separated by successive chromatographic runs.

Finally, debenzylation of these synthetic products (**22–24**, **26**, **27**, **29**, and **30**) was performed conventionally using Na in liquid NH_3 [16], which proved to be superior to hydrogenolysis with Pd-black catalyst [17] for removing the benzyl groups rapidly and completely. The products thus obtained were, however, considerably contaminated with inorganic salts, and therefore they were removed by successive acetylation, washing the products with water, and by deacetylation to give the final products **32**, **35**, and **38** (each, α,α structure) and **33**, **36**, and **39** (each, α,β structure). The structures were confirmed based on the ^1H and ^{13}C NMR spectroscopy (Tables 2, 4–6).

Interaction between cinnamyl alcohol and **32**, **35**, *or* **38**.—Before carrying out a broader study on the interaction of the (dimaltoside)s prepared here with several candidate compounds, we wanted initially to inspect the ^1H NMR spectra of the α,α-(dimaltoside)s (**32, 35**, and **38**) in the presence of cinnamyl alcohol. The reason for choice of this alcohol was based on its having a similar molecular length with that of the maltosides, together with the aromatic and flat structure. Our interest concerning the interaction was in the following points: that the slightly positively charged hydrogens in the dimaltoside molecules (such as H-1 or 1′) might attract the aromatic π-electrons of cinnamyl alcohol, and whether this phenomenon, if it occurred, could be detected in the ^1H NMR spectra. As it was found difficult to dissolve both dimaltoside and (an excess of) cinnamyl alcohol in D_2O, the maltoside was dissolved in CD_3OD and all of the ^1H-shifts were measured at 40 °C in the presence and absence of cinnamyl alcohol (sharp signals were obtained at that temperature). The results are shown in Tables 7 and 8.

Noteworthy is the fact that all of the skeletal protons shifted downfield roughly linearly with the concentration of cinnamyl alcohol added, and the protons in the spacer alkylenes were shifted upfield, although only to a slight extent. No indication of the sought-after chelation of a cinnamyl alcohol molecule between the two wings of the di(maltoside) molecule was observed. To clarify the spatial relationship, maltose (as an anomeric mixture) and methyl α-D-glucopyranoside were similarly measured with addition of cinnamyl alcohol, whereupon all of the proton signals of both compounds shifted downfield, as likewise observed for the skeletal protons in the (dimaltoside)s. Ethane-1,2-diol dimethyl ether and propane-1,3-diol were measured in the same manner and all protons were found to show upfield shifts (Table 8), a result similar to that for the spacer alkylenes.

These results suggest that the mode of interaction is different from that of cyclodextrins forming inclusion complexes with aromatic compounds (cyclodextrins usually show upfield shifts in the skeletal protons [18]). To assist in understanding the NMR spectroscopic feature, the electron-charge distributions for methyl α-D-glucopyranoside (I), ethane-1,2-diol dimethyl ether (II), propane-1,3-diol (III), methanol, and cinnamyl alcohol were calculated by MOPAC94/PM3 (see Experimental section). The results indicated that O*H*-hydrogens are strongly positive (~0.24) as compared to the C*H*-hydrogens (0.03~0.1 for

Table 4
^1H NMR chemical shifts[a] (δ, ppm, in $CDCl_3$) of *O*-benzylated α-linked maltosides (**13, 17**, and **19**) and α,α-linked (dimaltoside)s (**22, 26**, and **29**)

	13	**17**	**19**	**22**	**26**	**29**
H-1	4.76	4.70	4.73	4.83	4.78	4.76
H-2	3.60	3.58	3.58	3.58	3.58	3.60
H-3	4.07	4.04	4.07	4.09	4.09	4.09
H-4	3.97	3.99	4.01	4.06	4.05	4.04
H-5	3.98	3.87	3.87	3.86	3.88	3.88
H-6a	3.64	3.65	3.65	3.63	3.64	3.64
H-6b	3.76	3.79	3.81	3.84	3.84	3.83
H-1′	5.65	5.65	5.67	5.70	5.70	5.70
H-2′	3.48	3.48	3.48	3.48	3.48	3.48
H-3′	3.88	3.89	3.90	3.89	3.92	3.91
H-4′	3.64	3.62	3.63	3.65	3.64	3.64
H-5′	3.71	3.71	3.72	3.72	3.74	3.73
H-6′a	3.42	3.41	3.41	3.38	3.39	3.39
H-6′b	3.52	3.50	3.50	3.49	3.49	3.49
H-1″a	3.69	3.48	3.42	3.71	3.57	3.41
H-1″b	3.69	3.90	3.70	3.79	3.73	3.67
H-2″a	3.74	1.83	1.71	3.71	1.99	1.74
H-2″b	3.74	1.90	1.71	3.79	1.99	1.74
H-3″a		3.80	1.67		3.57	1.74
H-3″b		3.80	1.67		3.73	1.74
H-4″a			3.67			3.41
H-4″b			3.67			3.67
OH	2.80	2.58	1.94			

[a] Confirmed by ^1H–^1H COSY and, if necessary, by further HMQC.

Table 5
^{1}H NMR chemical shifts[a] (δ, ppm, in $CDCl_3$) of *O*-benzylated β-linked maltosides (**14, 18**, and **20**) and α,β-linked (dimaltoside)s (**23, 27**, and **30**)

	14	**18**	**20**	**23**		**27**		**30**	
				α	β	α	β	α	β
H-1	4.40	4.43	4.42	4.87	4.43	4.76	4.42	4.76	4.42
H-2	3.51	3.49	3.49	3.59	3.50	3.58	3.48	3.59	3.50
H-3	3.78	3.77	3.77	4.06	3.78	4.08	3.76	4.08	3.78
H-4	3.96	3.98	4.02	4.03	4.04	4.07	4.03	4.03	4.01
H-5	3.62	3.58	3.55	3.90	3.55	3.86	3.56	3.87	3.54
H-6a	3.68	3.73	3.77	3.62	3.70	3.60	3.74	3.62	3.75
H-6b	3.75	3.75	3.79	3.85	3.86	3.78	3.81	3.79	3.83
H-1′	5.60	5.62	5.64	5.65		5.70	5.65	5.71	5.65
H-2′	3.47	3.47	3.47	3.45	3.48	3.48	3.47	3.48	
H-3′	3.85	3.87	3.88	3.86		3.88	3.90	3.89	3.90
H-4′	3.60	3.61	3.62	3.63		3.64		3.63	
H-5′	3.69	3.71	3.75	3.73		3.71	3.75	3.72	3.75
H-6′a	3.42	3.43	3.44	3.38	3.42	3.37	3.42	3.39	3.43
H-6′b	3.55	3.55	3.57	3.48	3.56	3.48	3.55	3.50	3.56
H-1″a	3.83	3.79	3.61	3.72		3.54		3.40	
H-1″b	3.95	4.02	3.96	4.77		3.76		3.66	
H-2″a	3.68	1.85	1.74	3.77		2.00		1.75	
H-2″b	3.80	1.85	1.74	4.13		2.00		1.75	
H-3″a		3.73	1.68			3.65		1.75	
H-3″b		3.82	1.68			4.03		1.75	
H-4″a			3.64					3.56	
H-4″b			3.64					3.97	
OH	3.03	2.23	1.49						

[a] Confirmed by ^{1}H–^{1}H COSY and, if necessary, by further HMQC.
[b] α and β mean α- and β-linked maltoside portions, respectively.

Table 6
^{13}C NMR chemical shifts[a] (δ, ppm, in D_2O) of α,α-(**32, 35, 38**) and α,β-linked (dimaltoside)s (**33, 36**, and **39**)

	32	**35**	**38**	**33**		**36**		**39**	
				α^b	β^b	α^b	β^b	α^b	β^b
C-1	98.97	98.92	98.78	98.98	103.00	98.86	103.02	98.78	102.92
C-2	72.02	72.03	72.03	72.06	73.85	72.03	73.88	72.02	73.90
C-3	74.41	74.41	74.46	74.37	77.06	74.40	77.08	74.44	77.12
C-4	78.08	77.81	77.82	77.82	77.68	77.95	77.79	77.90	77.70
C-5	71.15	77.14	77.17	71.13	75.47	71.13	75.43	71.17	75.42
C-6	61.43	61.43	61.46	61.36	61.62	61.42	61.65	61.45	61.64
C-1′	100.66	100.50	100.50	100.52	100.46	100.58	100.47	100.53	100.44
C-2′	72.65	72.60	72.61	72.64	72.53	72.62	72.53	72.61	72.52
C-3′	73.77	73.75	73.74	73.78	73.71	73.76	73.71	73.75	73.71
C-4′	70.21	70.21	70.22	70.21		70.21		70.21	
C-5′	73.56	73.57	73.55	73.55	73.57	73.57		73.56	
C-6′	61.37	61.37	61.37	61.36		61.37		61.37	
C-1″	67.57	66.25	68.83	67.79		65.75		68.83	
C-2″	67.57	29.62	26.34	69.87		29.77		26.07	
C-3″		66.25	26.34			68.20		26.54	
C-4″			68.83					71.05	

[a] Confirmed by ^{1}H–^{1}H COSY and, if necessary, by further HMQC.
[b] α and β mean α- and β-linked maltoside portions, respectively.

alkyl-H and ~0.13 for arom.-H) or carbons [0.00–0.11 for alkyl carbons except for the anomeric carbon (0.18 in I) and C-2 carbons (−0.19 in III), and −0.07 to −0.2 for arom.-C], and all of the oxygens are strongly negative (−0.3 to ~−0.4). One explanation satisfying the foregoing numerical data would be that some of the CD_3OD molecules surrounding a maltoside molecule through hydrogen

Table 7
Chemical shifts[a] (δ, ppm) of **33, 35**, and **38** and four reference compounds[b] (9.0×10^{-3} mmol/mL) in CD_3OD at 40 °C

	33	**35**	**38**	Maltose		I
				α	β	
H-1	4.853	4.797	4.787	5.101	4.489	4.666
H-2	3.466	3.443	3.449	3.408	3.169	3.385
H-3	3.900	3.894	3.890	3.910	3.603	3.612
H-4	3.490	3.508	3.505	3.519		3.283
H-5	3.770	3.670	3.652	3.845	3.378	3.528
H-6a	3.804	3.807	3.808	3.787		3.672
H-6b	3.871	3.843	3.837	3.874		3.808
H-1′	5.135	5.168	5.156	5.157	5.150	
H-2′	3.457	3.441	3.444	3.439		
H-3′	3.676	3.642	3.636	3.654	3.614	
H-4′	3.280	3.268	3.271	3.267	3.272	
H-5′	3.727	3.710	3.708	3.708		
H-6′a	3.669	3.662	3.663	3.663		
H-6′b	3.834	3.837	3.832	3.822		
H-1″a	3.656	3.603	3.507			
H-1″b	3.936	3.848	3.760			
H-2″a,b		1.951	1.745			
OCH3						3.406
$HOCH_2CH_2CH_2OH$:		for OCH_2C	3.666,	for CCH_2C		1.748
$H_3COCH_2CH_2OCH_3$:		for CH_2	3.524,	for OCH_3		3.351

[a] Estimated error is ±0.0007 ppm.
[b] Maltose, methyl α-D-glucopyranoside (I), propane-1,3-diol, and ethane-1,2-diol dimethyl ether.

Table 8
Increase[a] of the chemical shifts in the ^1H NMR spectra of **32, 35, 38**, and four reference compounds[b] measured in CD_3OD (9.0 mM solution, 40 °C) after addition of cinnamyl alcohol[c]

	32	**35**	**38**	Maltose		I
				α	β	
H-1	1	6	3	4	1	2
H-2	8	13	10	5	8	5
H-3	7	12	11	5	3	6
H-4	5	9	9	3	3	5
H-5	3	9	7	4	−1	5
H-6a	7	9	9	3	3	5
H-6b	5	9	15	2	2	5
H-1′	4	9	8	3	2	
H-2′	7	12	12	6	6	
H-3′	11	15	15	4	7	
H-4′	7	13	10	4	4	
H-5′	8	14	13	5	5	
H-6′a	7	13	10	4	4	
H-6′b	9	10	12	4	4	
H-1″a	−8	−1	−4			
H-1″b	−1	−1	−4			
H-2″a,b		−3	−6			
OCH_3						−1
$HOCH_2CH_2CH_2OH$:		for OCH_2C−7,	for CCH_2C−2			
$H_3COCH_2CH_2OCH_3$:		for CH_2−6,	for OCH_3−5			

[a] $\Delta\delta$ (ppm)$\times10^3$ (estimated error is ±0.7).
[b] See Table 7.
[c] 24 Molar excess for **33, 35**, and **38**, and 12 molar excess for the other compounds were added, respectively.

bonding are substituted by some cinnamyl alcohol molecules through OD-hydrogen bonding (we used the usual term "hydrogen bonding" although deuterium plays the role) brought from the attractive forces working between the positively charged *H*O-hydrogen of cinnamyl alcohol and the negatively charged H*O*-oxygens of the maltoside. However, as the skeletal protons of the (dimaltoside)s show downfield shifts, suggesting operation of the magnetic anisotropy effect [19] via the cinnamyl plane, the foregoing explanation has little validity in view of the disposition of the cinnamyl plane; overall, cinnamyl alcohol is expected to be located closer to the di(maltoside) in order to satisfy the observed deshieldings. If the cinnamyl plane is arranged face to face to the maltoside plane, or takes a similar disposition, the dimaltoside skeleton protons should shift upfield, as seen in cyclodextrins when including an aromatic molecule [18]. Therefore, the cinnamyl plane must approach the maltoside plane from the perpendicular direction or more precisely, approach the skeleton hydrogens from the extended plane of cinnamyl alcohol, and not from the up (or down) face of the plane. However, such a disposition seemed difficult to realize by operation only of the hydrogen-bonding force of the DO-group of cinnamyl alcohol, as already described.

We considered, however, that such a situation would be possible if approach of the cinnamyl plane having a comparatively electron-deficient outside zone [originating from its seven acidic hydrogens interacting with the negatively charged oxygens of the maltoside moiety (O-2,3,6,2′,3′,4′,6′, at least)] is facilitated by the formation of *multiple* arom.-H···O bonds (more correctly, if such an approach would be slightly favored over a random one). This presumption was basically supported by MOPAC calculation to find energy-minimal geometries, which showed 3–6 kcal mol^{-1} of stabilization by such an approach (see A and C in Fig. 1). It seems this mode of attraction is not fully explained.

As regards the alkylene protons of the (dimaltoside)s, and also compounds II and III, they were shifted upfield, respectively, and thus there might be a slight preference for the alkylene chain to face up (or down) to the cinnamyl plane over the random approach; this may satisfy the anisotropic shielding. This explanation is valid if we consider that the weakly acidic alkylene hydrogens approach, perpendicularly, the electron-rich (by the π cloud) cinnamyl plane (see B in Fig. 1) by CH/π interaction [5], and if the situation is aided by the hydrophobic group assembly arising from the exclusion of both the spacer chain and the cinnamyl group from the hydrogen-bond network formed by CD_3OD molecules.

From the foregoing discussion, it may be deduced that the inclusion of an aromatic compound in a cyclodextrin cavity is initiated by the attachment of the guest compound by the extended hydroxyl groups of the cyclodextrin. However, compounds **32**, **35**, or **38** have no cavity for receiving a foreign molecule, and they, therefore, only draw the molecule near the outside oxygen atoms. We suppose this kind of initial attraction by the extended placement of oxygen atoms of carbohydrates may occur during the initial stage of some biological adhesions.

3. Experimental

General methods.—Optical rotations were determined with a Perkin–Elmer 241 polarimeter. ^{1}H- and ^{13}C-NMR spectra were recorded at 500 and 125.8 MHz with a Bruker AMX-500 spectrometer, using Me_4Si as the internal reference, respectively. The signals were mostly confirmed by ^{1}H–^{1}H COSY and HMQC. The ^{1}H NMR spectra of **32**, **35**, **38**, and of a mixture of the each compound and cinnamyl alcohol in CD_3OD were measured (5.9 data points/Hz) at 40 ± 0.05 °C in the absence of reference (the shifts were measured from the frequency of single Me_4Si in CD_3OD). TLC was performed on Silica Gel 60 F_{254} (Merck 5715 and

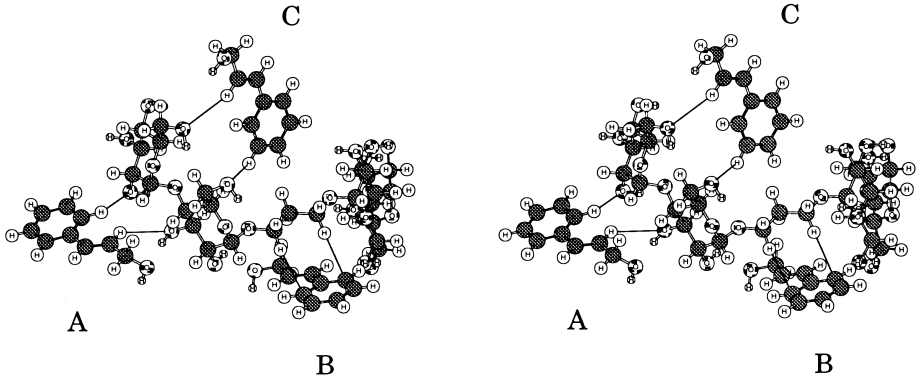


Fig. 1. Stereoview of a model of the interaction between **35** and cinnamyl alcohol, as generated by CAChe. The starting geometry of **35** (before minimization) having the shape of spread bird-wings (slightly curved inside) was chosen, and after energy-minimization, a molecule of cinnamyl alcohol was positioned close to the structure of **35**, in order, as much as possible, to reflect the situation as described in the text (three such relationships were chosen, that is, A: a cinnamyl alcohol was positioned along the edge of a maltoside including O-2, 3, 2′ with the cinnamyl O*H* close to O-2; B: along the spacer chain; C: near the O-6, 6′ atoms), then each combination was minimized (during the process, both **35** and cinnamyl alcohol minimized changed the conformations only slightly, mainly by altering the intermolecular atom–atom distances). The three final arrangements thus obtained are shown together. Characteristic points are that the pairs were stabilized by ΔH (heat of formation) 3.1 (A), 4.6 (B), and 6.1 kcal mol^{-1} (C), respectively, relative to the additive *H* values of the starting mixture (**35** and cinnamyl alcohol, both minimized). The distances (shown by solid lines) are as follows: (maltosyl and cinnamyl portions are denoted as M and Ci, respectively) A: O-3 (M)···H-2 (Ci) 2.99, O-2′ (M)···H-2′ (Ci) 1.88 Å; B: H-1″a (M)···C-2′ (Ci) 2.71, H-3″a (M)···C-6′ (Ci) 2.77 Å; and C: O-6 (M)···H-3′ (Ci) 3.34, O-6′ (M)···H-2 (Ci) 1.88 Å.

5717), and detected by charring with aq 50% H_2SO_4. Column chromatography was performed on Wakogel C-200.

Computation.—All calculations were performed on a Macintosh 9500 with CAChe (Sony Tektronix Corporation, Japan) using MOPAC94/PM3 based on MOPAC6 by J.J.P. Stewart. Geometry optimization was performed by the eigenvector following method (for Fig. 1). When optimization in MeOH was required, the structures obtained by the above MOPAC94/PM3 method were further optimized with the COSMO method by setting the dielectric constant as 32.63.

4-Methoxyphenylmethyl 2,3,6-tri-O-*acetyl-4*-O-*(2,3,4,6-tetra*-O-*acetyl*-α-D-*glucopyranosyl)*-β-D-*glucopyranoside* (**2**).—A mixture of **1** [6] (2.06 g, 2.95 mmol) and molecular sieves 3 Å (4.12 g) in benzene (30 mL) was stirred for 30 min, and 4-methoxyphenylmethanol (1.87 mL, 15.0 mmol), Ag_2CO_3 (2.44 g, 8.84 mmol), and I_2 (1.50 g, 5.89 mmol) were added, and the mixture was stirred overnight at room temperature. After filtration through a layer of Celite, the filtrate and the combined washings (benzene) were washed successively with aq 20% $Na_2S_2O_3$, aq $NaHCO_3$ (saturated), and water, dried (Na_2SO_4), and concentrated. The residue was chromatographed (1:2 acetone–hexane) to give **2** as a syrup (2.01 g, 90%), mp 108–109 °C (EtOH), $[\alpha]_D^{23}+23°$ (*c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$): δ (selected signals) 1.97, 1.98, 1.99, 2.00, 2.02, 2.10, and 2.17 (each s of 3 H, 7 Ac), 3.81 (s, 3 H, OMe), 4.56 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 5.40 (d, 1 H, $J_{1',2'}$ 4.0 Hz, H-1′). Anal. Calcd for $C_{34}H_{44}O_{19}$: C, 54.00; H, 5.86. Found: C, 53.84; H, 5.71.

4-Methoxyphenylmethyl 4-O-*(*α-D-*glucopyranosyl)*-β-D-*glucopyranoside* (**3**).—To a solution of **2** (1.50 g, 1.98 mmol) in 1:1 CH_2Cl_2–MeOH (45 mL) was added 1 M NaOMe in MeOH (5 mL), and the solution was kept for 1.5 h at room temperature. After neutralization with Dowex 50W (H^+) resin, the mixture was filtered, and the solution was concentrated. The residue was purified on a short column of silica gel (4:1 $CHCl_3$–MeOH) to give **3** as an amorphous powder (900 mg, 95%), $[\alpha]_D^{23}+24.6°$ (*c* 0.7, MeOH); ^1H NMR (D_2O): δ (selected signals) 3.86 (s, 3 H, OMe), 4.51 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 5.39 (d, 1 H, $J_{1',2'}$ 4.0 Hz, H-1′). Anal. Calcd for $C_{20}H_{30}O_{12}\cdot H_2O$: C, 50.00; H, 6.71. Found: C, 50.37; H, 6.93.

4-Methoxyphenylmethyl 2,3,6-tri-O-*benzyl-4*-O-*(2,3,4,6-tetra*-O-*benzyl*-α-D-*glucopyranosyl)*-β-D-*glucopyranoside* (**4**).—A solution of **3** (864 mg, 1.87 mmol) in DMF (25 mL) was stirred vigorously with NaH (1.05 g, 60% in mineral oil; 26 mmol) for 30 min at room temperature. After cooling to 0 °C, benzyl bromide (2.4 mL, 19.6 mmol) was added, and the mixture was stirred for 3 h at room temperature. TLC (3:1 $CHCl_3$–MeOH) of the solution gave a single spot at R_f 0.3. After addition of MeOH (10 mL), most of the solvent was removed by coevaporation with toluene, and an EtOAc solution of the residue was washed with water, dried (Na_2SO_4), and concentrated. The residue was chromatographed (5:1 hexane–EtOAc) to give **4** as a syrup (1.99 g, 98%), $[\alpha]_D^{25}+18.5°$ (*c* 1.4, $CHCl_3$); ^1H NMR ($CDCl_3$): δ (selected signals) 3.80 (s, 3 H, OMe), 4.43, 4.55, 4.57, 4.62, 4.72, 4.74, 4.82, and 4.83 (each ABq of 2 H, 8 PhCH_2), 4.51 (d, 1 H, *J* 8.0 Hz, H-1), 5.65 (d, 1 H, *J* 3.8 Hz, H-1′). Anal. Calcd for $C_{69}H_{72}O_{12}$: C, 75.80; H, 6.64. Found: C, 75.98; H, 6.56.

2,3,6-Tri-O-*benzyl-4*-O-*(2,3,4,6-tetra-O-benzyl*-α-D-*glucopyranosyl)*-D-*glucopyranose* (**5**).—A solution of **4** (3.02 g, 2.76 mmol) in 1:1:0.2 $CHCl_3$–CF_3CO_2H–H_2O (66 mL) was kept for 1 h at room temperature. Removal of the solvent by coevaporation with toluene gave a residue, which was chromatographed (3:2 hexane–EtOAc) to give **5** [12] as an amorphous powder (2.83 g, 94%), $[\alpha]_D^{21}+34°$ (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$): δ (selected signals) 3.10 [d, ∼0.63 H, HO-1 (α-anomer)], 5.22 [t, ∼0.63 H, $J_{1,2}=J_{1,OH}$ 3.3 Hz, H-1 (α–anomer)], 5.62 (d, 1 H, $J_{1',2'}$ 3.8 Hz, H-1′).

2,3,6-Tri-O-*benzyl-4*-O-*(2,3,4,6-tetra-O-benzyl*-α-D-*glucopyranosyl)*-α-D-*glucopyranosyl chloride* (**6**).—To a solution of **5** (534 mg, 0.55 mmol) in CH_2Cl_2 (5.9 mL), $SOCl_2$ (237 μL, 3.3 mmol) and DMF (64 μL. 0.83 mmol) were added, and the solution was kept overnight at room temperature. TLC (2:1 hexane–EtOAc) of the solution showed a single spot at R_f 0.65 (*cf*. **5**: R_f 0.4).

Concentration gave a residue, which was dissolved in 3:1 hexane–EtOAc and passed through a layer of silica gel. Concentration of the filtered solution gave **6** as an amorphous powder (500 mg, 92%), $[\alpha]_D^{22}+86°$ (*c* 1, $CHCl_3$) [lit. [12], $[\alpha]_D^{26}+89.5°$ (*c* 1.6, $CHCl_3$); obtained via a different route]; ^1H NMR ($CDCl_3$): δ (benzyl signals were omitted) 3.41 (dd, 1 H, H-6′a), 3.50 (dd, 1 H, H-2′), 3.53 (dd, 1 H, H–6′b), 3.63 (dd, 1 H, H-6a), 3.65 (t, 1 H, H-4′), 3.75 (m, 1 H, H-5′), 3.75 (dd, 1 H, H–2), 3.91 (dd, 1 H, H-6b), 3.92 (t, 1 H, H-3′), 4.08–4.18 (m, 3 H, H-3, 4, 5), 5.63 (d, 1 H, H-1′), 6.06 (d, 1 H, H-1). $J_{1,2}$ 3.8, $J_{2,3}$ 9.0, $J_{5,6a}$ 2.2, $J_{5,6b}$

3.5, $J_{6a,6b}$ 11, $J_{1'2'}$ 3.8, $J_{2',3'} \approx J_{3',4'} \approx J_{4',5'}$ 9.0–9.5, $J_{5',6'a}$ 2, and $J_{5',6'b}$ 3.0 Hz; ^{13}C NMR ($CDCl_3$): δ 93.27 (C-1), 80.10 (C-2), 81.26 (C-3), 71.86 (C-4), 73.16 (C-5), 68.29 (C-6,6′), 97.05 (C-1′), 79.50 (C-2′), 81.96 (C-3′), 77.71 (C-4′), and 71.18 (C-5′), 68.29 (C-6′). The ^1H and ^{13}C signals were confirmed by mononuclear COSY and HMQC experiments.

2,3,6-Tri-O-*benzyl-4*-O-*(2,3,4,6-tetra-O-benzyl-α*-D-*glucopyranosyl)*-D-*glucopyranosyl bromide* (**7**).—A mixture of **8** (20 mg, 0.02 mmol) and $TiBr_4$ (10.9 mg, 0.03 mmol) in 10:1 CH_2Cl_2–EtOAc (0.45 mL) was stirred overnight at room temperature. TLC (2:1 hexane–EtOAc) of the solution showed a spot at R_f 0.65 (*cf* **8**: R_f 0.55). After addition of CH_3CN (0.8 mL), the solution was poured on to powdered, anhydrous NaOAc (34 mg), and the mixture was stirred for 20 min at room temperature. After filtration with the aid of toluene, the filtrate was concentrated to give **7** as a syrup (20 mg), which was used without purification.

1-O-*Acetyl-2,3,6-tri*-O-*benzyl-4*-O-*(2,3,4,6-tetra*-O-*benzyl-α*-D-*glucopyranosyl)*-D-*glucopyranose* (**8**).—A mixture of **5** (380 mg, 0.39 mmol) and Ac_2O (55 μL, 0.6 mmol) in pyridine (5 mL) was kept for 1.5 h at room temperature. Methanol (2 mL) was added and the solution was concentrated by coevaporation with toluene to give a syrup, that was purified by chromatography (3.2:1 hexane–EtOAc) to give **8** as a syrup (395 mg, quant), $[\alpha]_D^{21} + 53°$ (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ (selected signals) 2.03 (1.3 H, Ac of β-anomer), 2.15 (1.7 H, Ac of α-anomer), 3.49 (dd, 0.43 H, H-2′ of β-anomer), 3.50 (dd, 0.57 H, H-2′ of α-anomer), 3.62 (t, 0.43 H, H-2 of β-anomer), 3.67 (t, 1 H, H-4′), 3.68 (ddd, 0.43 H, H-5 of β-anomer), 3.72 (dd, 0.57 H, H-2 of α-anomer), 3.77 (ddd, 1 H, H–5′), 3.82 (t, 0.43 H, H-3 of β-anomer), 3.91 (dd, 1 H, H-3′), 3.97 (ddd, 0.57 H, H-5 of α–anomer), 4.04 (d, 0.57 H, H-3 of α-anomer), 4.13 (t, 0.43 H, H-4 of β-anomer), 4.15 (t, 0.57 H, H-4 of α-anomer), 5.58 (0.43 H, H-1′ of β-anomer), 5.65 (d, 0.43 H, H-1 of β–anomer), 5.69 (d, 0.57 H, H-1′ of α-anomer), 6.36 (d, 0.57 H, H-1 of α-anomer); $J_{1,2}$ 3.8 (α) and 8.0 (β), $J_{2,3} = J_{3,4} = J_{4,5}$ 9.0, $J_{5,6a}$ 2.0, $J_{5,6b}$ 3.5, $J_{1',2'}$ 3.5 (α) and 3.8 (β), $J_{2',3'} = J_{3',4'} = J_{4',5'}$ 9.0 Hz. Anal. Calcd for $C_{63}H_{66}O_{12}$: C, 74.53; H, 6.55. Found: C, 74.65; H, 6.64.

Phenyl 2,3,6-tri-O-*benzyl-4*-O-*(2,3,4,6-tetra*-O-*benzyl-α*-D-*glucopyranosyl)–1-thio-α*-D-*glucopyranoside* (**9**).—To a cold (0 °C) solution of **8** (932 mg, 0.92 mmol) in CH_2Cl_2 (12 mL), $PhSSiMe_3$ (0.57 mL, 3.0 mmol) and $CF_3SO_2SiMe_3$ (0.36 mL, 1.85 mmol) were added, and the solution was kept for 4 h at room temperature. TLC (2:1 hexane–EtOAc) of the solution showed a single spot at R_f 0.65 (*cf*. **8**: R_f 0.55). After neutralization with triethylamine, the solution was washed with water, dried (Na_2SO_4), and concentrated. The residue was chromatographed with 3.5:1 hexane–EtOAc to give **9** as a syrup (978 mg, quant), $[\alpha]_D^{26} + 103°$ (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$): δ (selected signals) 3.50 (dd, 1 H, H-2′), 3.64 (t, 1 H, H-4′), 3.78 (ddd, 1 H, H-5′), 3.92 (dd, 1 H, H-2), 3.94 (t, 1 H, H-3′), 3.97 (t, 1 H, H-3), 4.06 (dd, 1 H, H-4), 4.41 (ddd, 1 H, H-5), 5.62 (d, 1 H, H-1′), 5.63 (d, 1 H, H-1); $J_{1,2}$ 6.0, $J_{2,3} \approx J_{3,4} \approx J_{4,5}$ 9–9.5, $J_{1',2'}$ 3.8, $J_{2',3'} = J_{3',4'} = J_{4',5'}$ 9–9.5 Hz. Anal. Calcd for $C_{67}H_{68}O_{10}S$: C, 75.54; H, 6.43; S, 3.01. Found: C, 75.77; H, 6.49; S, 3.21.

General procedure for 2-hydroxyethyl (**10**)*, 3-hydroxypropyl* (**11**)*, and 4-hydroxybutyl 2,3,6-tri*-O-*acetyl-4*-O-*(2,3,4,6-tetra*-O-*acetyl-α*-D-*glucopyranosyl)-β*-D-*glucopyranoside* (**12**).—A mixture of **1** (0.5 mmol), a corresponding diol (distilled or dried over molecular sieves 4 Å, 2.5–5 mmol), powdered Drierite ($CaSO_4$, 250 mg), and $Hg(CN)_2$ (1.5 mmol) in CH_2Cl_2 (3–4 mL) was stirred for 5.5 h under reflux. The mixture was filtered through a layer of Celite with the aid of CH_2Cl_2, and the solution was washed with aq $NaHCO_3$, and dried (Na_2SO_4). Concentration followed by chromatography (1:2.5 acetone–toluene or 2:1 toluene–acetone for **11** and **12**) gave the product **10** (73%) together with **21** (6.4%); and **11** (78%) and **12** (70%), respectively, as a syrup.

Compound **10**: $[\alpha]_D^{26} + 49.5°$ (*c* 0.9, $CHCl_3$). Anal. Calcd for $C_{28}H_{40}O_{19}$: C, 49.41; H, 5.92. Found: C, 49.42; H, 5.71.

Compound **11**: $[\alpha]_D^{24} + 44°$ (*c* 1, $CHCl_3$). Anal. Calcd for $C_{29}H_{42}O_{19}$: C, 50.14; H, 6.09. Found: C, 50.11; H, 6.01.

Compound **12**: $[\alpha]_D^{23} + 45°$ (*c* 0.9, $CHCl_3$). Anal. Calcd for $C_{30}H_{44}O_{19}$: C, 50.85; H, 6.26. Found: C, 50.56; H, 6.22.

General procedure for 2-hydroxyethyl (**13**)*, 3-hydroxypropyl* (**17**)*, and 4–hydroxybutyl 2,3,6-tri*-O-*benzyl-4*-O-*(2,3,4,6-tetra*-O-*benzyl-α*-D-*glucopyranosyl)-α*- (**19**) *and the corresponding* β-D-*glucopyranosides* (**14**, **18**, and **20**).—

Method A [from **6** *and Hg(CN)$_2$]*. A mixture of **6** (0.05 mmol), a corresponding diol (distilled or dried over molecular sieves 4 Å, 0.5 mmol), Drierite (30 mg), and $Hg(CN)_2$ (0.15 mmol) in CH_2Cl_2 (0.5 mL) was refluxed overnight. The solution was filtered through a Celite layer with the aid of

CH_2Cl_2, washed with aq $NaHCO_3$ (saturated), and dried (Na_2SO_4). Concentration of the solution gave a residue, which was chromatographed (3:1 hexane–MeCOEt) to give, in the case of ethane-1,2-diol, **13** (12%) and **14** (76%) each as a syrup.

Method B (from **6** *and* HgI_2–I_2*)*. A mixture of **6** (0.05 mmol), HgI_2 (0.15 mmol, dried in vacuo for 3 h at 80 °C), I_2 (0.1 mmol), and molecular sieves 3 Å (100 mg) in CH_2Cl_2 (0.7 mL) was stirred for 1 h, a corresponding diol (0.5 mmol) was added, and stirring was continued overnight at room temperature. Filtration, washing of the filtrate with aq 20% $Na_2S_2O_3$ and aq $NaHCO_3$ (saturated), and concentration gave a mixture of products, which was separated as described for Method A to give, in the case of ethane-1,2-diol, **13** (17%) and **14** (56%).

Method C (from **6** *and AgOTf)*. A mixture of a corresponding diol (0.5 mmol), *s*-collidine (0.1 mmol), and molecular sieves 4 Å (100 mg) in CH_2Cl_2 (0.6 mL) was stirred for 30 min at room temperature, cooled to −40 °C, AgOTf (0.15 mmol) was added, **6** (0.05 mmol) in CH_2Cl_2 (0.6 mL) was added dropwise under stirring, and stirring was continued overnight at room temperature. After filtration with the aid of CH_2Cl_2, the solution was washed with aq 1 M HCl and aq $NaHCO_3$, and dried (Na_2SO_4). Chromatography (12–15:1 toluene–acetone) of the products gave the corresponding α and β anomers each as a syrup. By using ethane-1,2-diol: **13** (43%) and **14** (35%); by propane-1,3-diol: **17** (51%) and **18** (30%); by butane-1,4-diol: **19** (47%) and **20** (43%).

Method D (from **9***)*. A mixture of **9** (0.05 mmol), a corresponding diol (0.5 mmol), and molecular sieves 4 Å (100 mg) in CH_2Cl_2 (0.4 mL) was stirred for 30 min at room temperature. The mixture was cooled to 0 °C, *N*-iodosuccinimide (0.15 mmol) was added, and stirring was continued for 30 min at the temperature. After cooling to −40 °C, CF_3SO_3H (2.5 μL) in CH_2Cl_2 (0.4 mL) was added dropwise, and the mixture was stirred for 4 h at 0 °C. Post work-up as described for Method B gave the corresponding α and β anomers, each as a syrup. From the reaction with ethane-1,2-diol: **13** (67%) and **14** (24%); from propane-1,3-diol: **17** (48%) and **18** (27%); from butane-1,4-diol: **19** (51%), **20** (27%).

Compound **13**: $[\alpha]_D^{23}$ + 33° (*c* 1.1, $CHCl_3$). Anal. Calcd for $C_{63}H_{68}O_{12}$: C, 74.39; H, 6.74. Found: C, 74.36; H, 6.48. Compound **14**: $[\alpha]_D^{23}$ + 27° (*c* 0.8, $CHCl_3$). Anal. Calcd for $C_{63}H_{68}O_{12}$: C, 74.39; H, 6.74. Found: C, 74.12; H, 6.72.

Compound **17**: $[\alpha]_D^{23}$ + 44° (*c* 1.2, $CHCl_3$). Anal. Calcd for $C_{64}H_{70}O_{12}$: C, 74.54; H, 6.84. Found: C, 74.66; H, 6.74. Compound **18**: $[\alpha]_D^{23}$ + 34° (*c* 1.1, $CHCl_3$). Anal. Calcd for $C_{64}H_{70}O_{12}$: C, 74.54; H, 6.84. Found: C, 74.26; H, 6.69.

Compound **19**: $[\alpha]_D^{23}$ + 45° (*c* 1.1, $CHCl_3$). Anal. Calcd for $C_{65}H_{72}O_{12}$: C, 74.69; H, 6.94. Found: C, 74.32; H, 6.84. Compound **20**: $[\alpha]_D^{23}$ + 32° (*c* 0.9, $CHCl_3$). Anal. Calcd for $C_{65}H_{72}O_{12}$: C, 74.69; H, 6.94. Found: C, 74.39; H, 6.90.

Reaction of **9** *with 2-*O*-(*t*-butyldimethylsilyl)-ethane-1,2-diol to give* **15** *and* **16**. A mixture of **9** (47 mg, 0.047 mmol), TBDMS-O$(CH_2)_2$OH (84 mg, 0.47 mmol), and molecular sieves 4 Å (100 mg) in CH_2Cl_2 (0.3 mL) was stirred for 30 min at room temperature, cooled to 0 °C, and treated successively with *N*-iodosuccinimide (32 mg, 0.14 mmol) and CF_3SO_3H (2.2 μL in 0.37 mL CH_2Cl_2) as described for Method D. After the usual work-up, chromatography (10:1 hexane–acetone) of the crude products gave a mixture of **15** and **16** (42 mg, 78%). ^{1}H NMR ($CDCl_3$): δ 0.04–0.11 (6 H, $SiMe_2$), 0.87–0.92 (9 H, CMe_3), 4.47 (d, 0.35 H, $J_{1,2}$ 8.0 Hz, H-1 of **16**), 4.87 (d, 0.65 H, $J_{1,2}$ 3.8 Hz, H-1 of **15**), 4.26–5.05 (14 H, CH_2Ph), 5.65 (d, 0.35 H, $J_{1',2'}$ 3.8 Hz, H-1′ of **16**), 5.69 (d, 0.65 H, $J_{1',2'}$ 4.0 Hz, H-1′ of **15**), 7.05–7.35 (35 H, 7 Ph).

*General procedure for 1,2-bis[*O*-[2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*α*-*D*-glucopyranosyl)-*β*-*D*-glucopyranosyl]]ethane-1,2-diol* (**21**)*, 1,3-bis[*O*-[2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*α*-*D*-glucopyranosyl)-*β*-*D*-glucopyranosyl]]propane-1,3-diol* (**25**)*, and 1,4-bis[*O*-[2,3,6-tri-*O*-acetyl-4-*O*–(2,3,4,6-tetra-*O*-acetyl-*α*-*D*-glucopyranosyl)-*β*-*D*-glucopyranosyl]]butane-1,4-diol* (**28**). A mixture of **1** (0.75 mmol) and **10, 11**, or **12** (0.5 mmol), Drierite (1.3 g), and $Hg(CN)_2$ (2.25 mmol) in CH_2Cl_2 (2 mL) was stirred under reflux for 3 h. Post treatment as described for **10** with chromatography (3∼4:1 toluene–acetone→2:1 hexane–acetone) gave **21** (70%), **25** (76%), and **28** (68%), respectively, as an amorphous powder.

Compound **21**: $[\alpha]_D^{26}$ + 49° (*c* 0.8, $CHCl_3$). Anal. Calcd for $C_{54}H_{74}O_{36}$: C, 49.92; H, 5.74. Found: C, 49.70; H, 5.75.

Compound **25**: $[\alpha]_D^{21}$ + 55° (*c* 1, $CHCl_3$). Anal. Calcd for $C_{55}H_{76}O_{36}$: C, 50.30; H, 5.83. Found: C, 50.59; H, 5.55.

Compound **28**: $[\alpha]_D^{21}$ + 47° (*c* 1, CHCl*3*). Anal. Calcd for $C_{56}H_{78}O_{36}$: C, 50.68; H, 5.92. Found: C, 50.44; H, 5.93.

*General procedure for 1,2-bis[*O*-[2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*–benzyl-α-D-glucopyranosyl)-α-D-glucopyranosyl]]ethane-1,2-diol* (**22**), *1-*O*-[2,3,6–tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α-D-glucopyranosyl]-2-*O*-[2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-β-D-glucopyranosyl]ethane-1,2-diol* (**23**); *1,3-bis[*O*-[2.3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α-D-glucopyranosyl]]-propane-1,3-diol* (**26**), *1-*O*-[2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α-D-glucopyranosyl]-3-*O*-[2,3,6-tri-*O*-benzyl-4-*O*-(2,3,-4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-β-D-glucopyranosyl]propane-1,3–diol* (**27**); *1,4-bis[*O*-[2,3,6-tri-*O*-benzyl-4-*O*-(2,3,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α-D-glucopyranosyl]]butane-1,4-diol* (**29**) *and 1-*O*-[2,3,6-tri-*O*–benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α-D-glucopyranosyl]-4-*O*-[2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-β-D-glucopyranosyl]butane-1,4-diol* (**30**). From **6**. A mixture of **13, 17**, or **19** (1.0 mmol), *s*-collidine (2.5 mmol) and molecular sieves 4 Å (2.0 g) in CH_2Cl_2 (25 mL) was stirred for 30 min at room temperature, cooled to −40 °C, AgOTf (3.0 mmol) was added, then compound **6** (1.1 mmol) in CH_2Cl_2 (15 mL) was added dropwise under stirring, and the mixture was stirred overnight at room temperature. Purification as described for Method C gave a mixture of products, which were separated by column chromatography (double developments with 3.5:1 hexane–EtOAc and 12–14:1 toluene–EtOAc) to give a pair of products **22** (42%) and **23** (14%); **26** (46%) and **27** (23%); and **29** (46%) and **30** (33%), each as a syrup, respectively, together with slight amounts of starting materials recovered.

From **9**. A mixture of **9** (1.1 mmol) and **13, 17** or **19** (1.0 mmol), and molecular sieves 4 Å (4.0 g) in CH_2Cl_2 (15 mL) was stirred for 1 h at room temperature, cooled to 0 °C, *N*-iodosuccinimide (3.0 mmol) was added, stirring was continued for 20 min in the cold, cooled to −40 °C, CF_3SO_3H (60 μL in 25 mL CH_2Cl_2) was added dropwise, and the mixture was stirred for 4 h at 0 °C. Purification as described for Method D followed by chromatography as described for the synthesis from **6** gave a pair of products **22** (44%) and **23** (20%); **26** (37%) and **27** (37%); and **29** (34%) and **30** (31%), respectively.

Compound **22**: $[\alpha]_D^{21} + 64°$ (*c* 0.9, $CHCl_3$). Anal. Calcd for $C_{124}H_{130}O_{22}$: C, 75.51; H, 6.64. Found: C, 75.41; H, 6.59. Compound **23**: $[\alpha]_D^{21} + 49°$ (*c* 1.2, $CHCl_3$). Anal. Calcd for $C_{124}H_{130}O_{22}$: C, 75.51; H, 6.64. Found: C, 75.23; H, 6.47.

Compound **26**: $[\alpha]_D^{23} + 71°$ (*c* 1, $CHCl_3$). Anal. Calcd for $C_{125}H_{132}O_{22}$: C, 75.58; H, 6.70. Found: C, 75.19; H, 6.69. Compound **27**: $[\alpha]_D^{23} + 42°$ (*c* 1, $CHCl_3$). Anal. Calcd for $C_{125}H_{132}O_{22}$: C, 75.58; H, 6.70. Found: C, 75.39; H, 6.63.

Compound **29**: $[\alpha]_D^{21} + 60°$ (*c* 1, $CHCl_3$). Anal. Calcd for $C_{126}H_{134}O_{22}$: C, 75.65; H, 6.75. Found: C, 75.61; H, 6.81. Compound **30**: $[\alpha]_D^{21} + 47°$ (*c* 1, $CHCl_3$). Anal. Calcd for $C_{126}H_{134}O_{22}$: C, 75.65; H, 6.75. Found: C, 75.35; H, 6.70.

*1-*O*-[2,3,6-Tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α–D-glucopyranosyl]-2-*O*-[2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-glucopyranosyl]ethane-1,2-diol* (**24**).—Compound **1** (25 mg, 0.036 mmol) was condensed with **13** (14 mg, 0.014 mmol) in CH_2Cl_2 (0.7 mL) in the presence of *s*-collidine (12 μL, 0.09 mmol), AgOTf (28 mg, 0.11 mmol), and molecular sieves 4 Å (30 mg) as described for **22** to give, after chromatography (6:1 toluene–acetone), **24** as a syrup (14 mg, 62% based on **13**), $[\alpha]_D^{22} + 54.0°$ (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ (selected signals; A and B denote the benzylated and acetylated portions of the maltosides, respectively) 1.96 (3 H), 2.00 (3 H), 2.02 (3 H), 2.07 (9 H), 2.08 (3 H) (each s, 7 Ac); 3.48 (dd, 1 H, H-2′A), 3.59 (dd, 1 H, H-2A); 3.58 (m, 1 H), 3.66 (m, 1 H), and 3.74 (m, 2 H) (H–1″a,b and H-2″a,b); 3.63 (m, 1 H, H-5B), 3.64 (t, 1 H, H-4′A), 3.88 (m, 1 H, H-5A), 3.89 (t, 1 H, H-3′A), 3.91 (m, 1 H, H-5′B), 4.02 (t, 1 H, H-4B), 4.04 (t, 1 H, H-4A), 4.07 (t, 1 H, H-3A), 4.08 (m, 1 H, H-5′A), 4.08 (dd, 1 H, H-6′aB), 4.20 (dd, 1 H, H–6aB), 4.24 (dd, 1 H, H-6′bB), 4.32 (dd, 1 H, H-6bB), 4.37 (dd 1 H, H-2B?), 4.39, 4.52, 4.52, 4.60, 4.61, 4.83, and 4.91 (each ABq of 2 H, CH_2Ph), 4.82 (d, 1 H, H-1A), 4.88 (dd, 1 H, H-2′B), 5.03 (t, 1 H, H-4′B), 5.06 (t, 1 H, H-3B), 5.41 (dd, 1 H, H-3′B), 5.48 (d, 1 H, H-1′B), 5.67 (d, 1 H, H-1′A), 5.82 (d, 1 H, H-1B); $J_{1''a,1''b} = J_{2''a,2''b}$ 12, $J_{1A,2A} = J_{1'A,2'A} = J_{1'B,2'B}$ 3.8, $J_{1B,2B}$ 5.8, $J_{2A,3A} = J_{2'A,3'A}$ 9, $J_{2B,3B} = J_{2'B,3'B}$ 9.5. ^{13}C NMR ($CDCl_3$): δ (selected signals) 96.83 (C-1A), 80.01 (C-2A), 81.90 (C–3A), 68.27 (C-4A), 69.90 (C-5A), 69.03 (C-6A), 96.73 (C-1′A), 79.43 (C-2′A), 82.01 (C-3′A), 77.71 (C-4′A), 71.08 (C-5′A), 68.27 (C-6′A), 96.86 (C-1B), 73.66 (C-2B), 68.93 (C-3B), 72.30 (C-4B), 73.18 (C-5B), 63.93 (C-6B), 95.02 (C-1′B), 70.25 (C-2′B), 69.83 (C-3′B), 68.33 (C-4′B), 67.47 (C-5′B), 61.84 (C-6′B), 62.39 and 66.50 (two bridge carbons). Anal. Calcd for $C_{89}H_{102}O_{29}$: C, 65.35; H, 6.29. Found: C, 65.35; H, 6.29.

*General procedure for 1,2-Bis[*O*-[4-*O*-(α-*D*-glucopyranosyl)-β-*D*-glucopyranosyl]]ethane-1,2-diol* (**31**), *1,3-bis[*O*-[4-*O*-(α-*D*-glucopyranosyl)-β-*D*-glucopyranosyl]]propane-1,3-diol* (**34**), *and 1,4-bis[*O*-[4-*O*-(α-*D*-glucopyranosyl)-β-*D*-glucopyranosyl]]butane-1,4-diol* (**37**).—To a solution of **21, 25** or **28** (0.5 mmol) in MeOH (20 mL) was added methanolic 1 M NaOMe (2.0 mL), and the solution was kept for 1 h at room temperature. Neutralization with Dowex 50W-X2 (H^+) resin, followed by concentration of the solution gave a solid, which was thoroughly dried in vacuo (for 5 days in the presence of P_2O_5 in a desiccator) to give **31, 34**, and **37** (each almost quant.) as an amorphous powder, respectively.

Compound **31**: TLC (4:1:1 1-propanol–AcOH–H_2O) $R_{f,\ \mathrm{maltose}}$ 0.3, $[\alpha]_D^{20}+78°$ (*c*, 1, H_2O). Anal. Calcd for $C_{26}H_{46}O_{22}$: C, 43.94; H, 6.52. Found: C, 43.48; H, 6.78.

Compound **34**: $[\alpha]_D^{20}+84°$ (*c* 1, H_2O). Anal. Calcd for $C_{27}H_{48}O_{22}\cdot 0.5H_2O$: C, 44.20; H, 6.73. Found: C, 44.02; H, 6.67.

Compound **37**: $[\alpha]_D^{21}+63°$ (*c* 1.1, H_2O). Anal. Calcd for $C_{28}H_{50}O_{22}\cdot 0.5H_2O$: C, 44.98; H, 6.88. Found; C, 44.81; H, 6.79.

*General procedure for 1,2-bis[*O*-[4-*O*-(α-*D*-glucopyranosyl)-α-*D*-glucopyranosyl]]ethane-1,2-diol* (**32**), *1,3-bis[*O*-[4-*O*-(α-*D*-glucopyranosyl)-α-*D*-glucopyranosyl]]propane-1,3-diol* (**35**), *and 1,4-bis[*O*-[4-*O*-(α-*D*-glucopyranosyl)–α-*D*-glucopyranosyl]]butane-1,4-diol* (**38**).—To liquid NH_3 (~10 mL) cooled to −55 °C, **22**, **26** or **29** (0.05 mmol) in oxolane (1.0 mL) was added, then Na (~100 mg) was added, and the deep-blue solution was kept for 30 min in the cold. After addition of 2:1 oxolane–MeOH until the solution become colorless, NH_3 and the solvents were evaporated under warming and finally under reduced pressure. A strongly basic aq solution of the residue was neutralized with Dowex 50W-X2 (H^+) resin, filtered, and the filtrate was concentrated. The residue dissolved in pyridine was acetylated with Ac_2O overnight at room temperature, following chromatography (3:1 toluene–acetone) of the product and deacetylated (Zemplén deacetylation) to give a deprotected product, which was purified as described for **31** to give **32** (75%), **35** (69%), and **38** (56%) as an amorphous powder of 0.5 hydrate, respectively.

Compound **32**: $[\alpha]_D^{21}+185°$ (*c* 1, H_2O). Anal. Calcd for $C_{26}H_{46}O_{22}\cdot 0.5H_2O$: C, 43.39; H, 6.58. Found: C, 43.63; H, 6.51.

Compound **35**: $[\alpha]_D^{21}+192°$ (*c* 1, H_2O). Anal. Calcd for $C_{27}H_{48}O_{22}\cdot 0.5\ H_2O$: C, 44.20; H, 6.73. Found: C, 44.24; H, 6.70.

Compound **38**: $[\alpha]_D^{22}+184°$ (*c* 1, H_2O). Anal. Calcd for $C_{28}H_{50}O_{22}\cdot 0.5H_2O$: C, 44.98; H, 6.88. Found: C, 44.90; H, 6.61.

*1-*O*-[4-*O*-(α-*D*-Glucopyranosyl)-α-*D*-glucopyranosyl]-2-*O*-[4-*O*-(α-*D*-glucopyranosyl)-β-*D*-glucopyranosyl]ethane-1,2-diol* (**33**).—From **23**. Compound **23** (50 mg, 0.025 mmol) was treated as described for **32** to give **33** as an amorphous powder (0.5 hydrate, 13 mg, 71%), $[\alpha]_D^{21}+125°$ (*c* 1, H_2O). Anal. Calcd for $C_{26}H_{46}O_{22}\cdot 0.5H_2O$: C, 43.39; H, 6.58. Found: C, 43.89; H, 6.71.

From 24. Zemplén deacetylation of **24** (10 mg, 6.11 μmol) followed by debenzylation of the product [7.3 mg, $[\alpha]_D^{22}+53°$ (*c* 0.5, $CHCl_3$)] as described for **32** gave **33** (2.5 mg, 58% based on **24**), identical with the specimen obtained from **23**.

*1-*O*-[4-*O*-(α-*D*-Glucopyranosyl)-α-*D*-glucopyranosyl]-3-*O*-[4-*O*-(α-*D*-glucopyranosyl)-β-*D*-glucopyranosyl]propane-1,3-diol* (**36**).—Debenzylation of **27** (88 mg, 0.044 mmol) as described for **32** gave **36** as an amorphous powder (0.5 hydrate, 21 mg, 65%), $[\alpha]_D^{21}+111°$ (*c* 1, H_2O). Anal. Calcd for $C_{27}H_{48}O_{22}\cdot 0.5H_2O$: C, 44.20; H, 6.73. Found: C, 44.08; H, 6.76.

*1-*O*-[4-*O*-(α-*D*-glucopyranosyl)-α-*D*-glucopyranosyl]-4-*O*-[4-*O*-(α-*D*-glucopyranosyl)-β-*D*-glucopyranosyl]butane-1,4-diol* (**39**).—Debenzylation of **30** (105 mg, 0.053 mmol) as described for **32** gave **39** as an amorphous powder (0.5 hydrate, 24 mg, 62%), $[\alpha]_D^{22}+117°$ (*c* 1, H_2O). Anal. Calcd for $C_{28}H_{50}O_{22}\cdot 0.5H_2O$: C, 44.98, H, 6.88. Found: C, 44.78; H, 6.76.

Atomic charges in most stable conformations of model compounds in a medium of dielectric constant 32.63 (MeOH) calculated by MOPAC 94/PM3.—Methyl α-*D*-glucopyranoside: H-1 (0.108), H-2 (0.111), H-3 (0.106), H-4 (0.104), H–5 (0.092), H-6a (0.077), H-6b (0.062), O*C*H_3 (0.060, 0.045, 0.033), *H*O-2 (0.235), *H*O-3 (0.237), *H*O-4 (0.237), *H*O-6 (0.240), C-1 (0.181), C-2 (0.001), C-3 (0.016), C-4 (0.026), C-5 (0.001), C-6 (0.059) *C*H_3 (0.053), O-1 (−0.329), O-2 (−0.360), O-3 (−0.362), O-4 (−0.358), O-5 (−0.289), O-6 (−0.387). H_3COCH_2-CH_2OCH_3: H-1a and 2b (0.082), H-1b and 2a (0.066), O*C*H_3 (0.055, 0.042, 0.035), C-1 and 2 (0.010), *C*H_3 (0.037), O-1 and 2 (−0.327). $HOCH_2CH_2CH_2OH$: H-1a and 3b (0.046), H-1b and 3a (0.061), H-2a and 2b (0.073), *H*O-1 and 3 (0.240), C-1 and 3 (0.075), C-2 (−0.190), O-1 and 3

(−0.401). H_3COH: OCH_3 (0.040, 0.026, 0.026), O*H* (0.243), CH_3 (0.075), *O*H (−0.410). Cinnamyl alcohol (trans): H-1a (0.070), H-1b (0.055), H-2 (0.132), H-3 (0.125), H–2′ and 6′ (0.133, 0.129), H-3′ and 5′ (0.127, 0.126), H-4′ (0.126), O*H* (0.242), C-1 (0.105), C-2 (−0.196), C-3 (−0.113), C-1′ (−0.072), C-2′ and 6′ (−0.110, −0.121), C-3′ and 5′ (−0.118, −0.123), C-4′ (−0.119), *O*H (−0.399).

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