Dehydrative Glycosylation Using Heptabenzyl Derivatives of Glucobioses and Lactose

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Dehydrative glycosylations of the 2-, 3-, 4-, and 6-OH groups of D-glucopyranose with hepta-*O*-benzyl derivatives of glucobioses (*O*-D-glucopyranosyl-(1→*n*)-D-glucopyranose; *n*=2, 3, 4, or 6) and lactose, in the presence of a ternary mixture of *p*-nitrobenzenesulfonyl chloride, silver trifluoromethanesulfonate, and triethylamine in dichloromethane showed that the selectivity of the reaction depended on the anomeric configuration and the linking position to the reducing tribenzylglucose moiety of the nonreducing tetrabenzylglucosyl residue and on the class of the OH group to be glycosylated. The use of a quaternary mixture of *p*-nitrobenzenesulfonyl chloride, silver trifluoromethanesulfonate, *N,N*-dimethylacetamide, and triethylamine made all but the β(1→2)-linked biosyl donor undergo α-condensation. Several new linear trisaccharides were obtained via debenzylation of the condensates.

In recent years, modern methods for glycosylation have been developed to construct complex natural and artificial oligosaccharidic structures.[1] In addition to attainment of higher efficiency and selectivity, attention has heen given to the simplification of the glycosylation process.[2] Direct use of protected glycose (DOH) donating a glycosyl residue (D) at the expense of a hemiacetal OH (1-OH) group, such as 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**22**) and its relatives, in glycosylation of an alcohol (AOH) accepting D to give a protected glycoside (DOA) is advantageous, when a necessitative control of self-condensations is realized, because pre-activation processes are omissible and such 1-OH derivatives usually have longer shelf-lives (Eq. 1; DOH=glycosyl donor, AOH=glycosyl acceptor, Rg= condensing reagent (or reagent mixture)).

$$\mathrm{DOH} + \mathrm{AOH} \xrightarrow{\mathrm{Rg}} \mathrm{DOA} + \mathrm{H_2O} \qquad (1)$$

The ternary mixture of *p*-nitrobenzenesulfonyl chloride (NsCl), silver trifluoromethanesulfonate (AgOTf), and triethylamine (Et_3N) in dichloromethane (abbreviated NST hereafter) performed dehydrative glycosylations between the donor **22** and acceptor alcohols to afford cross-condensates.[3] The quaternary mixture (NSDT) of NsCl, AgOTf, *N,N*-dimethylacetamide

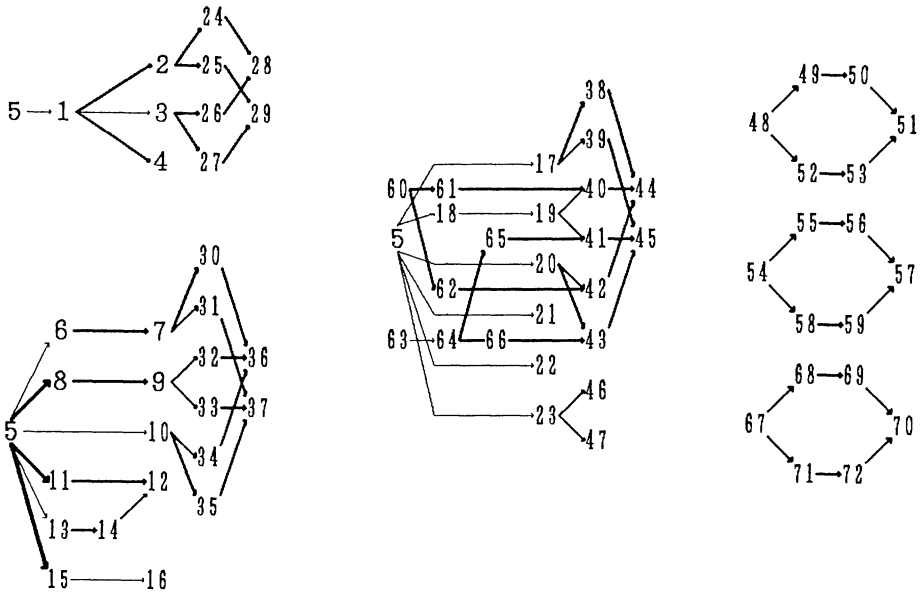

Fig. 1. Synthetic diagrams in which thin arrows show known processes.

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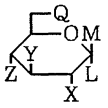
Table 1. Dehydrative Glycosylation Using 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranose (**22**)

Acceptors	Glycosides		Reagents	Yield/%(α/β)	
	α-Anomer	β-Anomer			
2	**24**	**25**	NST	82	(50/50)
			NSDT	94	(94/6)
3	**26**	**27**	NST	89	(47/53)
			NSDT	88	(95/5)
7	**30**	**31**	NST	92	(48/52)
			NSDT	95	(95/5)
9	**32**	**33**	NST	91	(49/51)
			NSDT	89	(93/7)
10	**34**	**35**	NST	96	(46/54)
			NSDT	87	(96/4)
17	**38**	**39**	NST	83	(26/74)
			NSDT	81	(67/33)
19	**40**	**41**	NST	73	(33/67)
			NSDT	68	(57/43)
20	**42**	**43**	NST	85	(34/66)
			NSDT	78	(74/26)
23	**46**	**48**	NST	83	(38/62)
			NSDT	89	(65/35)

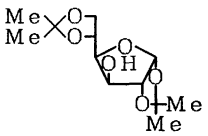
(AcNMe$_2$), and Et$_3$N in dichloromethane improved the glycosylation to afford α-anomers with acceptable selectivities.[4] When NST was applied to the condensation of heptabenzyl 1-OH derivatives of glucobiose (*O*-D-glucopyranosyl-(1→*n*)-D-glucopyranose; *n*=2, 3, 4, or 6) and lactose, **28**, **29**, **36**, **37**, **44**, **45**, **51**, **57**, and **70**, to the primary alcohol **21**,[5,6] the selectivity of the biosylation depended on the anomeric configuration of the nonreducing tetrabenzylglucosyl (Bn$_4$G) residue and its position linked to the reducing tribenzylglucose (Bn$_3$G) unit.[6] This report presents the results of the biosylations of the acceptors, **4**, **12**, **16**, and **21**, using the biosyl donors and the reagent mixtures NST and NSDT.

Acceptor Preparations. Some of the glycosyl acceptors were prepared through new procedures (Fig. 1). The 2-OH derivatives **2** and **4** were derived from acetate **1** following the through-process giving **3**.[7] All the 3-OH compounds, **7**, **9**, and **12**, were produced via controlled benzylations.[4,7,8]



AL = -CH$_2$-CH=CH$_2$
Bn = -CH$_2$CPh
ME = -CH$_2$CH$_2$OMe

	L	M	X	Y	Z	Q
1	H	OAc	OAc	OAc	OAc	OAc
2	H	OAL	OH	OBn	OBn	OBn
3	H	OME	OH	OBn	OBn	OBn
4	H	OBn	OH	OBn	OBn	OBn
5	OH(H)	H(OH)	OH	OH	OH	OH
6	OAL	H	OH	OH	OH	OH
7	OAL	H	OBn	OH	OBn	OBn
8	H	OAL	OAc	OAc	OAc	OAc
9	H	OAL	OBn	OH	OBn	OBn
10	H	OME	OBn	OH	OBn	OBn
11	H	OBn	OAc	OAc	OAc	OAc
12	H	OBn	OBn	OH	OBn	OBn
14	H	OAc	OAc	OAL	OAc	OAc
15	H	OBn	OH	OH	OH	OH
16	H	OBn	OBn	OBn	OH	OBn
17	OAL	H	OBn	OBn	OBn	OH
18	H	OAL	OH	OH	OH	OH
19	H	OAL	OBn	OBn	OBn	OH
20	H	OME	OBn	OBn	OBn	OH
21	OBn	H	OBn	OBn	OBn	OH
22	OH(H)	H(OH)	OBn	OBn	OBn	OBn
23	SEt	H	OBn	OBn	OBn	OH



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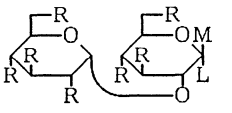
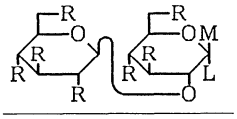
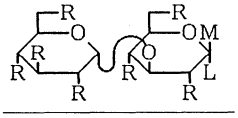


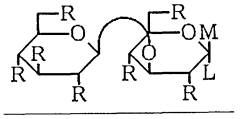
	L	M	R
24	H	OAL	OBn
26	H	OME	OBn
28	OH(H)	H(OH)	OBn
73	2BG	H	OBn
74	H	2BG	OBn
91	3BG	H	OBn
92	H	3BG	OBn
109	4BG	H	OBn
110	H	4BG	OBn
127	6BG	H	OBn
128	H	6BG	OBn
145	2G	H	OH
154	3G	H	OH
163	4G	H	OH
172	6G	H	OH
173	H	6G	OH



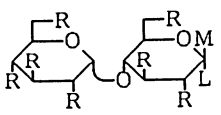
	L	M	R
25	H	OAL	OBn
27	H	OME	OBn
29	OH(H)	H(OH)	OBn
75	2BG	H	OBn
76	H	2BG	OBn
93	3BG	H	OBn
94	H	3BG	OBn
111	4BG	H	OBn
112	H	4BG	OBn
129	6BG	H	OBn
130	H	6BG	OBn
146	H	2G	OH
155	H	3G	OH
164	H	4G	OH
174	6G	H	OH
175	H	6G	OH



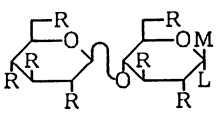
	L	M	R
30	OAL	H	OBn
32	H	OAL	OBn
34	H	OME	OBn
36	OH(H)	H(OH)	OBn
77	2BG	H	OBn
78	H	2BG	OBn
95	3BG	H	OBn
96	H	3BG	OBn
113	4BG	H	OBn
114	H	4BG	OBn
131	6BG	H	OBn
132	H	6BG	OBn
147	2G	H	OH
156	3G	H	OH
165	4G	H	OH
176	6G	H	OH
177	H	6G	OH



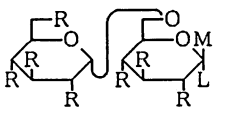
	L	M	R
31	OAL	H	OBn
33	H	OAL	OBn
35	H	OME	OBn
37	OH(H)	H(OH)	OBn
79	2BG	H	OBn
80	H	2BG	OBn
97	3BG	H	OBn
98	H	3BG	OBn
115	4BG	H	OBn
116	H	4BG	OBn
133	6BG	H	OBn
134	H	6BG	OBn
148	2G	H	OH
157	3G	H	OH
166	4G	H	OH
178	6G	H	OH
179	H	6G	OH



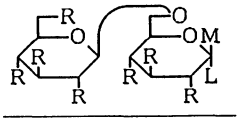
	L	M	R
48	OH(H)	H(OH)	OH
49	H	OAL	OAc
50	H	OAL	OBn
51	OH(H)	H(OH)	OBn
52	H	OME	OAc
53	H	OME	OBn
81	2BG	H	OBn
82	H	2BG	OBn
99	3BG	H	OBn
100	H	3BG	OBn
117	4BG	H	OBn
118	H	4BG	OBn
135	6BG	H	OBn
136	H	6BG	OBn
149	2G	H	OH
158	3G	H	OH
167	4G	H	OH
180	6G	H	OH
181	H	6G	OH



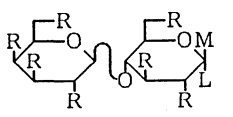
	L	M	R
54	OH(H)	H(OH)	OH
55	H	OAL	OAc
56	H	OAL	OBn
57	OH(H)	H(OH)	OBn
58	H	OME	OAc
59	H	OME	OBn
83	2BG	H	OBn
84	H	2BG	OBn
101	3BG	H	OBn
102	H	3BG	OBn
119	4BG	H	OBn
120	H	4BG	OBn
137	6BG	H	OBn
138	H	6BG	OBn
150	2G	H	OH
159	3G	H	OH
168	4G	H	OH
182	6G	H	OH
183	H	6G	OH



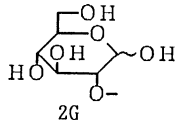
	L	M	R
38	OAll	H	OBn
40	H	OAll	OBn
42	H	OME	OBn
44	OH(H)	H(OH)	OBn
46	SEt	H	OBn
60	OH(H)	H(OH)	OH
61	H	OAll	OAc
62	H	OME	OAc
85	2BG	H	OBn
86	H	2BG	OBn
103	3BG	H	OBn
104	H	3BG	OBn
121	4BG	H	OBn
122	H	4BG	OBn
139	6BG	H	OBn
140	H	6BG	OBn
151	2G	H	OH
160	3G	H	OH
169	4G	H	OH
179	6G	H	OH
180	H	6G	OH

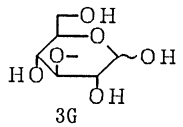


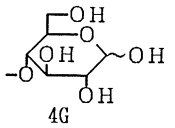
	L	M	R
39	OAL	H	OBn
41	H	OAL	OBn
43	H	OME	OBn
45	OH(H)	H(OH)	OBn
47	SEt	H	OBn
63	OH(H)	H(OH)	OH
64	H	OAc	OAc
65	H	OAL	OAc
66	H	OME	OAc
87	2BG	H	OBn
88	H	2BG	OBn
105	3BG	H	OBn
106	H	3BG	OBn
123	4BG	H	OBn
124	H	4BG	OBn
141	6BG	H	OBn
142	H	6BG	OBn
152	2G	H	OH
161	3G	H	OH
170	4G	H	OH
186	6G	H	OH
187	H	6G	OH

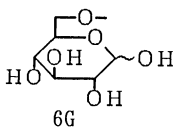


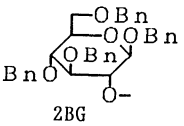
	L	M	R
67	OH(H)	H(OH)	OH
68	H	OAL	OAc
69	H	OAL	OBn
70	OH(H)	H(OH)	OBn
71	H	OME	OAc
72	H	OME	OBn
89	2BG	H	OBn
90	H	2BG	OBn
107	3BG	H	OBn
108	H	3BG	OBn
125	4BG	H	OBn
126	H	4BG	OBn
143	6BG	H	OBn
144	H	6BG	OBn
152	2G	H	OH
162	3G	H	OH
171	4G	H	OH
188	6G	H	OH
189	H	6G	OH

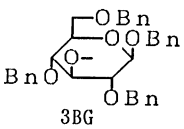


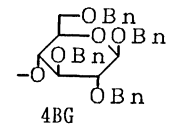


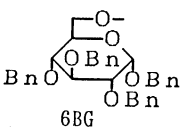












Biosyl Donors Preparations. To prepare benzylated bioses having a free hemiacetal OH group, an allyl residue[9] was used to mask the reducing OH group temporarily (Fig. 1). A 2-methoxyethyl (ME) group[7] was also used to study its utility in the preparation of such biosyl donors. The 1→4 linked biosyl donors, **51**, **57**, and **70**, were prepared from commodity sugars, **48**, **54**, and **67** (Fig. 1). The intermediary bioside acetates, **49**, **52**, **55**, **58**, **68**, and **71**, were prepared from the respective disaccharides via direct acetobromination.[10,11] For the α(1→6) linked **60**, this method was useful, but the β(1→6) **63** partly anomerized its interglycosidic linkage during the acetobromination. The 1→2, 1→3, and 1→6 linked biosyl donors, **28**, **29**, **36**, **37**, **44**, and **45**, were prepared via dehydrative glucosylations. The acceptors, **2**, **3**, **7**, **9**, **10**, **17**, **19**, and **20**, were condensed with **22** in the presence of NST to prepare the corresponding β-linked disaccharides, **25**, **27**, **31**, **33**, **35**, **39**, **41**, and **43**, whereas the use of NSDT afforded the α-linked condensates, **24**, **26**, **30**, **32**, **34**, **38**, **40**, and **42**, respectively, as summarized in Table 1.

The ME bioside derivatives mostly afforded the respective 1-OH derivatives in good yields; the yields of the 1-OH derivatives from α(1→3) linked **34** and β(1→3) linked **35**, however, remained rather low. All the allyl biosides, except for **40**, were smoothly transformed into the corresponding 1-OH derivatives.

Biosylations. Nine biosyl donors thus prepared were first condensed with the primary alcohol **21** in the presence of NST.[5,6] The α(1→2) linked **28** and the β(1→6) linked **45** selectively formed the corresponding α-glycosides **127** and **141**, respectively, while the β(1→2) linked **29** and the α(1→6) linked **44** mainly afforded the β-glycosides **130** and **140**, respectively. The α-selectivities of **36**, **37**, and **51** and the β-selectivities of **57** and **70** were marginal.[6] No correlations were observed between the selectivities of the biosylations and the anomeric ratios of the biose 1-OH derivatives as summarized in Table 2. In the biosylations of the secondary alcohols, **4**, **12**, and **16**, all donors but the β(1→2) linked **29** furnished the corresponding α-glycosides with good to excellent selectivities. The general tendencies of the biosyl donors, comparing to **22**,[3,4] to form α-condensates of the less-reactive acceptors appeared to be attributable to the fact that the condensation reactions are thermodynamically controlled by the anomeric effect[12] due to the slow formation of a glycosidic linkage from a fully dissociated biosyl sulfonate[4] and an incom-

ing OH group of an acceptor. The glycosylation using the donors without participating protecting groups with less-reactive secondary alcoholic acceptors under dissociative conditions usually afforded α-condensates predominantly.[13] On the other hand, the attack by the primary alcohol **21** to an anomeric center is kinetically controlled by the steric effect of its Bn_4G residue, as mentioned below.

The use of NSDT for the biosylation of **21** selectively produced the corresponding α-glycosides, but **29** still gave the β-product **130**, mainly. In the biosylation of **4**, **12**, and **16** in the presence of NSDT, the respective α-glycosides were produced with excellent or complete selectivities, although the total yields of the glycosides were slightly depressed. Again, **29** furnished the β-anomers with significantly high ratios. In the cases of 1→2 linked **28** and **29**, the yields of the condensates were generally low probably due to the hindrance by the

Table 2. Dehydrative Biosylation Using Heptabenzyl Bioses

Donors(α/β)	Acceptors	Glycosides		Reagents	Yield/%(α/β)
		α-Anomer	β-Anomer		
28(67/33)[c]	**4**	**73**	74	NST	63 (69/31)
				NSDT	27 (96/4)
	12	**91**	**92**	NST	59 (87/13)
				NSDT	25 (100/0)
	16	**109**	**110**	NST	66 (73/27)
				NSDT	14 (100/0)
	21	**127**	**128**	NST	70 (85/15)
				NSDT	51 (100/0)
29(—)[e]	**4**	**75**	**76**	NST	66 (31/69)
				NSDT	15 (48/52)
	12	**93**	**94**	NST	65 (33/67)
				NSDT	18 (48/52)
	16	**111**	**112**	NST	57 (22/78)
				NSDT	12 (31/69)
	21	**129**	**130**	NST	70 (13/87)
				NSDT	53 (21/79)
36(59/41)[d]	**4**	**77**	**78**	NST	79 (53/47)
				NSDT	65 (100/0)
	12	**95**	**96**	NST	79 (64/35)
				NSDT	52 (95/5)
	16	**113**	**114**	NST	71 (89/11)
				NSDT	44 (100/0)
	21	**131**	**132**	NST	84 (57/43)
				NSDT	71 (75/25)
37(69/31)[a]	**4**	**79**	**80**	NST	83 (82/18)
				NSDT	59 (94/6)
	12	**97**	**98**	NST	74 (84/16)
				NSDT	57 (100/0)
	16	**115**	**116**	NST	75 (81/19)
				NSDT	54 (100/0)
	21	**133**	**134**	NST	75 (59/41)
				NSDT	62 (70/30)
44(—)[e]	**4**	**85**	**86**	NST	83 (61/39)
				NSDT	46 (74/26)
	12	103	**104**	NST	72 (58/42)
				NSDT	42 (73/28)
	16	**123**	**124**	NST	66 (64/36)
				NSDT	38 (76/24)
	21	**139**	**140**	NST	76 (15/85)
				NSDT	48 (54/46)
45(64/36)[b]	**4**	**87**	**88**	NST	83 (91/9)
				NSDT	61 (100/0)
	12	**105**	**106**	NST	85 (89/11)
				NSDT	69 (100/0)
	16	**123**	**124**	NST	71 (91/9)
				NSDT	54 (100/0)
	21	**141**	**142**	NST	82 (82/18)
				NSDT	43 (94/6)

Table 2. (Continued)

Donors(α/β)	Acceptors	Glycosides		Reagents	Yield/%(α/β)
		α-Anomer	β-Anomer		
51(83/17)[d]	**4**	**81**	**82**	NST	87 (68/32)
				NSDT	73 (86/14)
	12	**99**	**100**	NST	81 (73/27)
				NSDT	63 (92/8)
	16	**117**	**118**	NST	67 (90/10)
				NSDT	50 (100/0)
	21	**135**	**136**	NST	79 (72/28)
				NSDT	65 (79/21)
57(76/24)[a]	**4**	**83**	**84**	NST	87 (90/10)
				NSDT	67 (100/0)
	12	**101**	**102**	NST	84 (53/47)
				NSDT	60 (100/0)
	16	**119**	**120**	NST	71 (55/45)
				NSDT	41 (98/2)
	21	**137**	**138**	NST	77 (39/61)
				NSDT	67 (77/23)
70(—)[e]	**4**	89	**90**	NST	76 (84/16)
				NSDT	57 (100/0)
	12	**107**	**108**	NST	83 (66/34)
				NSDT	63 (100/0)
	16	**125**	**126**	NST	62 (53/47)
				NSDT	49 (91/9)
	21	**143**	**144**	NST	61 (42/58)
				NSDT	55 (76/24)

a) $I\alpha/I\beta$, where $I\alpha$ is the integral value of ^{1}H NMR signals of H1 of the α-form of the donors and $I\beta$ is that of the β-form. b) $I'\alpha/I'\beta$, where $I'\alpha$ is the integral value of H1′ of the α-form of the donors and $I'\beta$ is that of the β-form. c) $I\alpha/I'\beta$. d) $I\alpha/(I'\alpha+I'\beta-I\alpha)$. e) Could not be determined.

Bn_4G residues vicinal to their reducing anomeric centers. The above-described condensation of the $\alpha(1\rightarrow6)$ linked donor **44** with **21** giving the β-glycoside **140**, the fully-benzylated derivative of the trisaccharide constituting nephritogenoside,[14] contrasted with the bromide-catalyzed[15] glycosylation using the $\alpha(1\rightarrow6)$ linked biosyl bromide derivative[16] which gave the α-condensate **139** with a good selectivity.

The above-described selectivities in the biosylation of **21** using the $1\rightarrow2$ and $1\rightarrow6$ linked donors implies that the fully benzylated 2-*O*-α- and 6-*O*-β-D-glucopyranosyl residues appear to restrict the course of the incomming nucleophile to the α-side of their C1*, whereas the protected 2-*O*-β- and 6-*O*-α-glucosyl residues do the same to the β-side. Inspection of molecular models showed that the plausible conformers of **28**, **29**, **44**, and **45**, shown in Fig. 2*, have factors which can kinetically control the steric course of the reaction.[17] Conformer K of **28** having $\phi\approx0°$ and $\psi\approx0°$ allows Bn2′ (the benzyl group at O2′, and so on) to stay on the β-side of Cl; Bn3 and Bn6′ will interact to rotate ϕ toward ca. 0° from the exo-anomeric effect favoring ca. $-60°$.[18,19] For **29**, conformers S_g with $\phi\approx60°$ and $\psi\approx180°$and S_e with

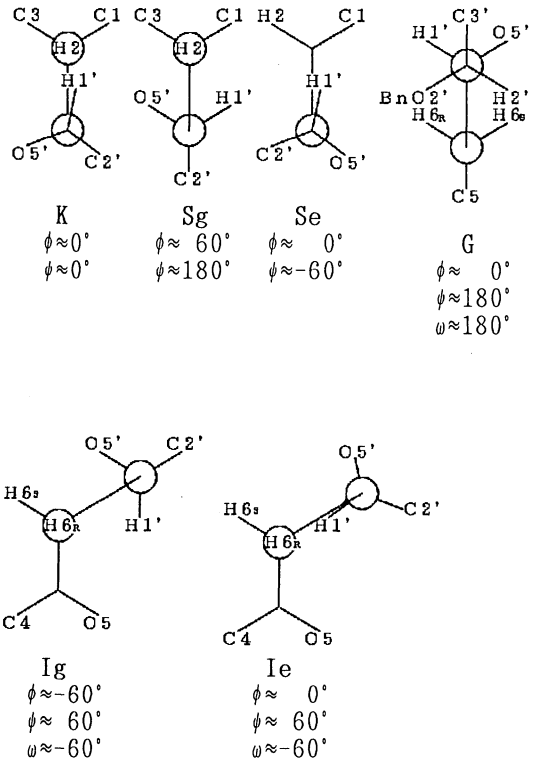


Fig. 2. Plausible limitting conformations of glycoside linkages of heptabenzyl $1\rightarrow2$ and $1\rightarrow6$ linked bioses which may bring forth selectivities of biosylations.

* The positions in Bn_4G are primed and those in Bn_3G are not. For **28** and **29**, ϕ and ψ are associated with H1′/C2 and C1′/H2, and, for **44** and **45**, ϕ, ψ, and ω with C1′/C6, C1′/C5, and O6/H5.

$\phi \approx 0°$ and $\psi \approx -60°$ place H1′ and Bn6′ on the α-side, respectively; Bn3 and Bn2′ will help ϕ rotate toward ca. 0° in S_e. In the case of **44**, conformers I_g with $\phi \approx -60°$, $\psi \approx 60°$, and $\omega = -60°$, and I_e with $\phi \approx 0°$, $\psi \approx 60°$, and $\omega \approx -60°$ will render Bn2′ sticking out into the α-side. In the I_e conformer, Bn4 and Bn6′ may interact to push ϕ toward ca. 0°. The conformers I_g and I_e resemble the metastable conformers 'GT4' and 'GT3" of **60**, respectively, which were calculated recently.[20] Conformer G for **45** with $\phi \approx 0°$, $\psi \approx 180°$, and $\omega \approx 180°$ possibly hangs Bn2′ over the β-side and is similar to the recently calculated conformer 'd' or 'gg' of **63**.[21] In **29**, the benzylated 2-*O*-β-glucosyl residue seems to be held tight enough to prevent the formation of an anomeric effect controlled transition state[12] even in the cases of less reactive acceptors, whereas the α-tetrabenzylglucosyloxy group at C6 in **44** relaxes to attain a stereoelectronically controlled glycosylation.

Synthetic Linear Trisaccharides. Debenzylation of the main condensates obtained hy dehydrative biosylation afforded the corresponding linear trisaccharides, including those naturally occuring and enzymatically synthesized, as well as several novel trisaccharides. A set of tentative assignments for the ^{13}C NMR chemical shifts of the synthetic trisaccharides were obtained as summarized in Table 3; the assignments were based on the correlation of the compiled sets of the data[22] while consulting the accumulated information[23] on the conformation of oligosaccharides.

Experimental

The solvent systems for column chromatography on silica gel (Kanto Chemical, No. 37047; gradient elution) and thin-layer chromatography on silica gel plate (Merck DC-Plastikfolien Kieselgel 60 F_{254}, Art. 5735) were chloroform–methanol (CM), DCE§–ethyl acetate (DE), hexane–ethyl acetate (HE), hexane–IPE§ (HI), and toluene–2-butanone (TB). The optical rotations were measured on a JASCO DIP-150

Table 3. ^{13}C MMR Spectral Data of Trisaccharides (75.5 MHz, in D_2O)[a]

C	**145**	**146**	**147**	**148**	**149**	**150**#	**151**	**152**	**153**#
1α	90.4	92.4	90.2	90.4	90.3	90.3	90.4	90.4	90.4
1β	97.2	95.5	97.0	97.2	97.0[4]	97.0[4]	97.2	97.0	97.2
2α	77.0	82.8	76.4	76.8[3]	76.9	77.0	77.1	77.3	77.1
2β	79.5	84.6	79.2	79.3	79.4	79.5	79.8	79.9	79.7
3α	72.7	72.5	72.4	72.3*	72.0[7]*	72.1	72.3	72.1[1]*	72.3
3β	75.3	76.8[0]*	75.3	75.4	75.3	75.3	75.4	75.3	75.4
4α	70.5	69.7	70.1	70.6	70.4	70.4	70.6	70.4[0]	70.6
4β	70.7	69.6	70.3[5]	70.7	70.5	70.6	70.8	70.6	70.7
5α	72.2	72.1	72.3	72.2*	72.1[3]*	72.0	72.2	72.0[6]*	72.1
5β	76.8	76.7[6]*	76.6	76.7[5]	76.6	76.6	76.7	76.6	76.8
6α	61.5	61.3	61.0	61.6	61.4	61.4	61.6	61.4	61.6
6β	61.8	61.4[3]	61.6	61.8	61.6	61.6	61.8	61.6[0]	61.8
1′α	94.6	103.6	97.1	97.2	97.0[0]	97.0[0]	97.4	97.5	97.1
1′β	95.7	102.9	98.6	98.6	98.3	98.3	98.8	98.8	98.5
2′α	76.7	82.1	70.9	71.9[7]	72.0[7]	72.0	72.3	72.1[8]	72.2
2′β	75.4	82.2	—	72.0[0]	—	—	—	72.2[3]	—
3′α	72.2	76.5[3]	80.5	82.8	74.0	72.2	74.1	73.5	72.5
3′β	—	—	80.6	82.9	—	—	—	73.6	—
4′α	70.3	70.1	70.7	68.9	77.5[1]	79.4	70.4[3]	69.9	79.2
4′β	70.2	70.2	70.3[9]	68.8	77.5[3]	—	70.3[7]	—	—
5′α	72.4	76.4[8]	72.0	72.6	71.2	71.4	71.5	71.8	71.5
5′β	72.5	76.6	72.1	72.5	71.1	71.2	71.4	71.6	71.4
6′α	61.3	61.5	60.9[3]	61.3	61.2	60.5	66.5	69.1	60.7[0]
6′β	61.2	61.6	60.8[9]	61.2	61.1	—	66.4	69.0	60.6[5]
1″α	97.5	104.0	100.1	103.8	100.4	103.4	98.9	103.9	103.9
1″β	96.4	—	100.0	—	—	—	—	—	—
2″	72.3	74.7	72.5	74.5	72.6	74.0	72.6	73.9	72.0
3″α	73.8[0]	76.3	73.7[3]*	76.6	73.7	76.4	74.1	76.5	73.6
3″β	73.8[3]	76.2	73.7[1]*	—	—	—	—	—	—
4″	70.4	70.3	70.6	70.6	70.2	70.3	70.5	70.4[4]	69.6
5″α	72.9	77.2	72.5*	77.0	73.5	76.8	72.8	76.7	76.4
5″β	72.8	—	72.6*	—	—	—	—	—	—
6″	61.4	61.5	61.4	61.7	61.3	61.4	61.5	61.5[6]	62.1

a) The carbons in the sugar moiety at the non-reducing end have a double prime number and those at the reducing end are numbered without prime, whereas the others are coded with a prime number. The unresolved signals are expressed by —. The signals marked by * are interchangeable. Data measured at 100.6 MHz are shown by #.

§ DCE=1,2-dichloroethane, IPE=diisopropyl ether.

Table 3. (Continued)

C	154#	155	156	157	158	159	160#	161#	162
1α	93.1	92.6	93.2	93.2	93.2	93.2	93.1	93.1	93.2
1β	96.9	96.2	97.0	97.0	96.9	97.0	96.8	96.8	97.0
2α	70.9	71.7	71.1	71.1	71.1[2]	71.1	70.9	71.0	71.1
2β	73.6	74.3	73.9	73.8	73.8[5]	73.8	73.7	73.7	73.8
3α	80.4	85.6	80.7	80.4	80.5	80.6	80.6	81.0	80.6
3β	83.0	87.9	83.2	82.9	83.1	83.2	83.1	83.4	83.2
4α	70.2*	69.2	70.7	71.1	71.0[6]	71.1	70.9	70.8	71.1
4β	70.0*	—	70.8	—	—	—	—	—	—
5α	72.0	72.3	72.2	72.3	72.2	72.2	72.0	72.0	72.2
5β	76.3	76.6	76.6	76.7	76.6	76.7	76.5	76.5	76.7
6α	61.2	61.7	61.0	61.4	61.2	61.4	61.2[0]	61.3	61.4
6β	61.3	61.5	61.2	61.6	61.6	61.5[7]	61.4	61.4	61.6
1′α	97.2	102.8	100.1[6]*	100.0	99.8	99.8	98.6[9]	100.1	99.8
1′β	—	103.1	100.2[0]*	99.9	—	—	98.7[2]	100.0	—
2′α	76.1	82.3	71.4	72.2	72.5	72.5	72.5*	72.5	72.4
2′β	76.2	82.5	71.3	—	72.4	72.4	72.4*	72.4	72.3
3′	72.0[8]	76.7	80.9	83.1	74.3	72.5	73.9*	73.7	72.6
4′α	70.7	70.3	71.0	68.9	77.7[4]	79.6	70.3	70.0	79.3
4′β	—	—	—	68.8	77.6[5]	79.5	70.4	—	79.2
5′α	72.3	76.8*	72.7	72.5	71.3	71.4	71.2	71.7	71.4
5′β	—	76.9*	72.5	—	—	—	71.3	—	—
6′α	61.2	61.8[4]	61.4	61.2	61.4	60.7	66.4	69.2	60.7
6′β	60.9	61.8[2]	61.6	61.3	—	60.6	66.3	69.1	60.6
1″α	96.8	104.2	100.2[1]	103.8	100.6	103.5	99.9	103.6	103.9
1″β	—	104.3	—	—	—	—	—	—	—
2″	72.1[4]	74.8	72.7	74.5	72.7	74.2	72.4	74.0	72.0
3″α	73.7	76.4[3]	73.9	76.6	73.8[9]	76.5	74.0*	76.5	73.6
3″β	—	76.4[0]	—	—	—	—	—	—	—
4″	70.2	70.6	70.5	70.6	70.3	70.5	70.4	70.5	69.6
5″	72.6	77.4	72.8	77.0	73.7	77.0	72.7	76.7	76.4
6″	61.2	61.6	61.5	61.7	61.5	61.6[0]	61.2[4]	61.6	62.1

Table 3. (Continued)

C	163	164	165	166	167	168	169	170#	171
1α	92.8	92.6	92.7	92.9	92.7	92.9	92.7	92.7	92.9
1β	96.8	96.5	96.6	96.8	96.6	96.8	96.6	96.2	96.8
2α	72.4	72.0	72.1	72.2	72.1	72.5	72.0[9]	72.1	72.4
2β	75.2	74.7	74.8	75.0	74.8	75.0	74.8	74.8	75.0
3α	74.3	72.1	74.0	74.3	74.0	74.2	74.0	74.0[3]	74.2
3β	77.4	75.1	77.0	77.2	77.0	77.2	77.0	77.0	77.2
4α	76.9	80.6	77.9	77.8	78.0	77.9	78.2	78.2	78.0
4β	76.8	80.5	77.8	77.5	77.7	77.7	77.9	78.0	77.8
5α	70.9	70.9	70.8	70.9	70.8	70.9	70.8	70.8	70.9
5β	75.5	75.7	75.4	75.5	75.4	75.5	75.4	75.4	75.5
6α	61.7	60.9[7]	61.4	61.6	61.4	61.5	61.5	61.5	61.6
6β	61.8	61.0[7]	61.5	61.7	61.5	61.7	61.6	61.6	61.7
1′α	97.7	102.0[7]	100.8	100.5	100.3[4]	100.3	100.6	100.6	100.3
1′β	97.6	102.1[4]	100.7	100.4	100.2[6]	100.2	100.5	100.5	100.4
2′α	76.2	80.4	71.3	72.3	72.4	72.3	72.5	72.5[3]	72.3
2′β	75.8	80.3	71.2	—	72.3	—	72.4	72.4[5]	—
3′α	72.0	77.0	80.4	83.1	74.1	72.4	73.9	72.5[3]	72.5
3′β	—	—	80.3	83.0	—	—	—	—	—
4′	70.4*	70.1	70.6	68.8	77.6	79.4	70.2	70.0	79.1
5′α	73.5	76.9	73.3[0]	73.5	72.0	72.4	72.1[3]	73.6	72.3
5′β	—	—	73.3[3]	—	—	—	—	—	—
6′α	61.3	61.6[8]	61.1	61.4	61.3	60.8	66.7	69.3	60.9
6′β	—	61.7[1]	—	—	—	—	—	—	—
1″α	97.3	103.5[2]	99.9	103.8	100.6	103.5	98.9	103.5	103.9
1″β	—	103.4[8]	—	—	—	—	—	—	—
2″	72.3	74.9	72.5	74.5	72.6	74.2	72.3	73.9[9]	72.0
3″	73.8	76.4	73.7	76.6	73.7	76.5	73.9	76.5	73.6
4″	70.3*	70.4	70.3	70.6	70.2	70.5	70.4	70.5	69.6
5″	72.8	76.7	72.6	77.0	73.5	77.0	72.6	76.7	76.4
6″	61.4	61.4	61.3	61.7	61.3	61.6	61.3	61.6	62.1

Table 3. (Continued)

C	172#	173#	174#	175	176	177	178	179	180
1α	93.0	93.0	93.0	93.0	93.2	93.1	93.2	93.1	93.0
1β	96.8	96.8	96.8	96.8	97.1	97.0	97.1	97.0	96.9
2α	72.2	72.3[0]	72.2	72.3	72.4	72.4	72.4	72.4	72.3
2β	74.9	74.9	74.9	74.9	75.1	75.0	75.1	75.0	74.9
3α	73.8	73.6[2]	73.8	73.4	74.1	73.7	74.0	73.7	73.8
3β	76.7	76.5	76.4	76.4[5]	77.0	76.7	77.0	76.7	76.8
4α	70.6	70.6	70.6	70.1	70.5	70.3[6]	70.5	70.4	70.4
4β	—	70.5	—	70.3	70.4	70.3[9]	70.6	70.5	70.2[2]
5α	70.8	71.0	70.9	71.2	71.0	71.4	71.0	71.4	70.9
5β	75.2	75.4	75.1	75.6	75.3	75.9	75.3	75.9	75.1
6α	66.9	69.4	67.2	69.4	66.6[3]	69.6	66.9	69.7	66.8
6β	67.0	69.7	—	69.5	66.5[8]	69.8	66.8	69.8	66.7
1′α	96.2	103.7	98.7	102.0	99.1	103.7[7]	98.9[3]	103.4	98.7
1′β	—	103.8	98.5	—	99.0	103.8[1]	98.8[9]	103.5	98.6
2′α	76.2	78.3	81.2	80.5	71.0	72.8	72.0	73.9	72.1
2′β	—	—	81.3	80.6	—	—	—	—	—
3′	72.2	75.3	72.7	76.4	80.7	83.0	83.4	85.4	74.3
4′α	70.3	70.2	70.2	70.4	71.1[3]	71.0	69.0	69.1	77.5
4′β	—	—	—	—	71.0[9]	—	—	—	—
5′α	72.5	76.6	72.3[3]	76.8[8]	72.6[2]	76.5[6]	72.6	76.5	71.1
5′β	—	—	72.2[7]	76.8	72.5[6]	76.5[9]	—	—	—
6′α	61.2*	61.5	61.6	61.7	61.3[1]	61.2*	61.4	61.7	61.3
6′β	—	61.6	—	—	—	—	—	—	—
1″α	96.9	98.7	104.6	103.2[3]	100.1	100.1	103.9	103.8	100.4
1″β	—	—	104.7	103.2[0]	—	—	—	—	—
2″	72.2	72.2[6]	74.1	74.5	72.7	72.6	74.5	74.5	72.6
3″α	73.7	73.5[6]	76.7	76.5[4]	73.9	73.9	76.6	76.5	73.7
3″β	73.6	—	—	—	—	—	—	—	—
4″	70.3	70.6	70.4	70.2	70.4	70.3	70.6	70.6	70.1[6]
5″	72.7	72.5	76.7	76.9[4]	72.7	72.7	77.0	77.0	73.5
6″	61.3*	61.1	61.2	61.5	61.2[5]	61.5*	61.7	61.7	61.3

Table 3. (Continued)

C	181	182#	183	184	185	186	187#	188	189#
1α	93.1	93.0	93.1	93.0	93.1	93.2	93.0	93.2	93.0
1β	97.0	96.9	97.0	96.9	97.0	97.1	96.8	97.1	96.8
2α	72.4	72.3	72.4	72.2[5]	72.4	72.4	72.3	72.4	72.3
2β	75.0	74.9	75.0	74.9	75.0	75.1	74.9	75.0	74.9
3α	73.7	73.8	73.7	73.9	73.7	74.0[3]	73.5	74.0	73.5
3β	76.6	76.8[0]	76.7	76.8	76.7	77.0	76.5	76.9	76.5
4α	70.4	70.4	70.5	70.4	70.4	70.6	70.3	70.6	70.3
4β	70.5	70.3	—	70.2[8]	70.3	70.4	70.4	70.4	—
5α	71.4	70.9	71.4	70.8	71.5	71.0	71.3	71.0	71.3
5β	75.9	75.1	75.9	75.0	75.9	75.3	75.8	75.3	75.7
6α	69.6	66.7	69.7	66.7	69.9[6]	67.0	69.8	66.8	69.5
6β	69.8	—	69.8	66.6	70.0[0]	66.9	69.7	—	69.7
1′α	103.4[9]	98.5	103.5	98.7	103.9[3]	99.1	103.6	98.7	103.3
1′β	103.5[2]	—	—	—	103.8[8]	99.0	103.7	—	—
2′	74.0	72.1	73.9	72.2	74.1	72.4	74.0	72.2	73.6
3′	77.1	72.5	75.2	74.2*	76.8	73.9[6]	76.8	72.7	75.1
4′	77.8	79.5	79.6	70.3[4]	70.5*	70.2	70.3	79.3	79.2
5′α	75.5[4]	71.3	75.8	71.1	75.3	71.8	75.7	71.4	75.6
5′β	75.5[0]	—	—	71.0	—	—	—	—	—
6′α	61.7	60.6	61.0	66.3	66.5	69.1[9]	69.4	60.8	60.9
6′β	—	—	—	—	—	69.1[7]	—	—	—
1″	100.6	103.4	103.6	98.6	98.9	103.6	103.4	103.9	103.8
2″	72.7	74.0	74.2	72.3[1]	72.5	74.1	73.9	72.0	71.8
3″	73.8	76.4	76.5	73.9*	74.1	76.9	76.4	73.6	73.4
4″	70.3	70.3	70.5	70.3[4]	70.6*	70.6	70.5	69.6	69.4
5″	73.7	76.8[3]	77.0	72.7	72.8	76.7	76.5	76.4	76.2
6″	61.5	61.4	61.6	61.3	61.4	61.7	61.6	62.1	61.9

Table 4. ^{1}H NMR Chemical Shifts of Anomeric Protons of Trisaccharides (300 MHz, in D_2O)

Compounds	H1		H1′		H1″		Compounds	H1		H1′		H1″	
	α *J*, Hz	β *J*, Hz	α *J*, Hz	β *J*, Hz	α *J*, Hz	β *J*, Hz		α *J*, Hz	β *J*, Hz	α *J*, Hz	β *J*, Hz	α *J*, Hz	β *J*, Hz
145	5.39	4.73	5.23	5.53	5.04	5.11	**168**	5.14	4.57	5.33	5.33	4.43	4.43
	3.5	8.0	3.5	3.5	3.5	3.5		3.5	8.0	3.5	3.5	7.5	7.5
146	5.35	4.64	4.64	4.74	4.73	4.73	**169**	5.14	4.58	5.33	5.33	4.88	4.88
	3.5	7.5	7.5	8.0	8.0	8.0		3.5	8.0	3.5	3.5	3.5	3.5
147	5.38	4.75	5.04	5.33	5.28	5.28	**170**[a]	5.12	4.55	5.30	5.30	4.39	4.39
	3.5	7.5	3.5	4.0	4.0	4.0		3.5	8.0	4.0	4.0	8.0	8.0
148	5.36	4.73	5.02	5.33	4.64	4.63	**171**	5.15	4.57	5.33	5.33	4.38	4.38
	3.5	7.5	3.5	4.0	8.0	8.0		3.5	7.5	3.5	3.5	7.5	7.5
149	5.36	4.72	5.02	5.31	5.35	5.34	**172**[a]	5.13	4.55	5.07	5.08	5.01	5.01
	3.5	8.0	3.5	4.0	3.5	3.5		3.5	8.0	4.0	4.0	4.0	4.0
150[a]	5.35	4.70	5.00	5.28	4.44	4.43	**173**[a]	5.12	4.55	4.52	4.54	5.25	5.28
	3.5	8.0	4.0	4.0	8.0	8.0		3.5	8.0	8.0	8.0	3.5	3.5
151	5.35	4.73	5.02	5.30	4.88	4.88	**174**[a]	5.14	4.55	5.06	5.07	4.54	4.53
	3.5	8.0	3.5	3.5	3.5	3.5		4.0	8.0	4.0	4.0	8.0	8.0
152	5.35	4.72	5.01	5.27	4.42	4.42	**175**	5.14	4.56	4.52	4.55	4.74	4.75
	3.5	7.5	3.5	3.5	7.5	7.5		3.5	8.0	7.5	7.5	8.0	8.0
153[a]	5.36	4.72	5.01	5.30	4.39[0]	4.39[3]	**176**	5.17	4.60	4.87	4.88	5.28	5.29
	3.5	8.0	3.5	3.5	8.0	8.0		4.0	8.0	3.5	3.5	4.0	4.0
154[a]	5.13	4.55	5.45	5.40	5.08	5.07	**177**	5.14	4.57	4.43	4.45	5.26	5.26
	3.5	7.5	3.5	3.5	3.5	3.5		3.5	8.0	7.5	8.0	3.5	3.5
155	5.20	4.64	4.67	4.69	4.73	4.73	**178**	5.17	4.60	4.88	4.89	4.63	4.63
	3.5	8.0	8.0	8.0	8.0	8.0		4.0	8.0	4.0	4.0	8.0	8.0
156	5.15	4.58	5.31	5.29	5.28	5.28	**179**	5.14	4.57	4.44	4.46	4.67	4.67
	3.5	8.0	3.5	3.5	4.0	4.0		3.5	7.5	8.0	8.0	8.0	8.0
157	5.16	4.59	5.32	5.30	4.64	4.64	**180**	5.16	4.59	4.88	4.89	5.34	5.34
	4.0	8.0	4.0	4.0	8.0	8.0		3.5	7.5	3.5	3.5	3.5	3.5
158	5.15	4.59	5.28	5.30	5.33	5.33	**181**	5.14	4.57	4.42	4.44	5.32	5.32
	3.5	8.0	4.0	4.0	3.5	3.5		3.5	8.0	8.0	8.0	3.5	3.5
159	5.15	4.58	5.29	5.27	4.44	4.45	**182**[a]	5.14	4.57	4.85	4.86	4.42	4.42
	3.5	8.0	4.0	4.0	8.0	8.0		3.5	8.0	3.5	3.5	8.0	8.0
160[a]	5.13	4.56	5.28	5.26	4.87	4.86	**183**	5.15	4.57	4.44	4.46	4.43	4.43
	3.5	8.0	4.0	3.5	3.5	3.5		3.5	8.0	7.5	7.5	8.0	8.0
161[a]	5.13	4.56	5.25	5.23	4.39	4.39	**184**	5.16	4.58	4.88	4.88	4.88	4.88
	3.5	8.0	4.0	4.0	7.5	7.5		4.0	7.5	3.5	3.5	3.5	3.5
162	5.15	4.58	5.30	5.27	4.38	4.39	**185**	5.14	4.56	4.44	4.46	4.88	4.88
	3.5	8.0	4.0	4.0	7.5	7.5		4.0	8.0	8.0	8.0	4.0	4.0
163	5.15	4.56	5.60	5.63	5.11	5.11	**186**	5.16	4.59	4.87	4.88	4.41	4.41
	3.5	7.5	3.5	3.5	3.5	3.5		3.5	8.0	3.5	3.5	8.0	8.0
164	5.14	4.57	4.54	4.54	4.74	4.74	**187**[a]	5.12	4.55	4.41	4.44	4.42	4.42
	3.5	8.0	7.5	7.5	7.5	7.5		3.5	8.0	7.5	7.5	8.0	8.0
165	5.15	4.58	5.33	5.33	5.28	5.28	**188**	5.15	4.58	4.87	4.88	4.37	4.37
	3.5	7.5	3.5	3.5	3.5	3.5		3.5	7.5	3.5	3.5	7.5	7.5
166	5.15	4.57	5.36	5.36	4.64	4.63	**189**[a]	5.12	4.55	4.42	4.44	4.35	4.35
	3.5	7.5	3.5	3.5	7.5	7.5		3.5	8.0	7.5	7.5	8.0	8.0
167	5.15	4.58	5.32	5.32	5.32	5.32							
	3.5	7.5	3.5	3.5	3.5	3.5							

a) Measured at 400 MHz.

Table 5. ^{1}H and ^{13}C NMR Chemical Shifts of Anomeric Protons and Carbons of Biosyl Donors (300 MHz, in $CDCl_3$)

Compds	H1		H1′		Cl		Cl′	
	α *J*, Hz	β *J*, Hz	α *J*, Hz	β *J*, Hz	α	β	α	β
28	5.30	4.8[a]	4.8[a]	5.46	90.1	97.4	95.5	97.7
	3.5	—	—	4.0				
29	5.45	4.7[a]	4.75[a]	4.75[a]	92.7	95.7	103.5	103.1
	3.5	—	—	—				
36	5.32	4.7[a]	5.59	5.59	90.5	97.8	97.4	97.3
	3.5	—	3.5	3.5				

Table 5. (Continued)

Compds	H1		H1′		Cl		Cl′	
	α J, Hz	β J, Hz	α J, Hz	β J, Hz	α	β	α	β
37	5.18	4.68	5.07	5.07	90.8	97.2	102.6	102.6
	3.5	7.5	7.5	7.5				
44	5.17	4.73	4.99	4.99	91.0	97.2	97.5	97.5
	3.5	7.5	3.5	3.5				
45	5.22	4.68	4.45	4.49	91.0	97.4	103.8	104.4
	3.0	7.5	7.5	7.5				
51	5.23[b]	4.8[a]	5.64	5.63	90.8	97.4	96.9	96.8
	2.5	—	3.5	3.5				
57	5.19	4.68	4.4[a]	4.4[a]	91.3	97.3	102.6	102.5
	3.5	7.5	—	—				
70	5.20	4.7[a]	4.37	4.37	91.4	97.3	102.8[2]	102.7[7]
	3.5	7.5	7.5	7.5				

a) Overlapping. b) Broadening.

Digital Polarimeter at ca. 25 °C within 10 min after dissolution of each sample. The other items were described earlier.[7,24]

Glucoside **6**[26] and the acceptors, **3**,[7] **10**,[7] **17**,[27] **20**,[7] **21**,[5,28] and **23**,[16] were prepared according to the published methods. The following compounds were obtained from commercial sources: **1**, **54**, and **60**, Tokyo Kasei Kogyo Co., Inc.; **5** and **48**, Wako Pure Chemical Industries, Ltd.; **13** and **63**, Aldrich Chemical Co., Inc.; **22**, Pfanstiehl Laboratory Inc.; **64**, ICN Pharmaceutical Inc.; and **67**, Koso Chemical Co. Ltd.

The ^{1}H and ^{13}C NMR spectra were recorded with a Varian VXR-300 spectrometer or a Varian XL-400 spectrometer, accompanied by the measurements of H,H-COSY and H,C-COSY spectra; for the protected saccharides, DEPT experiments were also carried out.[24] Table 3 contains the ^{13}C NMR chemical shifts of the synthetic trisaccharides, while the ^{1}H NMR data of the anomeric protons are presented in Table 4. The ^{1}H and ^{13}C NMR spectral data of the anomeric centers of the heptabenzyl 1-OH derivatives of the glucobioses are summarized in Table 5.[25]

Acceptor Preparations. Allyl 3,4,6-Tri-*O*-benzyl-β-D-glucopyranoside (2): A through-process similar to that used for the preparation of **3**,[7] using allyl alcohol, converted acetate **1** (5.0 g) into **2** (3.74 g, 60%), mp 31—33 °C, $[\alpha]_D$−7° (*c* 0.8, $CHCl_3$).

Anal. ($C_{30}H_{34}O_6$) C, H.

Benzyl 3,4,6-Tri-*O*-benzyl-β-D-glucopyranoside (4). Similarly, **1** (10 g) was transformed into **4** (2.9 g, 21%), mp 88—89 °C, $[\alpha]_D$−29° (*c* 0.3, $CHCl_3$) (lit,[29] mp 87—88 °C, $[\alpha]_D^{20}$−25° (*c* 1.2, $CHCl_3$)).

Anal. ($C_{34}H_{36}O_6$) C, H.

Allyl 2,4,6-Tri-*O*-benzyl-α-D-glucopyranoside (7). A controlled benzylation[8] of **6**[26] (6.60 g) through stirring in benzyl chloride (66 ml) containing NaH (ca. 60% suspension in oil, 3.6 g) at 100 °C for 3 h, followed hy chromatography with a TB system, gave **7** (9.09 g, 62%), $[\alpha]_D$+85° (*c* 4.5, $CHCl_3$).

Found: 73.01; C, 7.02%. Calcd for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99%.

Allyl 2,4,6-Tri-*O*-benzyl-β-D-glucopyranoside (9). Through a similar procedure described for **10**,[7] **5** (7.0 g) was first converted into **8** (10.9 g, 72%), mp 86—87 °C (lit,[26] mp 86 °C), via direct acetobromination[10] using acetyl bromide (38 ml) and acetic acid (17 ml), followed by evaporation to dryness, reaction with allyl alcohol (35 ml) in the presence of Ag_2CO_3 (14 g), and chromatography with a TB system. Compound **8** (2.7 g) was then stirred in benzyl chloride (27 ml) containing KOH powder (4.7 g) at 100 °C for 1 h, followed by chromatography with a TB system to afford **9** (2.13 g, 45% from **5**), $[\alpha]_D$+12° (*c* 1.2, $CHCl_3$).

Anal. ($C_{30}H_{34}O_6$) C, H.

Benzyl 2,4,6-Tri-*O*-benzyl-β-D-glucopyranoside (12). (A) The acceptor **12** was best produced by way of an improved preparation of **11**. A lyophilized bromide,[10,30] obtained from **5** (10 g) as described above for **8**, reacted with benzyl alcohol (11 ml) and $Hg(CN)_2$ (14 g) in nitromethane (46 ml), followed by processing and chromatography with a TB system, furnished **11** (18.3 g (75%), mp 99—101 °C (lit,[31] mp 101—104 °C)). This (5.0 g) was then heated in benzyl chloride (50 ml) containing KOH (5.12 g) with stirring at 140 °C for 1 h and then more KOH (5.12 g) was added to the mixture. After 1 h, another portion of KOH (5.12 g) was added to the mixture which was further stirred for 2 h. Processing and chromatography with a TB system afforded **12** (2.75 g, 40% from **5**), mp 35—36 °C, $[\alpha]_D$−2° (*c* 0.3, $CHCl_3$) (lit,[32] mp 30—35 °C, $[\alpha]_D^{20}$−3° (*c* 2.6, $CHCl_3$)).

Anal. ($C_{34}H_{36}O_6$) C, H.

(B) Modifying the reported lengthy process,[32,33] **13** was transformed into **12**. Acetal **13** (5.0 g) was refluxed in allyl bromide (20 ml) containing NaH (ca. 60% dispersion in oil, 1.6 g) for 2 h. After filtration and evaporation to dryness, the residue was heated in aq acetic acid (80%, 40 ml) at 95 °C for 5 h. Lyophilization and successive hot acetylation in acetic anhydride (58 ml) containing NaOAc (1.9 g), followed by chromatography with a TB system and crystallization with IPE furnished **14** (4.35 g, 58%), mp 118—119 °C (lit,[33] mp 119—120 °C) (Found: C, 52.39; H, 6.24%). This (0.50 g) was dissolved in DCE (5.0 ml) containing benzyl alcohol (0.26 ml) and $(C_2H_5)_2O \cdot BF_3$ (0.15 ml) was then added into the solution with stirring. After stirring at 20 °C for 1 h, the reaction mixture was processed and lyophilized, the product mixture was then agitated in benzyl chloride (5.0 ml) containing KOH (1.2 g) at 120 °C for 2 h. After processing and chromatography using an HE system, a homogeneous product was then refluxed in EBW[##] (7.0 ml) containing TRC[##] (0.10 g) over-

[##] EBW=a mixture of ethanol, benzene, and H_2O (7:3:1); TRC=tris(triphenylphosphine)rhodium(I) chloride.

night.[24,27] After evaporation to dryness, the residue was heated in acetone (35 ml) containing dil HCl (3%, 0.53 ml) at 50 °C for 0.5 h. Subsequent chromatography with a TB system furnished **12** (0.30 g, 27% from **13**).

Benzyl β-D-Glucopyranoside (15). Compound **15**, the precursor of the acceptor **16**,[34] was conveniently prepared from D-glucose (**5**). A reaction mixture containing **11** derived from **5** (10 g) as described above in procedure A for **12** was demercurated as usual and dissolved in dil methanolic sodium methoxide (0.3%, 150 ml). After neutralization with acetic acid and concentration, chromatography using a CM system afforded **15** (10.6 g, 71% from **5**), mp 119—121 °C (lit,[31] mp 123—125 °C) (Found: C, 57.60; H, 6.93%).

Allyl β-D-Glucopyranoside (18). Compound **18**, the precursor of **19**,[27] was readily produced from **5**. A processed reaction mixture containing **8** obtained from **5** (7.0 g) as described for **9** was treated with dil sodium methoxide (0.4%, 30 ml). Neutralization and chromatography with a CM system provided **18** (5.53 g, 65% from **5**), mp 101—102 °C (lit,[26] mp 100—101 °C) (Found: C, 49.10; H, 7.39%).

Biosyl Donor Preparations. Allyl *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-gluco-pyranoside (49). To a cooled mixture of acetyl bromide (4.0 ml) and acetic acid (15 ml), **48** (monohydrate, 1.0 g) was added and stirring was continued at 20 °C for 2 h. After concentration and quick co-evaporation with toluene at 40—45 °C, the residue was stirred in allyl alcohol (7 ml) in the presence of Ag_2CO_3 (1.2 g) overnight in the dark at room temp. Processing, chromatography with a TB system and crystallization with IPE gave **49** (1.38 g, 73%), mp 115—117 °C, $[\alpha]_D$+50° (*c* 0.2, $CHCl_3$) (lit, mp 106—107 °C,[35] mp 109—110 °C,[36] $[\alpha]_D^{25}$+50.4° (*c* 0.2, $CHCl_3$),[35] $[\alpha]_D^{26}$+47° (*c* 1.5 $CHCl_3$)[36]), ^{13}C NMR ($CDCl_3$) δ=61.5 (C6′), 62.8 (C6), 68.0 (C4′), 68.4 (C5′), 69.3 (C3′), 69.9 (2C, C2′, and allyl), 72.0 (C2), 72.1 (C5), 72.7 (C4), 75.4 (C3), 95.5 (C1′), and 99.0 (C1).

Anal. ($C_{29}H_{40}O_{18}$) C, H.

Similarly, **60** (0.30 g) and **67** (monohydrate, 3.0 g) were converted into **61** (0.40 g, 67%) and **68** (4.3 g, 76%), respectively. In the case of **54** (5.0 g) affording **55** (6.7 g (68%)), the acetobromination needed more reagents (acetyl bromide, 27 ml and acetic acid, 86 ml) and a longer reaction time (5.5 h).

Allyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (55). Mp 184—185 °C, $[\alpha]_D$−30° (*c* 0.8, $CHCl_3$) (lit,[37] mp 179 °C, $[\alpha]_D^{20}$−21° (*c* 1, $CHCl_3$)), ^{13}C NMR ($CDCl_3$) δ=61.6 (C6′), 61.9 (C6), 67.8 (C4′), 70.0 (allyl), 71.5 (C2), 71.6 (C2′), 72.0 (C5′), 72.5 (C3′), 72.7 (C5), 72.9 (C3), 76.5 (C4), 99.4 (C1), and 100.7 (C1′).

Anal. ($C_{29}H_{40}O_{18}$) C, H.

Allyl *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (61). $[\alpha]_D$+67° (*c* 1.2, $CHCl_3$), ^{13}C NMR ($CDCl_3$) δ=61.8 (C6′), 66.4 (C6), 67.4 (C5′), 68.5 (C4′), 69.2 (C4), 69.9 (allyl), 70.0 (C3′), 70.6 (C2′), 71.3 (C2), 72.6 (C5), 72.8 (C3), 95.6(C1′), and 99.2 (C1).

Anal. ($C_{29}H_{40}O_{18}$) C, H.

Allyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (68). $[\alpha]_D$−15° (*c* 1.3, $CHCl_3$) (lit,[38] $[\alpha]_D^{24}$−11.7° (*c* 1.8, $CHCl_3$), ^{13}C NMR ($CDCl_3$), δ=60.8 (C6′), 62.0 (C6), 66.6 (C4′), 69.1 (C2′), 70.0 (allyl), 70.7 (C5′), 71.0 (C3′), 71.7 (C2), 72.6 (C5), 72.8 (C3), 76.3 (C4), 99.3 (C1), and 101.0 (C1′).

Anal. ($C_{29}H_{40}O_{18}$) C, H.

The ME bioside acetates, **52**, **58**, **62**, and **71**, were similarly produced using MEOH.

2-Methoxyethyl *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (52). 86%, mp 99—102 °C, $[\alpha]_D$+47° (*c* 3.8, $CHCl_3$) (lit,[39] $[\alpha]_D^{20}$+43.2° (*c* 1.1, $CHCl_3$)), ^{13}C NMR ($CDCl_3$) δ=59.0 (ME), 61.5 (C6′), 62.9 (C6), 68.0 (C4′), 68.5 (C5′), 69.0 (ME), 69.3 (C3′), 70.0 (C2′), 71.6 (ME), 72.1 (2C, C2, and C5), 72.8 (C4), 75.4 (C3), 95.5 (C1′), and 100.4 (C1).

Anal. ($C_{29}H_{42}O_{19}$) C, H.

2-Methoxyethyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (58). 85%, mp 180—181 °C, $[\alpha]_D$−23° (*c* 0.7, $CHCl_3$), ^{13}C NMR ($CDCl_3$) δ=59.0 (ME), 61.5 (C6′), 61.9 (C6), 67.5 (C4′), 69.0 (ME), 71.0 (ME), 71.5 (C2), 71.6 (C2′), 72.0 (C5′), 72.5 (C3′), 72.7 (C5), 72.9 (C3), 76.4 (C4), and 100.7 (2C, C1, and C1′).

Anal. ($C_{29}H_{42}O_{19}$) C, H.

2-Methoxyethyl *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→6)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (62). 74%, $[\alpha]_D$+62° (*c* 0.9, $CHCl_3$), ^{13}C NMR ($CDCl_3$) δ=59.0 (ME), 61.8 (C6′), 66.5 (C6), 67.4 (C5′), 68.4 (C4′), 69.0 (ME), 69.3 (C4), 70.0 (C3′), 70.2 (C2′), 71.2 (C2), 71.6 (ME), 72.6 (C5), 72.8 (C3), 95.7 (C1′), and 100.6 (C1).

Found: C, 49. 80; H, 6.06%. Calcd for $C_{29}H_{42}O_{19}$: C, 50.12; H, 6.09%.

2-Methoxyethyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (71). 71%, mp 61—62 °C, $[\alpha]_D$−15° (*c* 2.1, $CHCl_3$) (lit,[40] $[\alpha]_D^{16}$−14.4° (*c* 3.80, $CHCl_3$)), ^{13}C NMR ($CDCl_3$) δ=59.0 (ME), 60.8 (C6), 62.0 (C6′), 66.6 (C4′), 69.0 (ME), 69.1 (C2′), 70.7 (C5′), 71.0 (C3′), 71.6^0 (ME), 71.6^3 (C2), 72.6 (C5),72.8 (C3), 76.2 (C4), 100.7 (C1), and 101.0 (C1′).

Anal. ($C_{29}H_{42}O_{19}$) C, H.

Allyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (65). To a stirring cold solution of **64** (ICN Pharmaceuticals Inc., 100 mg) in chloroform (0.17 ml), acetyl bromide (60 μl) and H_2O (13 μl) were added to give a homogeneous solution which was kept stirring at 20 °C for 1 h.[5,7] After lyophilization, the residue was stirred in allyl alcohol (0.52 ml) containing Ag_2CO_3 (197 mg) overnight, followed by chromatography with a TB system to give **65** (65 mg, 65%), mp 139—140 °C, $[\alpha]_D$−15° (*c* 0.5, $CHCl_3$), ^{13}C NMR ($CDCl_3$) δ=61.8 (C6′), 68.3 (2C, C4′, and C6), 69.1 (C4), 69.8 (allyl), 71.1 (C2′), 71.3 (C2), 71.9 (C5′), 72.7 (C3′), 72.8 (C3), 73.3 (C5), 99.3 (C1),and 100.7 (C1′).

Anal. ($C_{29}H_{40}O_{18}$) C, H.

2-Methoxyethyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (66). Acetate **64** (100 mg) was similarly converted into **66** using MEOH (93 m 91%), mp 127—129 °C, $[\alpha]_D$−5° (*c* 0.6, $CHCl_3$), ^{13}C NMR ($CDCl_3$) δ=58.9 (ME), 61.8 (C6′), 68.1 (C6), 68.3 (C4′), 68.9 (ME), 69.1 (C4), 71.1 (C2), 71.3 (C2′), 71.5 (ME), 71.9 (C5′), 72.7 (C3), 72.8 (C3′), 73.5 (C5), 100.6 (C1′), and 100.7 (C1).

Anal. ($C_{29}H_{42}O_{19}$) C, H.

Allyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (50). Acetate **49** (1.38 g) was stirred in benzyl chloride (18 ml) containing KOH (6.2 g) at 120 °C for 2 h, followed by processing and chromatography using a TB system to give **50** (1.15 g, 56%), $[\alpha]_D$+25° (*c* 0.7, $CHCl_3$) (lit,[36] $[\alpha]_D^{26}$+28° (*c* 3, $CHCl_3$)).

Anal. ($C_{64}H_{68}O_{11}$) C, H.

Similarly, the acetates, **52**, **55**, **58**, **61**, **62**, **65**, **66**, 68, and **71**, were transformed into the corresponding benzyl ethers, **53** (58%), **56** (67%), **59** (81%), **40** (65%), **42** (75%), **41** (69%), **43**

(78%), **69** (66%), and **72** (83%). Compounds **40**, **41**, **42**, and **43** were identical to the products described below.

2-Methoxyethyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (53). $[\alpha]_D$ +26° (*c* 1.1, $CHCl_3$) (lit,[39] $[\alpha]_D^{20}$+29.5° (*c* 1.4, $CHCl_3$)).

Anal. ($C_{46}H_{70}O_{12}$) C, H.

Allyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (56). Mp 105—108 °C, $[\alpha]_D$+10° (*c* 0.9, $CHCl_3$).

Anal. ($C_{64}H_{68}O_{11}$) C, H.

2-Methoxyethyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (59). Mp 99—100 °C, $[\alpha]_D$+17° (*c* 0.7, $CHCl_3$).

Anal. ($C_{64}H_{70}O_{11}$) C, H.

Allyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (69). Mp 75—77 °C, $[\alpha]_D$+11° (*c* 1.0, $CHCl_3$).

Anal. ($C_{64}H_{68}O_{11}$) C, H.

2-Methoxyethyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (72). Mp 79—80 °C, $[\alpha]_D$+8° (*c* 1.0, $CHCl_3$) (lit,[40] mp 82—83 °C, $[\alpha]_D^{16}$+10.2° (*c* 3.50, $CHCl_3$)).

Anal. ($C_{64}H_{70}O_{12}$) C, H.

The removal of an allyl group[27] from the bioside derivatives, **24** **25**, **30**, **31**, **32**, **33**, **38**, **39**, **40**, **41**, **50**, **56**, and **69**, giving the corresponding biosyl donors, **28**, **29**, **36**, **37**, **44**, **45**, **51**, **57**, and **70**, were typically carried out as follows: **51** (0.93 g) was refluxed in EBW (10 ml) containing TRC (70 mg) overnight, followed by lyophilization, giving a product mixture which was then heated in acetone (20 ml) containing dil HCl (3%, 0.2 ml) at 50 °C for 1 h, lyophilized and chromatographed with a TB system to give **28** (0.80 g, 90%).

***O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-D-glucopyranose (28).** 63%, $[\alpha]_D$+60° (*c* 2.3, $CHCl_3$).

Anal. ($C_{61}H_{64}O_{11}$) C, H.

***O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-D-glucopyranose (29).** 82%, mp 125—126 °C, $[\alpha]_D$+28° (*c* 0.8, $CHCl_3$).

Anal. ($C_{61}H_{64}O_{11}$) C, H.

***O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-D-glucopyranose (36).** 64% from **30** and 71% from **32**, $[\alpha]_D$+54° (*c* 3.3, $CHCl_3$) (lit,[36] $[\alpha]_D^{26}$+30.5° (*c* 1.4, $CHCl_3$).

Anal. ($C_{61}H_{64}O_{11}$) C, H.

***O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-D-glucopyranose (37).** 81% from **31** and 66% from **33**, $[\alpha]_D$+40° (*c* 1.0, $CHCl_3$).

Anal. ($C_{61}H_{64}O_{11}$) C, H.

***O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-D-glucopyranose (44).** 66% from **38** and 31% from **40**, $[\alpha]_D$+53° (*c* 2.5, $CHCl_3$).

Anal. ($C_{61}H_{64}O_{11}$) C, H.

***O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-D-glucopyranose (45).** 70% from **39** and 53% from **41**, mp 137—139 °C, $[\alpha]_D$+26° (*c* 2.7, $CHCl_3$).

Anal. ($C_{61}H_{64}O_{11}$) C, H.

***O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-D-glucopyranose (51).** $[\alpha]_D$+41° (*c* 1.4, $CHCl_3$) (lit,[36] $[\alpha]_D^{26}$+39.5° (*c* 1.5, $CHCl_3$)).

Anal. ($C_{61}H_{64}O_{11}$) C, H.

***O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-D-glucopyranose (57).** 67%, mp 108—110 °C, $[\alpha]_D$+20° (*c* 0.9, $CHCl_3$).

Anal. ($C_{61}H_{64}O_{11}$) C, H.

***O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-D-glucopyranose (70).** 68%, mp 102—105 °C, $[\alpha]_D$+10° (*c* 1.2, $CHCl_3$).

Anal. ($C_{61}H_{64}O_{11}$) C, H.

The perbenzylated ME biosides, **26**, **27**, **34**, **35**, **42**, **43**, **53**, **59**, and **72**, were converted into the corresponding 1-OH derivatives through the procedure published earlier,[7] using $TiCl_4$ (1.0 equiv) in dichloromethane (10 ml/g of substrate). The yields were as follows: **28** 64%, **29** 87%, **36** 45%, **37** 35%, **44** 88%, **45** 89%, **51** 75%, **57** 66%, and **70** 81%.

Dehydrative Glycosylation. Glycosylations using NST[3,5,41] and NSDT,[4] followed by processing and preliminary chromatography using a TB system, were performed in the manner described previously; adequate anomeric separations of the condensates were carried out by rechromatography using those systems specified below. The molar ratios of the materials used for the primary alcoholic acceptors, **17**, **19**, **20**, **21**, and **23** were donor(DOH) : acceptor(AOH) : NsCl : AgOTf : Et_3N=1.1 : 1.0 : 1.7 : 1.7 : 1.7 and DOH : AOH : NsCl : AgOTf : DMA : Et_3N=1.3 : 1.0 : 2.5 : 2.5 : 5.0 : 2.5. Those for the secondary alcohols, **2**, **3**, **4**, **7**, **9**, **10**, **12**, and **16**, were DOH : AOH : NsCl : AgOTf : Et_3N=1.3 : 1.0 : 2.5 : 2.5 : 2.5 and DOH : AOH : NsCl : AgOTf : DMA : Et_3N=1.3 : 1.0 : 2.5 : 2.5 : 2.5 : 2.5. The volume of dichloromethane was 8 to 12 ml/g of AOH. The glycosylations were carried out in 1 to 4 mmol scale for **22**, and 0.1 to 0.5 mmol scale for the biosyl donors. The results are summarized in Tables 1 and 2.

Allyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosides (24 and **25).** **24**, (faster-moving in a TB system), $[\alpha]_D$+41° (*c* 1.2, $CHCl_3$). **25**, mp 63—65 °C, $[\alpha]_D$+16° (*c* 1.7, $CHCl_3$).

Anal. **24** and **25** ($C_{64}H_{68}O_{11}$) C, H.

2-Methoxyethyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosides (26 and 27). **26**, (faster-moving in a TB system), $[\alpha]_D$+46° (*c* 1.5, $CHCl_3$).

Anal. ($C_{64}H_{70}O_{12}$) C, H.

27, mp 30—35 °C, $[\alpha]_D$+12° (*c* 0.9, $CHCl_3$).

Found: C, 74.15; H, 6.81%. Calcd for $C_{64}H_{70}O_{12}$: C, 74.54; H, 6.84%.

Allyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-α-D-glucopyranosides (30 and **31).** **30**, (slower-moving in an HE system), $[\alpha]_D$+67° (*c* 1.3, $CHCl_3$).

31, $[\alpha]_D$+45° (*c* 2.0, $CHCl_3$).

Anal. **30** and **31** ($C_{64}H_{68}O_{11}$) C, H.

Allyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranosides (32 and **33).** **32** (faster-moving in a DE system), $[\alpha]_D$+32° (*c* 1.5, $CHCl_3$) (lit,[36] $[\alpha]_D^{26}$+33° (*c* 2.2, $CHCl_3$).

33, $[\alpha]_D$+25° (*c* 2.1, $CHCl_3$).

Anal. **32** and **33** ($C_{64}H_{68}O_{11}$) C, H.

2-Methoxyethyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranosides (34 and **35).** **34** (faster-moving in a TB system), $[\alpha]_D$+33° (*c* 1.5, $CHCl_3$).

35, $[\alpha]_D$+26° (*c* 1.4, $CHCl_3$).

Anal. **34** and **35** ($C_{64}H_{70}O_{12}$) C, H.

Allyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranosides (38 and **39).** **38** (faster-moving in a TB system), mp 47—49 °C,

$[\alpha]_D$+73° (*c* 1.0, $CHCl_3$).

Found: C, 75.43; H, 6.73%. Calcd for $C_{64}H_{68}O_{11}$: C, 75.87; H, 6.76%.

39, mp 116—117 °C, $[\alpha]_D$+20° (*c* 0.7, $CHCl_3$).

Anal. ($C_{64}H_{68}O_{11}$) C, H.

Allyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranosides (40 and 41). **40** (faster-moving in a TB system), mp 85—87 °C, $[\alpha]_D$+26° (*c* 0.8, $CHCl_3$).

Anal. ($C_{64}H_{68}O_{11}$) C, H.

41, mp 143—145 °C, $[\alpha]_D$+12° (*c* 1.7, $CHCl_3$).

Found: C, 75.44; H, 6.76%. Calcd for $C_{64}H_{68}O_{11}$: C, 75.87; H, 6.76%.

2-Methoxyethyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranosides (42 and 43). **42** (slower-moving in an HE system), mp 87—89 °C, $[\alpha]_D$+36° (*c* 2.0, $CHCl_3$).

43, mp 132—134 °C, $[\alpha]_D$+12° (*c* 1.7, $CHCl_3$).

Anal. **42** and **43** ($C_{64}H_{70}O_{12}$) C, H.

Ethyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-1-thio-α-D-glucopyranosides (46 and 47). **46** (faster-moving in a TB system), mp 78—79 °C, $[\alpha]_D$+86° (*c*, 0.9, $CHCl_3$).

47, mp 92—94 °C, $[\alpha]_D$+53° (*c* 0.6, $CHCl_3$).

Anal. **46** and **47** ($C_{63}H_{68}O_{10}S$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosides (73 and 74). **73** (faster-moving in a TB system), $[\alpha]_D$+55° (*c* 2.9, $CHCl_3$).

74, $[\alpha]_D$+32° (*c* 0.8, $CHCl_3$).

Anal. **73** and **74** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosides (75 and 76). **75** (faster-moving in a TB system), $[\alpha]_D$+21° (*c* 1.1, $CHCl_3$).

Anal. ($C_{95}H_{98}O_{16}$) C, H.

76, $[\alpha]_D$+10° (*c* 1.6, $CHCl_3$).

Found:C, 75.96; H, 6.61%. Calcd for $C_{95}H_{98}O_{16}$: C, 76.28; H, 6.60%.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosides (77 and 78). **77** (slower-moving in an HI system), $[\alpha]_D$+49° (*c* 2.1, $CHCl_3$).

78, $[\alpha]_D$+36° (*c* 1.0, $CHCl_3$).

Anal. **77** and **78** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosides (79 and 80). **79** (slower-moving in a TB system), $[\alpha]_D$+43° (*c* 1.4, $CHCl_3$).

80, $[\alpha]_D$+36° (*c* 1.0, $CHCl_3$).

Anal. **79** and **80** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosides (81 and 82). **81** (faster-moving in a TB system), $[\alpha]_D$+52° (*c* 1.6, $CHCl_3$).

Anal. ($C_{95}H_{98}O_{16}$) C, H.

82, $[\alpha]_D$+32° (*c* 1.2, $CHCl_3$).

Found: C, 75.84; H, 6.62%. Calcd for $C_{65}H_{98}O_{16}$: C, 76.28; H, 6.60%.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosides (83 and 84). **83** (faster-moving in a DE system), $[\alpha]_D$+15° (*c* 0.5, $CHCl_3$).

84, mp 49—51 °C, $[\alpha]_D$+13° (*c* 0.3, $CHCl_3$).

Anal. **83** and **84** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosides (85 and 86). **85** (slower-moving in a TB system), $[\alpha]_D$+47° (*c* 0.8, $CHCl_3$).

86 $[\alpha]_D$+29° (*c* 0.3, $CCHCl_3$).

Anal. **85** and **86** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosides (87 and 88). **87** (faster-moving in an HE system), $[\alpha]_D$+30° (*c* 2.0, $CHCl_3$).

88, $[\alpha]_D$+23° (*c* 0.2, $CHCl_3$).

Anal. **87** and **88** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranosides (89 and 90). **89** (faster-moving in a DE system), $[\alpha]_D$+10° (*c* 1.8, $CHCl_3$).

90, $[\alpha]_D$+7° (*c* 0.4, $CHCl_3$).

Anal. **89** and **90** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranosides (91 and 92).

91 (faster-moving in a TB system), $[\alpha]_D$+41° (*c* 1.2, $CHCl_3$).

Found: C, 75.88; H, 6.59%. Calcd for $C_{95}H_{98}O_{16}$: C, 76.28; H, 6.60%.

92, mp 45—47 °C $[\alpha]_D$+24° (*c* 0.2, $CHCl_3$).

Anal. ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranosides (93 and 94). **93** (slower-moving in an HI system), $[\alpha]_D$+37° (*c* 0.2, $CHCl_3$).

94, $[\alpha]_D$+11° (*c* 1.0, $CHCl_3$).

Anal. **93** and **94** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranosides (95 and 96). **95** (faster-moving in an HI system), $[\alpha]_D$+42° (*c* 2.5, $CHCl_3$).

96, $[\alpha]_D$+19° (*c* 0.3, $CHCl_3$).

Anal. **95** and **96** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranosides (97 and 98). **97** (faster-moving in a TB system), $[\alpha]_D$+39° (*c* 0.8, $CHCl_3$).

98, $[\alpha]_D$+27° (*c* 0.2, $CHCl_3$).

Anal. **97** and **98** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranosides (99 and 100). **99** (faster-moving in a TB system), $[\alpha]_D$+41° (*c* 1.6, $CHCl_3$).

100, $[\alpha]_D$+26° (*c* 0.2, $CHCl_3$).

Anal. **99** and **100** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranosides (101 and 102). **101** (slower-moving in a TB system), $[\alpha]_D$+21° (*c* 1.0, $CHCl_3$).

102, $[\alpha]_D$+18° (*c* 0.3, $CHCl_3$).

Anal. **101** and **102** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranosides (103 and 104). **103** (slower-moving in a TB system), $[\alpha]_D$+40° (*c* 0.9, $CHCl_3$).

104, $[\alpha]_D$+18° (*c* 0.9, $CHCl_3$).

Anal. **103** and **104** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranosides (105 and **106). 105** (slower-moving in an HE system), $[\alpha]_D$+25° (*c* 1.6, $CHCl_3$).

106, $[\alpha]_D$+14° (*c* 0.2, $CHCl_3$).

Anal. **105** and **106** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-β-D-glucopyranosides (107 and **108). 107** (slower-moving in a TB system), $[\alpha]_D$+13° (*c* 1.9, $CHCl_3$).

108, $[\alpha]_D$+9° (*c* 0.4, $CHCl_3$).

Anal. **107** and **108** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (109 and **110). 109** (faster-moving in a TB system), $[\alpha]_D$+54° (*c* 1.0, $CHCl_3$).

Found: C, 75.90; H, 6.55%. Calcd for $C_{95}H_{98}O_{16}$: C, 76.28; H, 6.60%.

Anal. ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (111 and **112). 111** (faster-moving in a TB system), $[\alpha]_D$+28° (*c* 0.3, $CHCl_3$).

112, $[\alpha]_D$+5° (*c* 1.9, $CHCl_3$).

Found: **111**, C, 75.91; H, 6.57%. **112**, C, 75.88; H, 6.63%. Calcd for $C_{95}H_{98}O_{16}$: C, 76.28; H, 6.60%.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (113 and **114). 113** (faster-moving in a TB system), $[\alpha]_D$+44° (*c* 1.6, $CHCl_3$).

Anal. ($C_{95}H_{98}O_{16}$) C, H.

114, $[\alpha]_D$+17° (*c* 0.2, $CHCl_3$).

Found: C, 75.89; H, 6.68%. Calcd for $C_{95}H_{98}O_{16}$: C, 76.28; H, 6.60%.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (115 and **116). 115** (faster-moving in a TB system), $[\alpha]_D$+34° (*c* 1.9, $CHCl_3$).

116, $[\alpha]_D$+28° (*c* 0.3, $CHCl_3$).

Anal. **115** and **116** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (117 and **118). 117** (slower-moving in an HE system), $[\alpha]_D$+43° (*c* 1.9, $CHCl_3$).

118, $[\alpha]_D$+21° (*c* 0.2, $CHCl_3$).

Anal. **117** and **118** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (119 and **120). 119** (faster-moving in a DE system), $[\alpha]_D$+18° (*c* 2.0, $CHCl_3$).

120, $[\alpha]_D$+17° (*c* 0.6, $CHCl_3$).

Anal. **119** and **120** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (121 and **122). 121** (slower-moving in a TB system), $[\alpha]_D$+39° (*c* 1.0, $CHCl_3$).

Found: C, 75.90; H, 6.57%. Calcd for $C_{95}H_{98}O_{16}$: C, 76.28; H, 6.60%.

122, $[\alpha]_D$+27° (*c* 0.9, $CHCl_3$).

Anal. ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (123 and **124). 123** (slower-moving in an HE system), $[\alpha]_D$+18° (*c* 2.4, $CHCl_3$).

124, $[\alpha]_D$+14° (*c* 0.6, $CHCl_3$).

Anal. **123** and **124** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (125 and **126). 125** (faster-moving in a DE system), $[\alpha]_D$+11° (*c* 2.0, $CHCl_3$).

126, $[\alpha]_D$+9° (*c* 1.5, $CHCl_3$).

Anal. **125** and **126** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranosides (127 and **128). 127** (slower-moving in a TB system), $[\alpha]_D$+86° (*c* 3.5, $CHCl_3$).

Anal. ($C_{95}H_{98}O_{16}$) C, H.

128, $[\alpha]_D$+62° (*c* 0.9, $CHCl_3$) (lit,[42] $[\alpha]_D^{20}$+67° (*c* 0.6, $CHCl_3$)) (Found: C, 76.36; H, 6.64%).

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranosides (129 and **130). 129** (slower-moving in a TB system), $[\alpha]_D$+59° (*c* 0.5, $CHCl_3$).

Found: C, 75.88; H, 6.57%. Calcd for $C_{95}H_{98}O_{16}$: C, 76.28; H, 6.60%.

130, $[\alpha]_D$+22° (*c* 0.8, $CHCl_3$) (lit,[42] °C, $[\alpha]_D^{20}$+34° (*c* 2.6, $CHCl_3$)) (Found: C, 76.55; H, 6.69%).

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranosides (131 and **132). 131** (faster-moving in a TB system), $[\alpha]_D$+83° (*c* 3.2, $CHCl_3$).

132, mp 127—129 °C, $[\alpha]_D$+48° (*c* 2.3, $CHCl_3$).

Anal. **131** and **132** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranosides (133 and **134). 133** (faster-moving in a TB system), $[\alpha]_D$+67° (*c* 2.9, $CHCl_3$).

134, $[\alpha]_D$+35° (*c* 2.0, $CHCl_3$).

Anal. **133** and **134** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranosides (135 and **136). 135** (faster-moving in a TB system), $[\alpha]_D$+74° (*c* 1.0, $CHCl_3$).

Anal. ($C_{95}H_{98}O_{16}$) C, H.

136, $[\alpha]_D$+51° (*c* 0.5, $CHCl_3$).

Found: C, 75.95; H, 6.56%. Calcd for $C_{95}H_{98}O_{16}$: C, 76.28; H, 6.60%.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranosides (137 and **138). 137** (faster-moving in a TB system), mp 114—116 °C, $[\alpha]_D$+62° (*c* 1.7, $CHCl_3$).

138, mp 122—123 °C, $[\alpha]_D$+36° (*c* 1.7, $CHCl_3$).

Anal. **137** and **138** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranosides (139 and **140). 139** (faster-moving in a TB system), $[\alpha]_D$+81° (*c* 1.0, $CHCl_3$).

140, mp 116—118 °C, $[\alpha]_D$+51° (*c* 3.4, $CHCl_3$).

Anal. **139** and **140** ($C_{95}H_{98}O_{16}$) C, H.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranosides (141 and **142). 141** (faster-moving in a DE system), $[\alpha]_D$+53° (*c* 3.3, $CHCl_3$).

Anal. ($C_{95}H_{98}O_{16}$) C, H.

142, $[\alpha]_D$+38° (*c* 1.6, $CHCl_3$).

Found: C, 75.93; H, 6.63%. Calcd for $C_{95}H_{98}O_{16}$: C, 76.28; H, 6.60%.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranosides (143 and 144). **143** (slower-moving in a TB system), mp 72—74 °C, $[\alpha]_D$+53° (*c* 2.2, $CHCl_3$).

144, mp 93—95 °C, $[\alpha]_D$+27° (*c* 3.6, $CHCl_3$).

Anal. **143** and **144** ($C_{95}H_{98}O_{16}$) C, H.

α-Isomaltosylation of **21** using the bromide.[16] A solution of **46** (100.0 mg) in carbon tetrachloride (1.0 ml) was treated with a solution of Br_2 in carbon tetrachloride (1.95 mol cm^{-3}, 56 μl) at 20 °C for 4 min. After evaporation to dryness, the residue was dissolved in nitromethane (1.0 ml). To this solution, **21** (48.4 mg) and then 2,6-dimethylpyridine (12.0 μl) were added with stirring. After being left overnight, lyophilization and chromatography with a TB system afforded **139** (29.6 mg, 22%) and **140** (4.4 mg, 3.3%).

Synthetic Trisaccharides. *O*-α-D-Glucopyranosyl-(1→2)-*O*-α-D-glucopyranosyl-(1→2)-D-glucopyranose (145). Hydrogenation of **73** (41.4 mg) over Pd on C (10%, 40 mg) in acetic acid (6 ml) at ca. 25 °C overnight, followed by chromatography using a CM system, gave **145** (8.9 mg, 62%), mp 208—215 °C (decomp), $[\alpha]_D$+145° (*c* 0.5, H_2O) (lit,[29] mp 228—230 °C (decomp), $[\alpha]_D^{20}$+151° (*c* 1, H_2O (5 min)).

Anal. ($C_{18}H_{32}O_{16}\cdot H_2O$) C, H.

Similarly, the above-described undecabenzyl trioses, **76**, **77**, **79**, **81**, **83**, **85**, **87**, **89**, **91**, **94**, **95**, **97**, **99**, **101**, **103**, **105**, **107**, **109**, **112**, **113**, **115**, **117**, **119**, **121**, **123**, **125**, **127**, **128**, **129**, **130**, **131**, **132**, **133**, **134**, **135**, **136**, **137**, **138**, **139**, **140**, **141**, **142**, **143**, and **144**, were converted into the corresponding trisaccharides, **146**, **147**, **148**, **149**, **150**, **151**, **152**, **153**, **154**, **155**, **156**, **157**, **158**, **159**, **160**, **161**, **162**, **163**, **164**, **165**, **166**, **167**, **168**, **169**, **170**, **171**, **172**, **173**, **174**, **175**, **176**, **177**, **178**, **179**, **180**, **181**, **182**, **183**, **184**, **185**, **186**, **187**, **188**, and **189**, respectively.

***O*-β-D-Glucopyranosyl-(1→2)-*O*-β-D-glucopyranosyl-(1→2)-D-glucopyranose (146).** 58%, mp 188—194 °C (decomp), $[\alpha]_D$+18° (*c* 0.6, H_2O) (lit,[43] mp 218—223 °C, $[\alpha]_D$+16° (*c* 1.0, H_2O).

Anal. ($C_{18}H_{32}O_{16}$) C, H.

***O*-α-D-Glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→2)-D-glucopyranose (147).** 57%, mp 167—171 °C, $[\alpha]_D$+177° (*c* 0.7, H_2O) (lit,[44] mp 186—188 °C, $[\alpha]_D$+178.3° (*c* 0.6, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot H_2O$) C, H.

***O*-β-D-Glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→2)-D-glucopyranose (148).** 53%, $[\alpha]_D$+72° (*c* 0.3, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot 0.5H_2O$) C, H.

***O*-α-D-Glucopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→2)-D-glucopyranose (149).** 74 %, $[\alpha]_D$+156° (*c* 0.5, H_2O) (lit,[45] $[\alpha]_D^{22}$+162° (*c* 0.5, H_2O).

Found: C, 41.74; H, 6.57%. Calcd for $C_{18}H_{32}O_{16}\cdot H_2O$: C, 41.38; H, 6.71%.

***O*-β-D-Glucopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→2)-D-glucopyranose (150).** 69%, $[\alpha]_D$+69° (*c* 0.4, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot H_2O$) C, H.

***O*-α-D-Glucopyranosyl-(1→6)-*O*-α-D-glucopyranosyl-(1→2)-D-glucopyranose (151).** 58%, $[\alpha]_D$+148° (*c* 0.8, H_2O) (lit, $[\alpha]_D^{12}$+148° (*c* 1.8, H_2O),[46] $[\alpha]_D^{24}$+138° (H_2O)[47]).

Anal. ($C_{18}H_{32}O_{16}\cdot 1.5H_2O$) C, H.

***O*-β-D-Glucopyranosyl-(1→6)-*O*-α-D-glucopyranosyl-(1→2)-D-glucopyranose (152).** 82%, mp 173—176 °C, $[\alpha]_D$+60° (*c* 0.3, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot H_2O$) C, H.

***O*-β-D-Galactopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→2)-D-glucopyranose (153).** 81%, mp 184—198 °C (decomp), $[\alpha]_D$+64° (*c* 0.2, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot 0.5H_2O$) C, H.

***O*-α-D-Glucopyranosyl-(1→2)-*O*-α-D-glucopyranosyl-(1→3)-D-glucopyranose (154).** 58%, $[\alpha]_D$+162° (*c* 0.7, H_2O) (lit,[29] $[\alpha]_D^{21}$+159° (*c* 1.2, H_2O)).

Anal. ($C_{18}H_{32}O_{16}\cdot 0.5H_2O$) C, H.

***O*-β-D-Glucopyranosyl-(1→2)-*O*-β-D-glucopyranosyl-(1→3)-D-glucopyranose (155).** 72%, mp 164—165 °C (decomp), $[\alpha]_D$+13° (*c* 0.4, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot H_2O$) C, H.

***O*-α-D-Glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→3)-D-glucopyranose (156).** 50%, $[\alpha]_D$+178° (*c* 0.9, H_2O) (lit,[48] $[\alpha]_D^{27}$+182.7° (*c* 1.1, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot H_2O$) C, H.

***O*-β-D-Glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→3)-D-glucopyranose (157).** 84%, $[\alpha]_D$+59° (*c* 0.4, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot 1.5H_2O$) C, H.

***O*-α-D-Glucopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→3)-D-glucopyranose (158).** 59%, $[\alpha]_D$+152° (*c* 0.8, H_2O) (lit,[44] $[\alpha]_D$+149.4° (*c* 0.5, H_2O)).

Anal. ($C_{18}H_{32}O_{16}\cdot 0.5H_2O$) C, H.

***O*-β-D-Glucopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→3)-D-glucopyranose (159).** 79%, mp 154—156 °C, $[\alpha]_D$+71° (*c* 0.4, H_2O).

Found: C, 41.79; H, 6.70%. Calcd for $C_{18}H_{32}O_{16}\cdot 0.5H_2O$: C, 42.11; H, 6.48%.

***O*-α-D-Glucopyranosyl-(1→6)-*O*-α-D-glucopyranosyl-(1→3)-D-glucopyranose (160).** 66%, $[\alpha]_D$+151° (*c* 0.6, H_2O) (lit, $[\alpha]_D^{12}$+155° (*c* 0.7, H_2O),[46] $[\alpha]_D^{22}$+152° (*c* 2.0, H_2O)[49]).

Anal. ($C_{18}H_{32}O_{16}\cdot H_2O$) C, H.

***O*-β-D-Glucopyranosyl-(1→6)-*O*-α-D-glucopyranosyl-(1→3)-D-glucopyranose (161).** 78%, mp 179—183 °C, $[\alpha]_D$+67° (*c* 0. 2, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot H_2O$) C, H.

***O*-β-D-Galactopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→3)-D-glucopyranose (162).** 58%, mp 184—188 °C (decomp), $[\alpha]_D$+67° (*c* 0.3, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot H_2O$) C, H.

***O*-α-D-Glucopyranosyl-(1→2)-*O*-α-D-glucopyranosyl-(1→4)-D-glucopyranose (163).** 62%, mp 187—194 °C (decomp), $[\alpha]_D$+158° (*c* 0.8, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot 0.5H_2O$) C, H.

***O*-β-D-Glucopyranosyl-(1→2)-*O*-α-D-glucopyranosyl-(1→4)-D-glucopyranose (164).** 88%, mp 170—172 °C, $[\alpha]_D$−3° (*c* 0.5, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot H_2O$) C, H.

***O*-α-D-Glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→4)-D-glucopyranose (165).** 63%, $[\alpha]_D$+167° (*c* 1.1, H_2O) (lit,[50] $[\alpha]_D$+164° (*c* 1.1, H_2O)).

Anal. ($C_{18}H_{32}O_{16}\cdot 2.5H_2O$) C, H.

***O*-β-D-Glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→4)-D-glucopyranose (166).** 48%, $[\alpha]_D$+57° (*c* 0.3, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot 2H_2O$) C, H.

***O*-α-D-Glucopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→4)-D-glucopyranose (167).** 74%, $[\alpha]_D$+146° (*c* 0.7, H_2O) (lit,[51] $[\alpha]_D^{23}$+160° (*c* 2.36, H_2O)). The ^{13}CNMR spectrum (Table 3) agreed with that of commercial maltotriose (Tokyo Kasei Kogyo) as well as with the published data[52,53] (Found: C, 40.85; H, 6.55% ($C_{18}H_{32}O_{16}\cdot 1.5H_2O$)).

***O*-β-D-Glucopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-**

(1→4)-D-glucopyranose (168). 88%, mp 172—175 °C, $[\alpha]_D$+59° (*c* 0.4, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot 0.5H_2O$) C, H.

***O*-α-D-Glucopyranosyl-(1→6)-*O*-α-D-glucopyranosyl-(1→4)-D-glucopyranose (169).** 66%, mp 193—195 °C (decomp), $[\alpha]_D$+159° (*c* 0.9, H_2O) (lit, 221 °C (decomp),[54] 219—220 °C (decomp),[55] $[\alpha]_D^{20}$+161° (*c* 0.3, H_2O),[54] $[\alpha]_D^{20}$+162.1° (*c* 2.0, H_2O)[55]). The ^{13}C NMR spectrum (Table 3) agreed with the published data[52,53,56] (Found: C, 42.47; H, 6.83%).

***O*-β-D-Glucopyranosyl-(1→6)-*O*-α-D-glucopyranosyl-(1→4)-D-glucopyranose (170).** 53%, $[\alpha]_D$+83° (*c* 0.8, H_2O) (lit,[54] $[\alpha]_D$+70° (*c* 0.6, H_2O)).

Anal. ($C_{18}H_{32}O_{16}\cdot 2H_2O$) C, H.

***O*-β-D-Galactopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→4)-D-glucopyranose (171).** 67%, mp 198—206 °C (decomp) $[\alpha]_D$+75° (*c* 0.5, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot 0.5H_2O$) C, H.

***O*-α-D-Glucopyranosyl-(1→2)-*O*-α-D-glucopyranosyl-(1→6)-D-glucopyranose (172).** 48%, $[\alpha]_D$+142° (*c* 1.2, H_2O) (lit,[57] $[\alpha]_D$+150.5° (*c* 0.8, H_2O)). The ^{13}C NMR spectrum (Table 3) agreed with the published data.[57]

Anal. ($C_{18}H_{32}O_{16}\cdot 2.5H_2O$) C, H.

***O*-α-D-Glucopyranosyl-(1→2)-*O*-β-D-glucopyranosyl-(1→6)-D-glucopyranose (173).** 61%, $[\alpha]_D$+66° (*c* 0.4, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot H_2O$) C, H.

***O*-β-D-Glucopyranosyl-(1→2)-*O*-α-D-glucopyranosyl-(1→6)-D-glucopyranose (174).** 51%, $[\alpha]_D$+52° (*c* 0.5, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot 0.5H_2O$) C, H.

***O*-β-D-Glucopyranosyl-(1→2)-*O*-α-D-glucopyranosyl-(1→6)-D-glucopyranose (175).** 70%, $[\alpha]_D$−4° (*c* 0.8, H_2O) (lit,[42] $[\alpha]_D^{20}$−1° (*c* 0.8, H_2O)).

Anal. ($C_{18}H_{32}O_{16}\cdot H_2O$) C, H.

***O*-α-D-Glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→6)-D-glucopyranose (176).** 86%, $[\alpha]_D$+159° (*c* 1.4, H_2O) (lit,[49] $[\alpha]_D^{14}$+153° (*c* 2.5, H_2O)).

Anal. ($C_{18}H_{32}O_{16}\cdot 2H_2O$) C, H.

***O*-α-D-Glucopyranosyl-(1→3)-*O*-β-D-glucopyranosyl-(1→6)-D-glucopyranose (177).** 67%, $[\alpha]_D$+81° (*c* 0.2, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot H_2O$) C, H.

***O*-β-D-Glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→6)-D-glucopyranose (178).** 89%, mp 149—150 °C, $[\alpha]_D$+48° (*c* 0.5, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot 0.5H_2O$) C, H.

***O*-β-D-Glucopyranosyl-(1→3)-*O*-β-D-glucopyranosyl-(1→6)-D-glucopyranose (179).** 72%, mp 183—188 °C, $[\alpha]_D$−3° (*c* 0.6, H_2O) (lit,[58] mp 216—217 °C, $[\alpha]_D$−6° (H_2O)).

Anal. ($C_{18}H_{32}O_{16}\cdot 0.5H_2O$) C, H.

***O*-α-D-Glucopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→6)-D-glucopyranose (180).** 54%, $[\alpha]_D$+144° (*c* 0.9, H_2O) (lit, $[\alpha]_D^{20}$+128° (*c* 2, $CHCl_3$),[59] $[\alpha]_D$+136° (*c* 1.6, H_2O)[60]). The ^{13}C NMR data were coincident with those previously publisbed[52] (Found: C, 41.15; H, 6. 71% ($C_{18}H_{32}O_{16}\cdot H_2O$)).

***O*-α-D-Glucopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-D-glucopyranose (181).** 54%[α]$_D$+63° (*c* 0.7, H_2O) (lit,[61] $[\alpha]_D$+62° (*c* 1.2, H_2O)).

Anal. ($C_{18}H_{32}O_{16}\cdot 2H_2O$) C, H.

***O*-β-D-Glucopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→6)-D-glucopyranose (182).** 54%, mp 177—180 °C (decomp), $[\alpha]_D$+51° (*c* 0.4, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot 2.5H_2O$) C, H.

***O*-β-D-Glucopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-D-glucopyranose (183).** 72%, mp 239—244 °C (decomp), $[\alpha]_D$+8° (*c* 1.0, H_2O) (lit,[62] mp 247—252 °C (decomp), $[\alpha]_D^{22}$+15.0° (H_2O)) (Found:C, 42.44; H, 6.69%).

***O*-α-D-Glucopyranosyl-(1→6)-*O*-α-D-glucopyranosyl-(1→6)-D-glucopyranose (184).** 49%, $[\alpha]_D$+148° (*c* 1.3, H_2O) (lit, $[\alpha]_D^{25}$+144° (*c* 2.0, H_2O),[46] $[\alpha]_D^{25}$+145° (H_2O)[63]). The ^{13}C NMR spectrum (Table 3) was coincident with that of commercial isomaltotriose (Tokyo Kasei Kogyo) as well as that of the published data[64] (Found: C, 39.84; H, 6.52% ($C_{18}H_{32}O_{16}\cdot 2H_2O$)).

***O*-α-D-Glucopyranosyl-(1→6)-*O*-β-D-glucopyranosyl-(1→6)-D-glucopyranose (185).** 45%, $[\alpha]_D$+64° (*c* 0.6, H_2O) (lit,[46] $[\alpha]_D^{12}$+65° (*c* 1.8, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot H_2O$) C, H.

***O*-β-D-Glucopyranosyl-(1→6)-*O*-α-D-glucopyranosyl-(1→6)-D-glucopyranose (186).** 70%, $[\alpha]_D$+66° (*c* 1.0, H_2O) (lit,[65] $[\alpha]_D^{22}$+71.9° (*c* 1.1, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot 2H_2O$) C, H.

***O*-β-D-Glucopyranosyl-(1→6)-*O*-β-D-glucopyranosyl-(1→6)-D-glucopyranose (187).** 63%, mp 155—159 °C, $[\alpha]_D$−6° (*c* 0.6, H_2O) (lit,[66] mp 143—151 °C, $[\alpha]_D^{20}$−1.1° (*c* 0.9, H_2O)). The ^{13}C NMR spectrum (Table 3) was coincident with that of the published data[53,67] (Found: C, 40.04; H, 6.68% ($C_{18}H_{32}O_{16}\cdot 2H_2O$)).

***O*-β-D-Galactoyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→6)-D-glucopyranose (188).** 51%, mp 185—187 °C, $[\alpha]_D$+63° (*c* 0.7, H_2O).

Anal. ($C_{18}H_{32}O_{16}\cdot H_2O$) C, H.

***O*-β-D-Galactopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-D-glucopyranose (189).** 84%, mp 218—222 °C (decomp), $[\alpha]_D$+13° (*c* 0.7, H_2O) (lit,[62] mp 257 °C (decomp), $[\alpha]_D$+34.7° (H_2O)).

Anal. ($C_{18}H_{32}O_{16}\cdot 0.5H_2O$) C, H.

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