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2-Methoxyethyl Group for Protection of Reducing Hydroxyl Group of Aldose

Shinkiti KOTO,* Naohiko MORISHIMA,† Kazuhiro TAKENAKA, Kumi KANEMITSU, Noriko SHIMOURA, Miyuki KASE, Shizuko KOJIRO, Teiko NAKAMURA, Tomoko KAWASE, and Shonosuke ZEN
School of Pharmaceutical Sciences, Kitasato University, Shirokane, Minato-ku, Tokyo 108
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A variety of benzylated 1-OH derivatives, having an acetyl or an allyl group, of D-glucose, D-galactose, D-mannose, D-xylose, L-arabinose, L-fucose, and L-rhamnose, were synthesized from the corresponding protected 2-methoxyethyl glycosides through a brief treatment with $TiCl_4$ in dichloromethane and a subsequent hydrolysis of the intermediary 1-Cl derivatives on a silica-gel column.

Benzyl derivatives of aldose, whose reducing OH group is unprotected, are useful as a precursor of activated glycosyl donors in glycoside synthesis.[1] Under certain conditions,[2] such 1-OH derivatives can perform cross-condensation with alcohols as acceptors to give the corresponding glycosides. Several kinds of protecting groups for the reducing OH group have been proposed for the synthesis of 1-OH derivatives.[3] This report describes the 2-methoxyethyl (ME) group as a novel protecting group for the reducing OH group of aldose (Figs. 1 and 2).

Regeneration of the Reducing OH Group of the Protected 2-Methoxyethyl Glycosides. The isolation of a significant amount (22%) of the 1-OH derivative **4** in a study of rapid (4 s at room temp) anomerization of 2-benzyloxyethyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside with $TiCl_4$ in CH_2Cl_2 indicated that such a reaction could be useful in preparing **4** and similar compounds.[4] Later, a facile conversion of the glucoside **3** into the chloride **5** was observed upon its treatment with $TlCl_4$ in CH_2Cl_2 for 5 min at room temp.[5] The reaction mixture containing **5**, thus obtained, was adsorbed on a silica-gel column and eluted afterwards to give the hydrolyzate **4**.[5] The treatment of **3** with a slightly reduced amount (0.7 equiv) of $TiCl_4$ for 5 min at room temp was best for removing the ME group; **4** was obtained in a 66% yield. A longer reaction time and a larger quantity of the reagent diminished the yield of **4**, due to a concurrent formation of debenzylation products. A similar treatment of the α-anomer **8** with 1,2-cis disposition also afforded **4**, but required more reagent (1.0 equiv) to remove the ME group; thus the yield of **4** was low (41%). This procedure was then applied to the other 1,2-trans aldoside derivatives, **35**, **72**, **103**, **127**, **154**, and **181**, to produce the corresponding 1-OH derivatives, **36**, **73**, **104**, **128**, **155**, and **182**, in moderate yields.

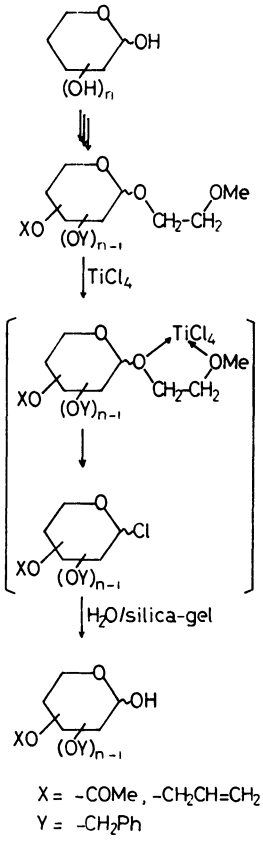


Fig. 1. General scheme.

The benzylated ME glycosides having one acetyl group, **10**, **16**, **23**, **28**, **38**, **49**, **59**, **66**, **75**, **80**, **81**, **98**, **106**, **119**, **129**, **141**, **145**, **156**, **168**, **172**, **183**, **191**, and **200**, and those having one allyl group, **13**, **18**, **25**, **30**, **41**, **51**, **61**, **68**, **78**, **84**, **95**, **100**, **109**, **112**, **121**, **132**, **143**, **147**, **159**, **170**, **174**, **186**, **193**, and **197**, were also converted into the corresponding 1-OH derivatives. The syntheses of the particular 1-OH derivatives, 3-*O*-acetyl-2,4-di-*O*-benzyl-D-xylopyranose[6] and 3-*O*-acetyl-2,4-di-*O*-benzyl-6-deoxy-D-glucopyranose,[7] have been reported before. They may be useful synthones for a linear portion of various oligosaccharides.

Preparation of Protected 2-Methoxyethyl Glycosides. The starting acetylated ME glycoside **33**, the precursor of **35** and **43**, was conveniently prepared from D-galactose (**32**) via a through-process of acetobromination with AcBr in AcOH[8] and a subsequent condensation with 2-methoxyethanol (MEOH) over Ag_2CO_3; the furanoside **34** was separated during chromatography. The fucoside acetate **152** was similarly synthesized from L-fucose (**151**) but L-arabinose (**123**) formed the furanoside **125** seriously;

† Present address: School of Nursing, Kitasato University, Kitasato, Sagamihara 228.

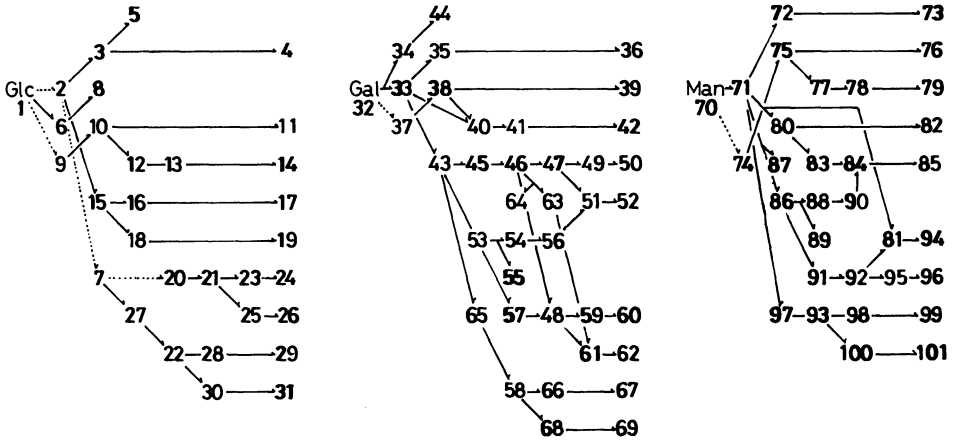


Fig. 2-i. Synthetic diagram.
(Broken arrows show known processes.)

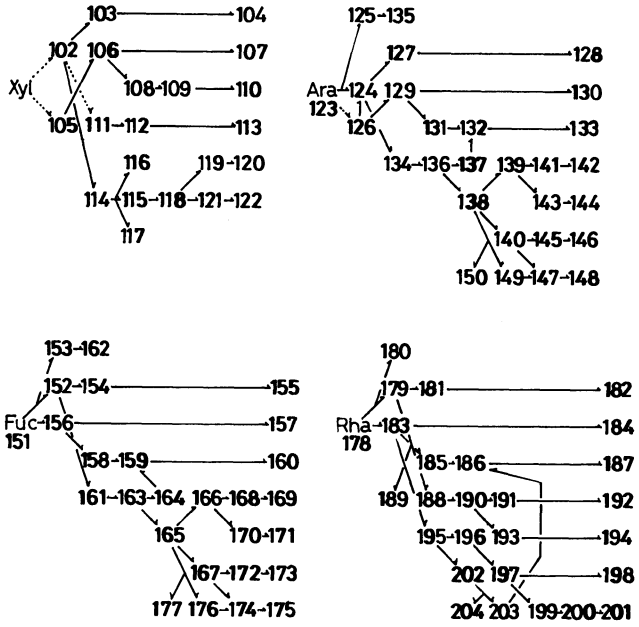
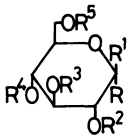


Fig. 2-ii. Synthetic diagram.
(Broken arrows show known processes.)



	R	R^1	R^2	R^3	R^4	R^5
1		H,OH	H	H	H	H
2	H	OME	Ac	Ac	Ac	Ac
3	H	OME	Bn	Bn	Bn	Bn
4		H,OH	Bn	Bn	Bn	Bn
5	Cl	H	Bn	Bn	Bn	Bn
6	OME	H	H	H	H	H
7	H	OME	H	H	H	H
8	OME	H	Bn	Bn	Bn	Bn
9	H	OAc	Ac	Ac	Ac	Ac
10	H	OME	Ac	Bn	Bn	Bn
11		H,OH	Ac	Bn	Bn	Bn
12	H	OME	H	Bn	Bn	Bn
13	H	OME	All	Bn	Bn	Bn
14		H,OH	All	Bn	Bn	Bn
15	H	OME	Bn	H	Bn	Bn
16	H	OME	Bn	Ac	Bn	Bn

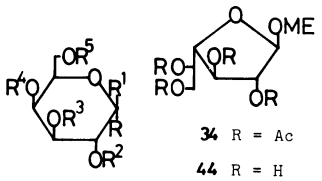
	R	R^1	R^2	R^3	R^4	R^5
17		H,OH	Bn	Ac	Bn	Bn
18	H	OME	Bn	All	Bn	Bn
19		H,OH	Bn	All	Bn	Bn
20	H	OME	Bn	Bn	H	H
21	H	OME	Bn	Bn	H	Bn
22	H	OME	Bn	Bn	Bn	H
23	H	OME	Bn	Bn	Ac	Bn
24		H,OH	Bn	Bn	Ac	Bn
25	H	OME	Bn	Bn	All	Bn
26		H,OH	Bn	Bn	All	Bn
27	H	OME	H	H	H	Tr
28	H	OME	Bn	Bn	Bn	Ac
29		H,OH	Bn	Bn	Bn	Ac
30	H	OME	Bn	Bn	Bn	All
31		H,OH	Bn	Bn	Bn	All

All = $-CH_2CH=CH_2$ ME = $-CH_2CH_2OMe$
Bn = $-CH_2Ph$ Bd = $=CH(Ph)$
Tr = $-CPh_3$ Ip = $=CMe_2$

CM = chloroform - methanol DME = 1,2-dimethoxyethane
HE = hexane - ethyl acetate DMP = 2,2-dimethoxypropane
TB = toluene - 2-butanone IPE = diisopropyl ether

the pyranoside **124** was eventually synthesized from the acetate **126**[9] via a convenient bromination using AcBr and H_2O in $CHCl_3$.[10] Methanolysis of the acetates **33**, **124**, and **152** afforded the starting ME glycosides, **43**, **134**, and **161**, respectively. The mannoside **71**, on the other hand, was prepared by a direct condensation of D-mannose (**70**) and MEOH in the presence of $MeSO_3H$. The rhamnoside **179** was similarly obtained.

The 2-acetate **10** prepared from the acetate **9** via a rearrangement of a benzylated orthoester[11] was converted into the 2-*O*-allyl ether **13** through deacetylation and allylation. Such a process was used for obtaining the other 2-acetates, **38**, **75**, **106**, **129**, **156**, and **183**, and the corresponding 2-*O*-allyl ethers, **41**, **78**, **109**, **132**, **159**, and **186**. In the case of **151** and **178**, peracetylation prior to the bromination as in the cases of the hexoses could be omitted, both were directly

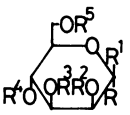


34 R = Ac

44 R = H

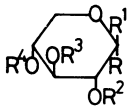
	R	R^1	R^2	R^3	R^4	R^5
32	H,OH	H	H	H	H	
33	H	OME	Ac	Ac	Ac	Ac
35	H	OME	Bn	Bn	Bn	Bn
36	H,OH	Bn	Bn	Bn	Bn	
37	H	OAc	Ac	Ac	Ac	Ac
38	H	OME	Ac	Bn	Bn	Bn
39	H,OH	Ac	Bn	Bn	Bn	
40	H	OME	H	Bn	Bn	Bn
41	H	OME	All	Bn	Bn	Bn
42	H,OH	All	Bn	Bn	Bn	
43	H	OME	H	H	H	H
45	H	OME	H	Ip		H
46	H	OME	Bn	H	H	Bn
47	H	OME	Bn	H	Bn	Bn
48	H	OME	Bn	Bn	H	Bn
49	H	OME	Bn	Ac	Bn	Bn
50	H,OH	Bn	Ac	Bn	Bn	
51	H	OME	Bn	All	Bn	Bn

	R	R^1	R^2	R^3	R^4	R^5
52	H,OH	Bn	All	Bn	Bn	
53	H	OME	H	H	Bd	
54	H	OME	H	All	Bd	
55	H	OME	All	H	Bd	
56	H	OME	Bn	All	H	H
57	H	OME	Bn	Bn	H	H
58	H	OME	Bn	Bn	Bn	H
59	H	OME	Bn	Bn	Ac	Bn
60	H,OH	Bn	Bn	Ac	Bn	
61	H	OME	Bn	Bn	All	Bn
62	H,OH	Bn	Bn	All	Bn	
63	H	OME	Bn	H	All	Bn
64	H	OME	Bn	All	H	Bn
65	H	OME	H	H	H	Tr
66	H	OME	Bn	Bn	Bn	Ac
67	H,OH	Bn	Bn	Bn	Ac	
68	H	OME	Bn	Bn	Bn	All
69	H,OH	Bn	Bn	Bn	All	



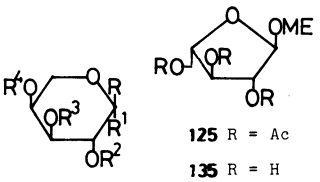
	R	R^1	R^2	R^3	R^4	R^5
70	H,OH	H	H	H	H	
71	OME	H	H	H	H	H
72	OME	H	Bn	Bn	Bn	Bn
73	H,OH	Bn	Bn	Bn	Bn	
74	OAc	H	Ac	Ac	Ac	Ac
75	OME	H	Ac	Bn	Bn	Bn
76	H,OH	Ac	Bn	Bn	Bn	
77	OME	H	H	Bn	Bn	Bn
78	OME	H	All	Bn	Bn	Bn
79	H,OH	All	Bn	Bn	Bn	
80	OME	H	Bn	Ac	Bn	Bn
81	OME	H	Bn	Bn	Ac	Bn
82	H,OH	Bn	Ac	Bn	Bn	
83	OME	H	Bn	H	Bn	Bn
84	OME	H	Bn	All	Bn	Bn
85	H,OH	Bn	All	Bn	Bn	

	R	R^1	R^2	R^3	R^4	R^5
86	OME	H	H	H	Bd	
87	OME	H	Bd		Ac	Ac
88	OME	H	H	All	Bd	
89	OME	H	All	H	Bd	
90	OME	H	Bn	All	H	H
91	OME	H	Bn	Bn	H	H
92	OME	H	Bn	Bn	H	Bn
93	OME	H	Bn	Bn	Bn	H
94	H,OH	Bn	Bn	Ac	Bn	
95	OME	H	Bn	Bn	All	Bn
96	H,OH	Bn	Bn	All	Bn	
97	OME	H	H	H	H	Tr
98	OME	H	Bn	Bn	Bn	Ac
99	H,OH	Bn	Bn	Bn	Ac	
100	OME	H	Bn	Bn	Bn	All
101	H,OH	Bn	Bn	Bn	All	



	R	R^1	R^2	R^3	R^4
102	H	OME	Ac	Ac	Ac
103	H	OME	Bn	Bn	Bn
104	H,OH	Bn	Bn	Bn	
105	H	OAc	Ac	Ac	Ac
106	H	OME	Ac	Bn	Bn
107	H,OH	Ac	Bn	Bn	
108	H	OME	H	Bn	Bn
109	H	OME	All	Bn	Bn
110	H,OH	All	Bn	Bn	
111	H	OME	Bn	H	Bn
112	H	OME	Bn	All	Bn

	R	R^1	R^2	R^3	R^4
113	H,OH	Bn	All	Bn	
114	H	OME	H	H	H
115	H	OME	H	H	Tr
116	H	OME	Tr	Ac	Ac
117	H	OME	Ac	Tr	Ac
118	H	OME	Bn	Bn	H
119	H	OME	Bn	Bn	Ac
120	H,OH	Bn	Bn	Ac	
121	H	OME	Bn	Bn	All
122	H,OH	Bn	Bn	All	



125 R = Ac

135 R = H

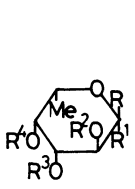
	R	R^1	R^2	R^3	R^4
123	H,OH	H	H	H	
124	OME	H	Ac	Ac	Ac
126	OAc	H	Ac	Ac	Ac
127	OME	H	Bn	Bn	Bn
128	H,OH	Bn	Bn	Bn	
129	OME	H	Ac	Bn	Bn
130	H,OH	Ac	Bn	Bn	
131	OME	H	H	Bn	Bn
132	OME	H	All	Bn	Bn
133	H,OH	All	Bn	Bn	
134	OME	H	H	H	H
136	OME	H	H	Ip	
137	OME	H	All	H	H

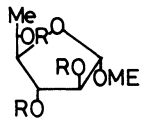
	R	R^1	R^2	R^3	R^4
138	OME	H	Bn	H	H
139	OME	H	Bn	H	Bn
140	OME	H	Bn	Bn	H
141	OME	H	Bn	Ac	Bn
142	H,OH	Bn	Ac	Bn	
143	OME	H	Bn	All	Bn
144	H,OH	Bn	All	Bn	
145	OME	H	Bn	Bn	Ac
146	H,OH	Bn	Bn	Ac	
147	OME	H	Bn	Bn	All
148	H,OH	Bn	Bn	All	
149	OME	H	Bn	H	All
150	OME	H	Bn	All	H

transformed into the 2-acetates, **156** and **183**, respectively.

Kinetic benzylation of the diol **20**[7] mainly gave the 4-OH compound **21**, the precursor **23** and **25**. A similar method was appled to the diols, **57** and **91**, obtained from the acetals, **53** and **86**, for preparing the 4-OH derivatives, **48** and **92**, which were then changed into the corresponding acetates, **59** and **81**, and the allyl ehers, **61** and **95**.

The 6-OH compound **22** obtained through conventional tritylation of the glucoside **7**[12] was derived into the acetate **28** and the allyl ether **30**. A similar process was applied to **43** and **71** to synthesize the other 6-OH

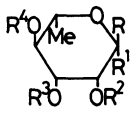




153 R = Ac
162 R = H

	R	R^1	R^2	R^3	R^4
151		H,OH	H	H	H
152	H	OME	Ac	Ac	Ac
154	H	OME	Bn	Bn	Bn
155		H,OH	Bn	Bn	Bn
156	H	OME	Ac	Bn	Bn
157		H,OH	Ac	Bn	Bn
158	H	OME	H	Bn	Bn
159	H	OME	All	Bn	Bn
160		H,OH	All	Bn	Bn
161	H	OME	H	H	H
163	H	OME	H	Ip	
164	H	OME	All	H	H
165	H	OME	Bn	H	H

	R	R^1	R^2	R^3	R^4
166	H	OME	Bn	H	Bn
167	H	OME	Bn	Bn	H
168	H	OME	Bn	Ac	Bn
169		H,OH	Bn	Ac	Bn
170	H	OME	Bn	All	Bn
171		H,OH	Bn	All	Bn
172	H	OME	Bn	Bn	Ac
173		H,OH	Bn	Bn	Ac
174	H	OME	Bn	Bn	All
175		H,OH	Bn	Bn	All
176	H	OME	Bn	H	All
177	H	OME	Bn	All	H



	R	R^1	R^2	R^3	R^4
178		H,OH	H	H	H
179	OME	H	H	H	H
180	H	OME	H	H	H
181	OME	H	Bn	Bn	Bn
182		H,OH	Bn	Bn	Bn
183	OME	H	Ac	Bn	Bn
184		H,OH	Ac	Bn	Bn
185	OME	H	H	Bn	Bn
186	OME	H	All	Bn	Bn
187		H,OH	All	Bn	Bn
188	OME	H	H	Tr	H
189	OME	H	Ac	Ac	Tr
190	OME	H	Bn	H	Bn
191	OME	H	Bn	Ac	Bn

	R	R^1	R^2	R^3	R^4
192		H,OH	Bn	Ac	Bn
193	OME	H	Bn	All	Bn
194		H,OH	Bn	All	Bn
195	OME	H	Ip		H
196	OME	H	H	H	All
197	OME	H	Bn	Bn	All
198		H,OH	Bn	Bn	All
199	OME	H	Bn	Bn	H
200	OME	H	Bn	Bn	Ac
201		H,OH	Bn	Bn	Ac
202	OME	H	H	H	Bn
203	OME	H	All	H	Bn
204	OME	H	H	All	Bn

Table 1. ^{1}H NMR Data (Chemical Shifts (δ) and Coupling Constants (Hz)) of Monoacetate of 2-Methoxyethyl Aldoside Derivatives

Compd	H-1	$J_{1,2}$	H-2	$J_{2,3}$	H-3	$J_{3,4}$	H-4	$J_{4,5}$	H-5	$J_{5,6a}$	$J_{5,6b}$	H-6a	$J_{6a,6b}$	H-6b	OMe	OAc
10	4.56	8	*5.20*	9	3.68	9	—		—			—		—	3.36	1.98
16	4.50	8	3.35	9.5	*5.21*	9.5	3.62	9.5	3.50	2.5	3.5	3.72	10.5	3.70	3.39	1.86
23	4.48	7.5	3.52	9	—	9.5	*4.96*	9.5	—			—		—	3.39	1.84
28	4.46	7.5	3.48	9	—		—		—	1.5	4.5	*4.35*	12	*4.20*	3.39	2.04
38	4.45	8	*5.41*	10	—	3	3.98	0	—			—		—	3.35	2.06
49	4.47	8	3.78	10.5	*4.89*	3	3.95	1	—			—		—	3.37	1.91
59	4.44	7	3.52	10	—	3	*5.58*	1	—			—		—	3.38	2.08
66	4.42	7.5	3.87	10	3.54	2.5	3.79	0	—	6.5	6	*4.23*	11	*4.07*	3.39	1.97
75	4.91	2	*5.46*	3.5	4.04	8.5	—		—			—		—	3.36	2.12
80	4.92	2.5	3.85	4	*5.26*	9	4.04	9	—	4	2	3.79	10	3.70	3.35	1.95
81	4.92	1.5	—		—	10	*5.39*	10	—			—		—	3.36	1.93
98	4.91	2	3.89	3	3.97	9	3.93	10	3.83	4	4	*4.30*	12	*4.32*	3.35	2.06

Table 1. (Continued)

Compd	H-1	$J_{1,2}$	H-2	$J_{2,3}$	H-3	$J_{3,4}$	H-4	$J_{4,5a}$	$J_{4,5b}$	H-5a	$J_{5a,5b}$	H-5b	OMe	OAc
106	4.41	7.5	*4.94*	9.5	3.59	9.5	—	4.5	9	3.99	11	3.26	3.34	1.98
119	4.45	7	3.49	9	3.61	9	*4.91*	5.5	9	4.04	11	3.19	3.39	1.96
129	4.47	5	*5.29*	7.5	3.60	3	3.73	5	2	3.99	12	3.38	3.35	2.05
141	4.47	6	3.79	8	*4.95*	4	3.84	2.5	2	4.02	12.5	3.44	3.38	2.03
145	4.36	7.5	3.68	9.5	3.56	4	*5.28*	2	1.5	4.00	13.5	3.48	3.39	2.15

Compd	H-1	$J_{1,2}$	H-2	$J_{2,3}$	H-3	$J_{3,4}$	H-4	$J_{4,5}$	H-5	$J_{5,6}$	H-6	OMe	OAc
156	4.40	8	*5.36*	10	3.53	3	3.61	1.5	3.49	6.5	1.23	3.34	2.04
168	4.44	7.5	3.77	10.5	*4.87*	3	3.66	1	3.61	6.5	1.22	3.37	1.93
172	4.42	7.5	—	10	3.56	3.5	*5.33*	1	3.65	6.5	1.22	3.38	2.17
183	4.79	2	*5.46*	4	3.99	10	3.46	10	—	6.5	1.35	3.38	2.16
191	4.80	2	3.89	3.5	*5.22*	10	3.62	10	3.80	6	1.33	3.36	1.96
200	4.82	2	3.86	3	3.80	10	*5.22*	10	—	6.5	1.20	3.36	2.02

Table 2. ^{1}H NMR Data (Chemical Shifts (δ) and Coupling Constants (Hz) of Monoacetate of 1-OH Aldose Derivatives

Compd	H-1	$J_{1,2}$	H-2	$J_{2,3}$	H-3	$J_{3,4}$	H-4	$J_{4,5}$	H-5	$J_{5,6a}$	$J_{5,6b}$	H-6a	$J_{6a,6b}$	H-6b	OAc
17α	5.24	4	3.51	10	*5.44*	9.5	—		—			—		—	1.93
17β	4.69	8	3.30	10	*5.21*	9.5	—		—			—		—	1.87
24α	5.20	3.5	—	9.5	3.94	9.5	*5.00*	10	4.10	3.5	5	—		—	1.87
24β	4.72	7.5	—		—	9.5	*4.96*	9.5	—			—		—	1.86
39α	4.57	4	*5.34*	10	3.98	3	—		—	6	6	3.57	9	3.47	2.07
39β	—	8	*5.18*	10	3.57	3	—		—			—		—	2.08
50α	5.31	3.5	4.00	10.5	*5.25*	3	4.03	1	4.29	6.5	6.5	—		—	1.97
50β	4.73	7.5	3.73	10	*4.90*	3	3.95	1	—			—		—	1.92

Table 2. (Continued)

Compd	H-1	$J_{1,2}$	H-2	$J_{2,3}$	H-3	$J_{3,4}$	H-4	$J_{4,5}$	H-5	$J_{5,6a}$	$J_{5,6b}$	H-6a	$J_{6a,6b}$	H-6b	OAc
60α	5.28	4	3.77	10	3.94	3.5	*5.61*	1	4.33	6.5	6.5	—		—	2.06
60β	4.68	7.5	—		—	3	*5.54*	1	3.74	6.5	6.5	—		—	2.09
67α	5.29	4	4.05	10	3.92	3	3.89	1	—			—		—	1.99
67β	4.64	7.5	3.79	9	3.56	3	3.81	1.5	3.61	7	5.5	*4.19*	11	—	1.99
76α	5.22	2	*5.37*	4	4.04	9.5	3.74	10	—			—		—	2.15
76β	—		—		—		—		—			—		—	2.21
82α	5.26	1.5	3.88	3.5	*5.31*	9.5	—	10	4.10	6	3	—		—	1.97
82β	4.77	1.5	3.93	3	*4.97*	10	—	10	3.49	2.5	4.5	—		—	1.95
94α	5.24	2	3.78	3	3.87	10.5	*5.28*	10.5	4.07	7.5	2.5	3.61	10.5	3.48	1.92
94β	—	1.5	3.83	3	—	9	*5.33*	9	—			—		—	1.92
99α	5.25	2	3.82	3	3.99	9	3.95	9	4.03	2	5	*4.39*	12	*4.26*	2.05
99β	—	1.5	3.87	3	3.65	10	3.85	10	3.51	2.5	6	*4.37*	12	*4.24*	2.04

Compd	H-1	$J_{1,2}$	H-2	$J_{2,3}$	H-3	$J_{3,4}$	H-4	$J_{4,5a}$	$J_{4,5b}$	H-5a	$J_{5a,5b}$	H-5b	OAc
107α	5.31	4	*4.80*	10	3.96	9	—			—		—	2.05
107β	—		—		—		—			—		—	2.03
120α	5.10	3	3.52	7.5	3.91	7.5	—			—		—	2.00
120β	—	5.5	3.40	7.5	3.70	7.5	*4.90*	4.5	7.5	4.12	12	3.36	2.00
130α	4.75	3	*5.25*	9	—		—			—		—	2.10
130β	5.40	3	*5.05*	6	—		—	8	4	4.08	11.5	3.63	2.07
142α	4.74	5.5	3.73	8.5	*5.01*	3.5	—	4.5	2	4.02	13	3.50	2.04
142β	5.15	2.5	3.84	8	*5.31*	3.5	—	2.5	5	3.93	12	3.72	2.07
146α	—		—		—		—			—		—	2.12
146β	5.23	4	3.95	9	3.78	4	*5.34*	2	4	4.03	13	3.72	2.13

Table 2. (Continued)

Compd	H-1	$J_{1,2}$	H-2	$J_{2,3}$	H-3	$J_{3,4}$	H-4	$J_{4,5}$	H-5	$J_{5,6}$	H-6	OAc
157α	5.46	4	*5.35*	10.5	3.99	3	3.90	0	4.14	6.5	1.16	2.10
157β	4.49	8	*5.18*	10	3.59	3	3.63	1	3.55	6.5	1.23	2.10
169α	5.29	4	4.01	10.5	*5.24*	3	3.76	1	4.23	6.5	1.17	1.98
169β	—	8	3.72	10.5	*4.88*	3.5	3.69	1	3.66	6.5	1.23	1.94
173α	5.25	4	3.78	10	3.93	3.5	*5.41*	1	4.27	6.5	1.15	2.10
173β	4.12	7.5	3.53	10	3.59	3	*5.34*	1	3.68	6.5	1.22	2.18
184α	5.13	2	*5.39*	3.5	4.01	10	3.45	10	—	6	1.32	2.16
184β	—	1.5	*5.53*	3.5	3.63	9	—	—	—	6	1.36	2.22
192α	5.16	2	3.89	3.5	*5.26*	10	3.64	10	4.02	6	1.33	1.97
192β	—	1.5	3.95	3	*4.96*	10	3.60	10.5	3.44	6	1.36	1.98
201α	5.20	2	3.81	3	3.85	9.5	*5.23*	9.5	3.96	6.5	1.20	2.03
201β	—		—	3	3.54	10	*5.17*	10	3.40	6.5	1.22	2.05

compounds **58** and **93**, and their derivatives, **66**, **68**, **98**, and **100**.

The diol **46** obtained through isopropylidenation of **43** was selectively benzylated with $PhCH_2Cl$ and KOH in 1,2-dimethoxyethane (DME) to furnish the 3-OH derivative **47**, the precursor of **49** and **51**. Such mild benzylation was useful in the monobenzylation of the diols, **138**, **165**, and **202**, which were derived from the corresponding acetals, **136**, **163**, and **195**, to give **139**, **166**, and **190**, respectively. A similar reaction using allyl bromide instead of $PhCH_2Cl$ worked well in the synthesis of the monoallyl ethers, **63**, **149**, **176**, and **203**, from the correspoinding diols, **46**, **138**, **165**, and **202**. This kinetic allylation was usefully applied to the acetals, **53** and **86**, to synthesize the monoallyl ethers, **54** and **88**, the precursors of **51** and **84**, respectively. The kinetic benzylation using $PhCH_2Cl$ and LiOH[13] for the diols, **138** and **165**, mainly afforded the 4-OH derivatives, **140** and **167**, respectively.

A controlled reaction of the acetate **2** with $PhCH_2Cl$ in the presence of a limited amount of NaOH mainly gave the 3-OH compound **15** (ca. 40%), the precursor of **16** and **18**. A similar reaction of the acetate **33**, but using DME as diluent, afforded the 2-OH derivative **40** (ca. 25%) as the main product. A kinetic benzylation of **71** with $PhCH_2Cl$ and KOH, followed by acetylation and chromatography, mainly furnished the 3-acetate **80** (35%), whereas the use of LiOH instead of KOH brought forth a preferential formation of the 4-acetate **81** (25%).[11]

Tritylation[14] of the xyloside **114** mainly gave the 4-*O*-trityl ether **115** (25%), the precursor of the 4-OH compound **118**, whereas the rhamnoside **179** formed the 3-*O*-substituted glycoside **188** (51%), the precursor of the 3-OH derivative **190**.

The 4-*O*-acetyl derivative **200** was prepared throgh deallylation and reacetylation of the 4-*O*-allyl ether **197**, which was readily obtained from the acetal **195**. The acetals, **136** and **163**, provided alternative routes to the 2-*O*-allyl derivatives, **132** and **159**, respectively.

All the structures of the derivatives of the ME glycosides are to be evident, since the ^1H NMR spectra of the monoacetates were consistently assigned; every proton on the carbon bearing OAc group definitely deshielded (Tables 1 and 2).

Thus, the ME group is considered to be an alternative choice for the protection of the hemiacetal OH group of aldose.[3] In the preparation of various derivarives of the ME glycosides, several kinetic substitutions of the polyols[15] (Fig. 3) were usefully carried out. The ME glycoside derivatives in which one OH group remains unprotected might be of use as

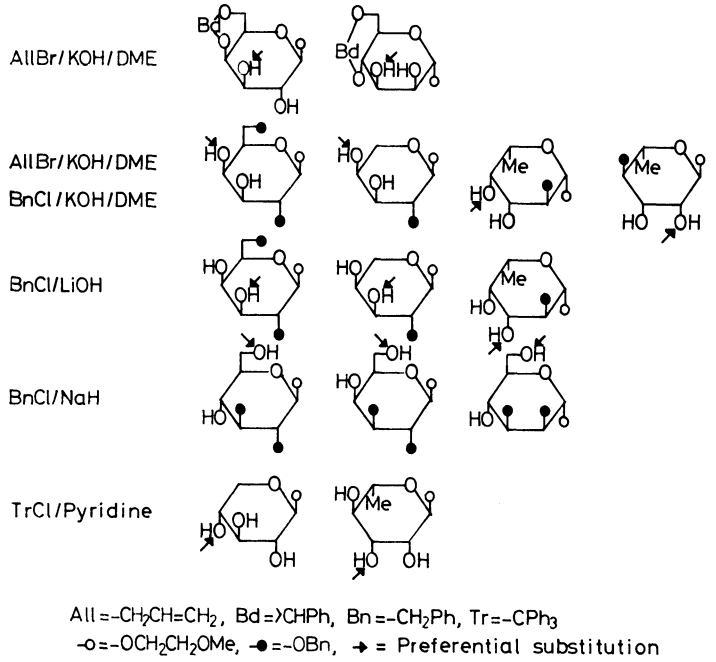


Fig. 3. Kinetic substitution of polyols.

acceptors in oligosaccharide synthesis.

Experimental

The ^{1}H NMR spectra were measured with a Varian VXR-300 spectrometer. The optical rotations were measured at room temp (20—25 °C). The other items were described previously.[16]

The aldoses used were the products of Wako Pure Chemicals Industries, Ltd., whereas the hexose acetates, **9**, **37**, and **74**, were available from Kyowa Pure Chemicals Industries, Ltd.

Synthesis of 1-OH Derivatives. To a stirring solution of a well-dried, protected 2-methoxyethyl aldoside (0.1—2 mmol) in dry CH_2Cl_2 (10 ml mmol^{-1} of substrate) was added $TiCl_4$ (0.7 equiv) at room temp to give a colored (pale yellow to reddish brown) solution. After 5 min, iced H_2O and then toluene were added to the solution. The organic layer was washed well with H_2O and dried over Na_2SO_4 briefly. After evaporation, the residue was adsorbed on a column of silica gel (40 g/g of substrate). After standing overnight, the column was eluted with toluene–2-butanone (TB) system (gradient) to give the corresponding 1-OH derivative. Compounds **4**[17] (66% from **3** and 41% from **8** (1.0 equiv of $TiCl_4$)), **11**[10] (77%), **29**[18] (76%), **36**[17] (74%), **73**[17] (66%), **85**[11] (70%), **96**[11] (67%), and **113**[6] (70%) were identified with the respective compounds prepared before.

2-*O*-Allyl-3,4,6-tri-*O*-benzyl-D-glucopyranose (**14**). 70%, mp 136—137 °C (from diisopropyl ether (IPE)), $[\alpha]_D$ +25° (*c* 0.4, $CHCl_3$) (lit,[19] mp 137—139 °C, $[\alpha]_D$ +25.7° ($CHCl_3$)) (Found: C, 73.37; H, 7.00%).

3-*O*-Acetyl-2,4,6-tri-*O*-benzyl-D-glucopyranose (**17**). 60%, mp 124—126 °C (from IPE), $[\alpha]_D$ +42° (*c* 1.4, $CHCl_3$)

Anal. ($C_{29}H_{32}O_7$) C, H.

3-*O*-Allyl-2,4,6-tri-*O*-benzyl-D-glucopyranose (**19**). 62%, mp 115—116 °C (from IPE), $[\alpha]_D$ +30° (*c* 1.0, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ=3.52 (dd, $J_{1,2}$=3.5 Hz, $J_{2,3}$=10 Hz, H-2α), 3.82 (dd, $J_{3,4}$=9 Hz, H-3α), 5.20 (H-1α), 6.00 (m, allyl).

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

4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-D-glucopyranose (**24**). 63% mp 118—119 °C (from IPE), $[\alpha]_D$ +13° (*c* 0.6, $CHCl_3$) (lit,[20] 111—112 °C, $[\alpha]_D$ +9.4° ($CHCl_3$)) (Found: C, 70.66; H, 6.57%).

4-*O*-Allyl-2,3,6-tri-*O*-benzyl-D-glucopyranose (**26**). 62%, mp 108—110 °C (from IPE), $[\alpha]_D$ +35° (*c* 2.0, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ=3.36 (dd, $J_{1,2}$=7.5 Hz, $J_{2,3}$=9 Hz, H-1β), 3.54 (dd, $J_{1,2}$=3.5 Hz, $J_{2,3}$=9.5 Hz, H-2α), 3.90 (dd, $J_{3,4}$=9 Hz, H-3α), 5.21 (H-1α), 5.81 (m, allyl).

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

6-*O*-Allyl-2,3,4-tri-*O*-benzyl-D-glucopyranose (**31**). 66%, mp 133—135 °C (from IPE), $[\alpha]_D$ +13° (*c* 2.0, $CHCl_3$) (lit,[21] mp 132—134 °C, $[\alpha]_D$ +11.7° ($CHCl_3$)) (Found: C, 73.51; H, 7.01%).

2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-D-galactopyranose (**39**). 56%, $[\alpha]_D$ +43° (*c* 1.7, $CHCl_3$) (lit,[22] $[\alpha]_D$ +45° ($CHCl_3$)) (Found: C, 70.45; H, 6.50%).

2-*O*-Allyl-3,4,6-tri-*O*-benzyl-D-galactopyranose (**42**). 76%, mp 88—90 °C (from hexane), $[\alpha]_D$ +16° (*c* 1.5, $CHCl_3$) (lit,[23] mp 90—92 °C, $[\alpha]_D$ +19.4° ($CHCl_3$)), ^{1}H NMR ($CDCl_3$) δ=3.48 (dd, $J_{2,3}$=9 Hz, $J_{3,4}$=2.5 Hz, H-3β), 3.64 (dd, $J_{1,2}$=7 Hz, H-2β), 3.85 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=3 Hz, H-3α), 3.96 (dd, $J_{1,2}$=4 Hz, H-2α), 4.61 (d, H-1β), 5.36 (d, H-1α), 5.93 (m, allyl) (Found: C, 73.23; H, 7.00%).

3-*O*-Acetyl-2,4,6-tri-*O*-benzyl-D-galactopyranose (**50**). 68%, $[\alpha]_D$ +56° (*c* 3.0, $CHCl_3$).

Anal. ($C_{29}H_{32}O_7$) C, H.

3-*O*-Allyl-2,4,6-tri-*O*-benzyl-D-galactopyranose (**52**). 64%, $[\alpha]_D$ +8° (*c* 2.8, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ=3.44 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=3 Hz, H-3β), 3.70 (dd, $J_{1,2}$=8 Hz, $J_{2,3}$=10 Hz, H-2β), 3.80 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=3 Hz, H-3α), 3.86 (d, $J_{4,5}$=0 Hz, H-4β), 3.93 (dd, $J_{4,5}$=1 Hz, H-4α), 3.98 (dd, $J_{1,2}$=4 Hz, H-2α), 4.10 (m, $J_{5,6a}$=$J_{5,6b}$=6.5 Hz, H-5α), 4.64 (d,

H-1β), 5.25 (d, H-1α).

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

4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-D-galactopyranose (**60**). 53%, $[\alpha]_D$ +26° (*c* 1.5 $CHCl_3$).

Found: C, 70.21; H, 6.54%. Calcd for $C_{29}H_{32}O_7$: C, 70.71; H, 6.55%.

4-*O*-Allyl-2,3,6-tri-*O*-benzyl-D-galactopyranose (**62**). 60%, mp 91—93 °C (from hexane), $[\alpha]_D$ +18° (*c* 1.4, $CHCl_3$) (lit,[24] mp 95—96 °C, $[\alpha]_D$ +19.3° ($CHCl_3$)), ^1H NMR ($CDCl_3$) δ=3.49 (dd, $J_{2,3}$=9.5 Hz, $J_{3,4}$=3 Hz, H-3β), 3.70 (dd, $J_{1,2}$=8 Hz, $J_{2,3}$=9.5 Hz, H-2β), 3.98 (dd, $J_{1,2}$=3.5 Hz, $J_{2,3}$=9.5 Hz, H-2α), 4.64 (d, H-1β), 5.27 (d, H-1α), 5.89 (m, allyl) (Found: C, 73.17; H, 7.00%).

6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-D-galactopyranose (**67**). 43%, mp 81—82 °C, $[\alpha]_D$ +7° (*c* 0.5, $CHCl_3$) (lit,[25] $[\alpha]_D$ +14° ($CHCl_3$)) (Found: C, 70.93; H, 6.89%).

6-*O*-Allyl-2,3,4-tri-*O*-benzyl-D-galactopyranose (**69**). 34%, $[\alpha]_D$ +19° (*c* 0.3, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.77 (dd, $J_{1,2}$= 7.5 Hz, $J_{2,3}$=9.5 Hz, H-2β), 3.91 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=2.5 Hz, H-3α), 3.97 (dd, $J_{4,5}$=1 Hz, H-4α), 4.04 (dd, $J_{1,2}$=3.5 Hz, H-2α), 4.14 (m, $J_{5,6a}$=$J_{5,6b}$=6.5 Hz, H-5α), 4.67 (d, H-1β), 5.29 (d, H-1α), 5.85 (m, allyl).

Found: C, 73.11; H, 6.85%. Calcd for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99%.

2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-D-mannopyranose (**76**). 54%, $[\alpha]_D$ +6° (*c* 1.1, $CHCl_3$) (lit,[26] $[\alpha]_D$ +10.2° ($CHCl_3$)) (Found: C, 70.47; H, 6.56%).

2-*O*-Allyl-3,4,6-tri-*O*-benzyl-D-mannopyranose (**79**). 66%, $[\alpha]_D$ +23° (*c* 0.9, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.57 (dd, $J_{2,3}$=3 Hz, $J_{3,4}$=10.5 Hz, H-3β), 3.64 (dd, $J_{5,6b}$=2 Hz, $J_{6a,6b}$= 10.5 Hz, H-6bα), 3.76 (dd, $J_{1,2}$=2 Hz, $J_{2,3}$=3 Hz, H-2α), 3.71 (dd, $J_{5,6a}$=6.5 Hz, H-6aα), 3.78 (dd, $J_{3,4}$=9 Hz, $J_{4,5}$=10 Hz, H-4α), 3.88 (dd, $J_{4,5}$=9 Hz, H-4β), 3.95 (dd, H-3α), 4.33 (m, H-5α), 5.25 (d, H-1α).

Found: C, 72.97; H, 7.10%. Calcd for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99%.

3-*O*-Acetyl-2,4,6-tri-*O*-benzyl-D-mannopyranose (**82**). 70%, $[\alpha]_D$ −8° (*c* 1.0, $CHCl_3$)

Anal. ($C_{29}H_{32}O_7$) C, H.

4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-D-mannopyranose (**94**). 78%, $[\alpha]_D$ +1.3° (*c* 0.5, $CHCl_3$).

Anal. ($C_{29}H_{32}O_7$) C, H.

6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-D-mannopyranose (**99**). 59%, $[\alpha]_D$ +23° (*c* 0.8, $CHCl_3$).

Found: C, 70.24; H, 6.53%. Calcd for $C_{29}H_{32}O_7$: C, 70.71; H, 6.55%.

6-*O*-Allyl-2,3,4-tri-*O*-benzyl-D-mannopyranose (**101**). 74%, $[\alpha]_D$ +20° (*c* 0.5, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.44 (m, $J_{4,5}$=10 Hz, $J_{5,6}$=2.5 and 4.5 Hz, H-5β), 3.63 (dd, $J_{2,3}$=2.5 Hz, $J_{3,4}$=10 Hz, H-3β), 3.81 (dd, $J_{1,2}$=2 Hz, $J_{2,3}$=3 Hz, H-2α), 3.86 (t, $J_{3,4}$=$J_{4,5}$=9.5 Hz, H-4α), 3.94 (t, H-4β), 3.98 (dd, H-3α), 5.26 (d, H-1α), 5.90 (m, allyl).

Found: C, 73.01; H, 7.05%. Calcd for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99%.

2,3,4-Tri-*O*-benzyl-D-xylopyranose (**104**). 80%, mp 138—139 °C (from IPE), $[\alpha]_D$ +15° (*c* 2.0, $CHCl_3$) (lit,[27] 130—131 °C, $[\alpha]_D$ +25.1° (CH_2Cl_2)) (Found: C, 74.02; H, 6.74%).

2-*O*-Acetyl-3,4-di-*O*-benzyl-D-xylopyranose (**107**). 51%, $[\alpha]_D$ +30° (*c* 0.8, $CHCl_3$).

Anal. ($C_{21}H_{24}O_6$) C, H.

2-*O*-Allyl-3,4-di-*O*-benzyl-D-xylopyranose (**110**). 71%, mp 56—58 °C, $[\alpha]_D$ +9° (*c* 0.8, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.21 (dd, $J_{1,2}$=7.5 Hz, $J_{2,3}$=9 Hz, H-2β), 3.26 (dd, $J_{4,5ax}$=10 Hz, $J_{5eq,5ax}$=11.5 Hz, H-5axβ), 3.42 (dd, $J_{1,2}$=4 Hz, $J_{2,3}$=9 Hz, H-2α), 3.68 (dd, $J_{4,5eq}$=5 Hz, $J_{5eq,5ax}$=11 Hz, H-5eqα), 3.84 (dd, $J_{4,5eq}$=4.5 Hz, H-5eqβ), 5.94 (m, allyl).

Found: C, 71.81; H, 6.99%. Calcd for $C_{22}H_{26}O_5$: C, 71.33; H, 7.07%.

4-*O*-Acetyl-2,3-di-*O*-benzyl-D-xylopyranose (**120**). 78%, $[\alpha]_D$ −4° (*c* 0.7, $CHCl_3$)

Found: C, 67.26; H, 6.48%. Calcd for $C_{21}H_{24}O_6$: C, 67.73; H, 6.50%.

4-*O*-Allyl-2,3-di-*O*-benzyl-D-xylopyranose (**122**). 56%, mp 49—51 °C, $[\alpha]_D$ +6° (*c* 0.6, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.25 (dd, $J_{4,5ax}$=10 Hz, $J_{5eq,5ax}$=12 Hz, H-5axβ), 3.30 (dd, $J_{1,2}$=7 Hz, $J_{2,3}$=9 Hz, H-2β), 3.47 (dd, $J_{1,2}$=4 Hz, $J_{2,3}$=9 Hz, H-2α), 3.82 (t, $J_{3,4}$=9 Hz, H-3α), 4.00 (dd, $J_{4,5eq}$=4.5 Hz, H-5eqβ), 4.65 (d, H-1β), 5.12 (d, H-1α), 5.90 (m, allyl).

Anal. ($C_{22}H_{26}O_5$) C, H.

2,3,4-Tri-*O*-benzyl-L-arabinopyranose (**128**). 71%, mp 76—81 °C (from hexane), $[\alpha]_D$ +36° (*c* 1.4, $CHCl_3$) (lit,[28] mp 83—86 °C, $[\alpha]_D$ +51.1° (CH_2Cl_2)) (Found: C, 74.04; H, 6.75%).

2-*O*-Acetyl-3,4-di-*O*-benzyl-L-arabinopyranose (**130**). 48%, $[\alpha]_D$ +60° (*c* 0.3, $CHCl_3$)

Anal. ($C_{21}H_{24}O_6$) C, H.

2-*O*-Allyl-3,4-di-*O*-benzyl-L-arabinopyranose (**133**). 51%, $[\alpha]_D$ +31° (*c* 0.3, $CHCl_3$).

Found: C, 71.80; H, 7.24%. Calcd for $C_{22}H_{26}O_5$: C, 71.33; H, 7.07%.

3-*O*-Acetyl-2,4-di-*O*-benzyl-L-arabinopyranose (**142**). 63%, $[\alpha]_D$ +67° (*c* 0.9, $CHCl_3$).

Anal. ($C_{21}H_{24}O_6$) C, H.

3-*O*-Allyl-2,4-di-*O*-benzyl-L-arbinopyranose (**144**). 60%, $[\alpha]_D$ +24° (*c* 0.8, $CHCl_3$)

Anal. ($C_{22}H_{26}O_5$) C, H.

4-*O*-Acetyl-2,3-di-*O*-benzyl-L-arabinopyranose (**146**). 69%, $[\alpha]_D$ +44° (*c* 0.7, $CHCl_3$).

Anal. ($C_{21}H_{24}O_6$) C, H.

4-*O*-Allyl-2,3-di-*O*-benzyl-L-arabinopyranose (**148**). 51%, $[\alpha]_D$ +21° (*c* 0.6, $CHCl_3$).

Anal. ($C_{22}H_{26}O_5$) C, H.

2,3,4-Tri-*O*-benzyl-L-fucopyranose (**155**). 63%, mp 104—105 °C (from IPE), $[\alpha]_D$ −27° (*c* 0.5, $CHCl_3$) (lit,[29] mp 102—103 °C, $[\alpha]_D$ −26.5° ($CHCl_3$) (Found: C, 74.36; H, 6.91%).

2-*O*-Acetyl-3,4-di-*O*-benzyl-L-fucopyranose (**157**). 37%, $[\alpha]_D$ −31° (*c* 0.6, $CHCl_3$).

Found: C, 68.82; H, 6.92%. Calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78%.

2-*O*-Allyl-3,4-di-*O*-benzyl-L-fucopyranose (**160**). 37%, $[\alpha]_D$ −20° (*c* 0.6, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.14 (d, $J_{5,6}$=6.5 Hz, H-6α), 1.18 (d, $J_{5,6}$=6.5 Hz, H-6β), 3.49 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=3 Hz, H-3β), 3.52 (m, $J_{4,5}$=1 Hz, H-5β), 3.56 (d, $J_{3,4}$= 2.5 Hz, $J_{4,5}$=1 Hz, H-4α), 3.57 (d, H-4β), 3.62 (dd, $J_{1,2}$=7.5 Hz, H-2β), 3.82 (dd, $J_{2,3}$=10 Hz, H-3α), 3.96 (dd, $J_{1,2}$=4 Hz, H-2α), 4.10 (m, H-5α), 4.57 (d, H-1β), 5.40 (d, H-1α).

Found: C, 72.24; H, 7.16%. Calcd for $C_{23}H_{28}O_5$: C, 71,85; H, 7.34%.

3-*O*-Acetyl-2,4-di-*O*-benzyl-L-fucopyranose (**169**). 72%, $[\alpha]_D$ −80° (*c* 0.7, $CHCl_3$).

Anal. ($C_{22}H_{26}O_6$) C, H.

3-*O*-Allyl-2,4-di-*O*-benzyl-L-fucopyranose (**171**). 56%, $[\alpha]_D$ −17° (*c* 0.6, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.15 (d, $J_{5,6}$=6.5 Hz, H-6α), 1.21 (d, $J_{5,6}$=6.5 Hz, H-6β), 3.45 (dd, $J_{2,3}$=10 Hz,

$J_{3,4}$=2.5 Hz, H-3β), 3.54 (m, $J_{4,5}$=1 Hz, H-5β), 3.58 (dd, H-4β), 3.66 (dd, $J_{3,4}$=5 Hz, $J_{4,5}$=1 Hz, H-4α), 3.68 (dd, $J_{1,2}$=7.5 Hz, H-2β), 3.79 (dd, $J_{2,3}$=10 Hz, H-3α) 3.98 (dd, $J_{1,2}$=4 Hz, H-2α), 4.11 (m, H-5α), 4.61 (d, H-1β), 5.25 (H-1α), 5.98 (m, allyl).

Anal. ($C_{23}H_{28}O_5$), C, H.

4-*O*-Acetyl-2,3-di-*O*-benzyl-L-fucopyranose (**173**). 70%, $[\alpha]_D$ −57° (*c* 0.9, $CHCl_3$).

Anal. ($C_{22}H_{26}O_6$) C, H.

4-*O*-Allyl-2,3-di-*O*-benzyl-L-fucopyranose (**175**). 32%, $[\alpha]_D$ −27° (*c* 0.6, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ=1.22 (d, $J_{5,6}$=6.5 Hz, H-6α), 1.29 (d, $J_{5,6}$=6.5 Hz, H-6β), 3.59 (dd, $J_{3,4}$=3 Hz, $J_{4,5}$=1 Hz, H-4α), 3.84 (dd, $J_{2,3}$=10 Hz, H-3α), 3.97 (dd, $J_{1,2}$=4 Hz, H-2α), 4.11 (m, H-5α), 5.25 (d, H-1α).

Anal. ($C_{23}H_{28}O_5$) C, H.

2,3,4-Tri-*O*-benzyl-L-rhamnopyranose (**182**). 78%, mp 94—95 °C (from IPE), $[\alpha]_D$ −12° (*c* 0.5, $CHCl_3$)(lit,[30] mp 90—92 °C, $[\alpha]_D$ −15.4° ($CHCl_3$)) (Found: C, 74.51; H, 6.94%).

2-*O*-Acetyl-3,4-di-*O*-benzyl-L-rhamnopyranose (**184**). 76%, $[\alpha]_D$ +10° (*c* 0.7, $CHCl_3$).

Anal. ($C_{22}H_{26}O_6$) C, H.

2-*O*-Allyl-3,4-di-*O*-benzyl-L-rhamnopyranose (**187**). 63%, $[\alpha]_D$ −20° (*c* 0.7, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ=1.31 (d, $J_{5,6}$=6.5 Hz, H-6α), 1.34 (d, $J_{5,6}$=6.5 Hz, H-6β), 3.36 (m, $J_{4,5}$=10 Hz, H-5β), 3.56 (t, $J_{3,4}$=$J_{4,5}$=10 Hz, H-4α), 3.78 (dd, $J_{1,2}$=2 Hz, $J_{2,3}$=3 Hz, H-2α), 3.91 (dd, H-3α), 5.19 (d, H-1α).

Found: C, 71.46; H, 7.36%. Calcd for $C_{23}H_{28}O_5$: C, 71.85; H, 7.34%.

3-*O*-Acetyl-2,4-di-*O*-benzyl-L-rhamnopyranose (**192**). 79%, $[\alpha]_D$ +20° (*c* 1.0, $CHCl_3$)

Anal. ($C_{22}H_{26}O_6$) C, H.

3-*O*-Allyl-2,4-di-*O*-benzyl-L-rhamnopyranose (**194**). 63%, $[\alpha]_D$ −22° (*c* 1.0, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ=1.31 (d, $J_{5,6}$=6.5 Hz, H-6α), 1.34 (d, $J_{5,6}$=6.5 Hz, H-6β), 3.53 (t, $J_{3,4}$=$J_{4,5}$=9.5 Hz, H-4β), 3.58 (t, $J_{3,4}$=$J_{4,5}$=9 Hz, H-4α), 3.85 (dd, $J_{1,2}$=1.5 Hz, $J_{2,3}$=2 Hz, H-2β), 3.92 (m, H-5α).

Found: C, 71.65; H, 6.99%. Calcd for $C_{23}H_{28}O_5$: C, 71.85; H, 7.34%.

4-*O*-Allyl-2,3-di-*O*-benzyl-L-rhamnopyranose (**198**). 72% $[\alpha]_D$ −27° (*c* 0.9, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ=1.32 (d, $J_{5,6}$=6.5 Hz, H-6α), 1.34 (d, $J_{5,6}$=6 Hz, H-6β), 3.32 (m, $J_{4,5}$=9 Hz, H-5β), 3.46 (t, $J_{3,4}$=9 Hz, H-4β), 3.50 (t, $J_{3,4}$=$J_{4,5}$=9.5 Hz, H-4α), 3.52 (dd, $J_{2,3}$=2.5 Hz, H-3β), 3.79 (dd, $J_{1,2}$=$J_{2,3}$=3 Hz, H-2α), 3.82 (dd, $J_{1,2}$=1.5 Hz, H-2β), 3.85 (dd, H-3α), 3.91 (m, H-5α), 5.15 (H-1α).

Anal. ($C_{23}H_{28}O_5$) C, H.

4-*O*-Acetyl-2,3-di-*O*-benzyl-L-rhamnopyranose (**201**). 85% $[\alpha]_D$ −13° (*c* 0.9, $CHCl_3$).

Anal. ($C_{22}H_{26}O_6$) C, H.

Formation of the Chloride 5. To a stirring solution of **3** (46 mg) in CH_2Cl_2 (0.77 ml) was added $TiCl_4$ (8.5 µl, 1.0 equiv) at room temp. After 5 min, iced H_2O and toluene were successively added and the organic layer was washed well with H_2O. After a brief treatmetnt with Na_2SO_4, the solution was concentrated up to give a sirup (43 mg) whose ^{1}H NMR spectrum measured in $CDCl_3$ showed a characteristic doublet of **5** at δ=6.09 ($J_{1,2}$=4 Hz, H-1). TLC indicated that the mixture contained **5** as the dominant product and slower-moving partially debenzylated products.

Synthesis of 2-Methoxyethyl Glycosides and Their Derivatives.

2-Methoxyethyl α-D-glucopyranoside (**6**). A mixture of **1** (200 mg), MEOH (2 ml), and $MeSO_3H$ (200 µl) was heated at 100 °C for 6 h. After neutralizaton with $NaHCO_3$ (0.40 g) and concentration, chromatography with $CHCl_3$–MeOH (CM) system (gradient) gave, after the elution of **7** (14 mg, 5%), **6** (217 mg, 82%), $[\alpha]_D$ +108° (*c* 1.2, H_2O)(lit,[31] $[\alpha]_D$ +94° (H_2O), ^{1}H NMR (D_2O) δ=3.30 (s, OMe), 3.43 (dd, $J_{1,2}$=4 Hz, $J_{2,3}$=10 Hz, H-2), 4.82 (d, H-1) (Found: C, 45.20; H, 7.82%).

2-Methoxyethyl α-D-Mannopyranoside (**71**). A similar reaction of **70** (10 g) and MEOH (100 ml) containing $MeSO_3H$ (3.0 ml) for 2 h at 100 °C, followed by processing and chromatography (CM system), gave **71** (10.8 g, 82%), $[\alpha]_D$ +29° (*c* 1.4, H_2O), ^{1}H NMR (D_2O) δ=3.31 (s, OMe), 3.88 (dd, 1H, $J_{1,2}$=1.5 Hz, $J_{2,3}$=3.5 Hz, H-2), 4.80 (d, H-1).

Found: C, 44.76; H, 7.56%. Calcd for $C_9H_{18}O_7$: C, 45.37; H, 7.62%.

2-Methoxyethyl α- and β-L-Rhamnopyranosides (**179** and **180**). A reaction of **178** (monohydrate, 10 g) with MEOH (40 ml) in the presence of H_2SO_4 (0.1 ml) for 3.5 h at 80 °C, followoed by processing and chromatography (CM system), afforded **180** (1.5 g, 12%), $[\alpha]_D$ +29° (*c* 0.3, H_2O), ^{1}H NMR (D_2O) δ=1.23 (d, $J_{5,6}$=6 Hz, H-6), 3.31 (s, OMe), 3.89 (dd, $J_{2,3}$=3 Hz, $J_{3,4}$=8 Hz, H-3), 3.93 (d, $J_{1,2}$=0 Hz, H-2), 4.58 (s, H-1), and then **179** (7.6 g, 62%), $[\alpha]_D$ −28° (*c* 1.2, H_2O), ^{1}H NMR (D_2O) δ=1.21 (d, $J_{5,6}$=6.5 Hz, H-6), 3.31 (S, OMe), 3.35 (t, $J_{3,4}$=$J_{4,5}$=10 Hz, H-4), 3.69 (dd, $J_{2,3}$=3.5 Hz, H-3), 3.88 (dd, $J_{1,2}$=1.5 Hz, H-2), 4.72 (d, H-1).

Anal. ($C_9H_{18}O_6$) **179**, C, H. **180**, C, H.

2-Methoxyethyl 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranoside (**33**) and 2,3,5,6-Tetra-*O*-acetyl-β-D-galactofuranoside (**34**). To a cold mixture of AcBr (17 ml) and AcOH (11 ml) was added **32** (3.0 g); the suspension was then stirred at 25 °C for 1.5 h. After evaporation and co-evaporation with toluene, the residue was dissolved in cold MEOH (18 ml) and powdery Ag_2CO_3 (7.5 g) was added to the stirring solution. The suspension was stirred in the dark at room temp overnight. After filtration and concentration, the residue was chromatographed (TB system) to afford **34** (0.41 g, 6%), $[\alpha]_D$ −31° (*c* 3.4, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ=2.03, 2.05, 2.07, 2.10 (4s, OAc), 3.35 (s, OMe), 4.18 (dd, $J_{5,6b}$=7 Hz, $J_{6a,6b}$=12 Hz, H-6b), 4.25 (dd, $J_{3,4}$=6 Hz, $J_{4,5}$=3.5 Hz, H-4), 4.32 (dd, $J_{5,6a}$=4.5 Hz, H-6a), 4.97 ($J_{2,3}$=2 Hz, H-3), 5.05 (d, $J_{1,2}$=1 Hz, H-1), 5.07 (dd, H-2), 5.34 (m, H-5), and then **33** (3.61 g, 53%), $[\alpha]_D$ −13° (*c* 4.9, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ=1.97, 2.04, 2.05, 2.14 (4s, OAc), 3.35 (s, OMe), 4.55 (d, $J_{1,2}$=8 Hz, H-1), 5.01 (dd, $J_{2,3}$=9.5 Hz, $J_{3,4}$=3.5 Hz, H-3), 5.21 (dd, H-2), 5.37 (dd, $J_{4,5}$=1 Hz, H-4).

Found: **33**, C, 50.12; H, 6.52%. **34**, C, 49.75; H, 6.38%. Calcd for $C_{17}H_{26}O_{11}$: C, 50.24; H, 6.45%.

2-Methoxyethyl 2,3,4-Tri-*O*-acetyl-β-L-fucopyranoside (**152**) and 2,3,5-Tri-*O*-acetyl-β-L-fucofuranoside (**153**). To chilled AcBr (4 ml) was added **151** (1 g) and the mixture was stirred for 1 h at 25 °C. After evaporation and co-evaporation with toluene, the bromide was then treated with MEOH (5.5 ml) and Ag_2CO_3 (2.7 g). Processing and chromatography (TB system) furnished **153** (0.20 g, 9%), $[\alpha]_D$ +21° (*c* 0.7, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ=1.30 (d, $J_{5,6}$=6.5 Hz, H-6), 2.07, 2.08, 2.09 (3s, OAc), 3.38 (s, OMe), 4.11 (dd, $J_{3,4}$=6.5 Hz, $J_{4,5}$=4 Hz, H-4), 4.99 (dd, $J_{2,3}$=2 Hz, H-3), 5.07 (d, $J_{1,2}$=1 Hz, H-1), 5.09 (dd, H-2), 5.14 (m, H-5), and then **152** (1.59 g, 75%), $[\alpha]_D$ −12° (*c* 2.6, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ=1.20 (d, $J_{5,6}$=6.5 Hz, H-6), 1.96, 2.04, 2.15 (3s, OAc), 3.34 (s, OMe), 3.79 (m, $J_{4,5}$=1 Hz, H-5), 4.51 (d, $J_{1,2}$=8 Hz, H-1), 5.00 (dd, $J_{2,3}$=11.5

Hz, $J_{3,4}$=4 Hz, H-3), 5.18 (dd, H-2), 5.21 (dd, H-4).

Anal. ($C_{15}H_{24}O_9$) **152**, C, H. **153**, C. H.

2-Methoxyethyl 2,3,4-Tri-*O*-acetyl-α-L-arabinopyranoside (**124**). To a stirring solution of **126**[9] (0.49 g) in $CHCl_3$ (1.5 ml) was added AcBr (0.61 ml) and then H_2O (0.12 ml) at 0 °C. The mixture was stirred for 0.5 h at room temp. After evaporation and co-evaporation with toluene, the bromide was treated with MEOH (1.5 ml) containing Ag_2CO_3 (0.70 g) overnight, followed by chromatoraphy (TB system) to yield **124** (0.40 g, 78%), $[\alpha]_D$ −21° (*c* 2.8, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=2.01, 2.04, 2.09 (3s, OAc), 3.34 (s, OMe), 3.61 (dd, $J_{4,5b}$=2 Hz, $J_{5a,5b}$=13.5 Hz, H-5b), 4.01 (dd, $J_{4,5a}$=4 Hz, H-5a), 4.48 (d, $J_{1,2}$=7 Hz, H-1), 5.02 (dd, $J_{2,3}$=9.5 Hz, $J_{3,4}$=4 Hz, H-3), 5.18 (dd, H-2), 5.23 (t, H-4).

Anal. ($C_{14}H_{22}O_9$) C, H.

Attempt to prepare **124** directly from **123** (1.0 g) through the procedure described for **152** provided 2-methoxyethyl 2,3,5-tri-*O*-acetyl-α-L-arabinofuranoside (**125**) (0.74 g, 33%), $[\alpha]_D$ −41° (*c* 4.1, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=2.07 (s, 9H, OAc), 3.36 (s, OMe), 4.19 (dd, $J_{4,5b}$=5.5 Hz, $J_{5a,5b}$=10.5 Hz, H-5b), 4.24 (m, $J_{3,4}$=5 Hz, $J_{4,5a}$=2.5 Hz, H-4), 4.40 (dd, H-5a), 4.95 (dd, $J_{2,3}$=1.5 Hz, H-3), 5.06 (d, $J_{1,2}$=0 Hz H-1), 5.11 (d, H-2) (Found: C, 49.97; H, 6.66%) and then **124** (0.79 g, 35%).

2-Methoxyethyl β-D-galactopyranoside (**43**) and β-D-galactofuranoside (**44**). A filtrate obtained after removing the silver salts described for **33**, starting from **32** (3.0 g), was concentrated and redissolved in MeOH (40 ml). The solution was treated with dil NaOMe (7%, 4 ml) overnight. After neutralizatin with AcOH, evaporation and chromatography (CM system) delivered **44** (0.80 g, 12%), $[\alpha]_D$ −41° (*c* 1.4, H_2O), ^1H NMR (D_2O) δ=3.32 (s, OMe), 4.94 (d, $J_{1,2}$=2 Hz, H-1), and then **43** (3.83 g, 58%), $[\alpha]_D$ +4° (*c* 2.1, H_2O) (lit,[32] $[\alpha]_D$ +8.4° (H_2O)), ^1H NMR (D_2O) δ=3.30 (s, OMe), 3.35 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=3 Hz, H-3), 3.43 (dd, $J_{1,2}$=8 Hz, H-1), 3.82 (d, $J_{4,5}$=0 Hz, H-4), 4.32 (d, H-1).

Found: **43**, C, 42.16; H, 7.55%. **44**, C, 42.19; H, 7.44%. Calcd for $C_9H_{18}O_7 \cdot H_2O$: C, 42.18; H, 7.87%.

2-Methoxyethyl β-L-Fucopyranoside (**161**) and β-L-Fucofuranoside (**162**). A similar deacetylation of a reaction mixture obtained from **151** (5 g) as described for **152**, followed by chromatography (CM system), produced **162** (0.63 g, 9%), $[\alpha]_D$ +63° (*c* 1.0, H_2O), ^1H NMR (D_2O) δ=1.17 (d, $J_{5,6}$=6.5 Hz, H-6), 3.31 (s, OMe), 4.00 (dd, $J_{1,2}$=1.5 Hz, $J_{2,3}$=3 Hz, H-2), 4.93 (d, H-1), and then **161** (5.64 g, 83%), $[\alpha]_D$ +1.2° (*c* 2.2, H_2O), ^1H NMR (D_2O) δ=1.18 (d, $J_{5,6}$=6.5 Hz, H-6), 3.32 (s, OMe), 3.41 (dd, $J_{1,2}$=8 Hz, $J_{2,3}$=10.5 Hz, H-2), 3.56 (dd, $J_{3,4}$=4 Hz, H-3), 4.31 (d, H-1).

Anal. ($C_9H_{18}O_6$) **161**, C, H. **162**, C, H.

2-Methoxyethyl α-L-Arabinopyranoside (**134**). Similarly, a reaction mixture obtained from **126** (1.0 g), followed by chromatography (CM system), gave forth **134** (0.57 g, 87%), $[\alpha]_D$ −8° (*c* 3.8, H_2O), ^1H NMR (D_2O) δ=3.32 (s, OMe), 3.48 (dd, $J_{1,2}$=7.5 Hz, $J_{2,3}$=10 Hz, H-2), 3.84 (dd, $J_{4,5eq}$=2 Hz, $J_{5eq,5ax}$=12 Hz, H-5eq), 4.28 (d, H-1).

Anal. ($C_8H_{16}O_6$) C, H.

An attempt to obtain **134** directly from **123** (12 g) via acetobromination with AcBr (48 ml), 2-methoxyethylation with MEOH (72 ml) and Ag_2CO_2 (36 g), and deacetylation followed by chromatography (CM system), afforded 2-methoxyethyl α-L-arabinofuranoside (**135**) (5.96 g, 36%), $[\alpha]_D$ −39° (*c* 1.2, H_2O), ^1H NMR (D_2O) δ=3.31 (s, OMe), 3.86 (dd, $J_{2,3}$=4 Hz, $J_{3,4}$=6.5 Hz, H-3), 4.02 (dd, $J_{1,2}$=1.5 Hz, H-2), 4.95 (d, H-1) (Found: C, 46.20; H 7.82%), and then **134** (6.4 g, 38%).

2-Methoxyethyl β-D-Xylopyranoside (**114**). Deacetylation of **102**[6] (1.00 g) with dil NaOMe (0.6%), followed by chromatography (CM system), furnished **114** (0.55 g, 88%), $[\alpha]_D$ −45° (*c* 1.8, H_2O) (lit,[33] $[\alpha]_D$ −50.4° (MeOH)), ^1H NMR (D_2O) δ=3.20 (dd, $J_{1,2}$=7.5 Hz, $J_{2,3}$=9 Hz, H-2), 3.23 (dd, $J_{4,5ax}$=9.5 Hz, $J_{5eq,5ax}$=12 Hz, H-5ax), 3.31 (s, OMe), 3.36 (t, $J_{3,4}$=9 Hz, H-3), 3.54 (m, $J_{4,5eq}$=5 Hz, H-4), 3.88 (dd, H-5eq), 4.14 (d, H-1)(Found: C, 45.65; H, 7.86%).

2-Methoxyethyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranoside (**8**). A mixture of **6** (77 mg), powdered KOH (0.51 g, 7 equiv of OH) and $PhCH_2Cl$ (2.0 ml) was stirred for 2 h at 120 °C, followed by usual processing and chromatography with hexane–ethyl acetate (HE) system (gradient), to yield **8** (170 mg, 88%), $[\alpha]_D$ +23° (*c* 2.4, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.37 (s, OMe), 4.82 (d, $J_{1,2}$=4 Hz, H-1).

Anal. ($C_{37}H_{42}O_7$) C, H.

Similar benzylations of **71** and **179** furnished **72** (86%) and **181** (70%), respectively.

2-Methoxyethyl 2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranoside (**72**). $[\alpha]_D$ +25° (*c* 1.0, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.34 (s, OMe), 3.89 (dd, $J_{1,2}$=2 Hz, $J_{2,3}$=2.5 Hz, H-2), 3.94 (dd, $J_{3,4}$=9.5 Hz, H-3), 4.00 (t, $J_{4,5}$=9.5 Hz, H-4), 4.94 (d, H-1).

Anal. ($C_{37}H_{42}O_7$) C, H.

2-Methoxyethyl 2,3,4-Tri-*O*-benzyl-α-L-rhamnopyranoside (**181**). $[\alpha]_D$ −30° (*c* 0.7, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.35 (d, $J_{5,6}$=6 Hz, H-6), 3.35 (s, OMe), 3.99 (s, $J_{1,2}$=$J_{2,3}$=0 Hz, H-2), 4.82 (s, H-1).

Found: C, 72.81; H, 7.36%. Calcd for $C_{30}H_{36}O_6$: C, 73.15; H, 7.37%.

2-Methoxyethyl 2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranoside (**3**). A mixture of **2**[12] (100 mg), crushed KOH (386 mg, 7 equiv OAc), and $PhCH_2Cl$ (1.5 ml) was stirred for 2 h at 120 °C, followed by processing and chromatogrphy (HE system), to yield **3** (86 mg, 58%), mp 68—70 °C, $[\alpha]_D$ +7° (*c* 1.6, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.42 (s, OMe), 4.49 (d, $J_{1,2}$=7.5 Hz, H-1).

Anal. ($C_{37}H_{42}O_7$) C, H.

Similar reactions of **33**, **102**,[6] **124**, and **152**, afforded **35** (41%), **103** (78%), **127** (82%), and **154** (80%), respectively.

2-Methoxyethyl 2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranoside (**35**). $[\alpha]_D$ −6° (*c* 1.8, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.37 (s, OMe), 3.52 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=3 Hz, H-3), 3.84 (dd, $J_{1,2}$=8 Hz, H-2), 3.89 (d, $J_{4,5}$=0 Hz, H-4), 4.40 (d, H-1).

Found: C, 73.67; H, 7.05%. Calcd for $C_{37}H_{42}O_7$: C, 74.22; H, 7.07%.

2-Methoxyethyl 2,3,4-Tri-*O*-benzyl-β-D-xylopyranoside (**103**). $[\alpha]_D$ +10° (*c* 1.3, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.21 (dd, $J_{4,5ax}$=10 Hz, $J_{5aq,5ax}$=11.5 Hz, H-5ax), 3.39 (s, OMe), 3.41 (dd, $J_{1,2}$=7.5 Hz, $J_{2,3}$=9.5 Hz, H-2), 3.58 (t, $J_{3,4}$=9.5 Hz, H-3), 3.94 (dd, $J_{4,5eq}$=4.5 Hz, H-5eq), 4.39 (d, H-1).

Found: C, 72.38; H, 4.39%. Calcd for $C_{29}H_{34}O_6$: C, 72.78; H, 7.16%.

2-Methoxyethyl 2,3,4-Tri-*O*-benzyl-α-L-arabinopyranoside (**127**). $[\alpha]_D$ +6° (*c* 1.5, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.27 (dd, $J_{4,5ax}$=1.5 Hz, $J_{5eq,5ax}$=13 Hz, H-5ax), 3.39 (s, OMe), 3.52 (dd, $J_{2,3}$=9 Hz, $J_{3,4}$=4 Hz, H-3), 3.84 (dd, $J_{1,2}$=7.5 Hz, H-2), 4.04 (dd, $J_{4,5eq}$=3 Hz, H-5eq), 4.37 (d, H-1).

Anal. ($C_{29}H_{34}O_6$) C, H.

2-Methoxyetheyl 2,3,4-Tri-*O*-benzyl-β-L-fucopyranoside (**154**). $[\alpha]_D$ +7° (*c* 1.6, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.19 (d,

$J_{5,6}$=6.5 Hz, H-6), 3.38 (s, OMe), 3.46 (m, $J_{4,5}$=1 Hz, H-5), 3.52 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=2.5 Hz, H-3), 3.83 (dd, $J_{1,2}$=7.5 Hz, H-2), 4.38 (d, H-1).

Found: C, 72.57; H, 7.36%. Cacld for $C_{30}H_{36}O_6$: C, 73.15; H, 7.37%.

2-Methoxyethyl 3,4-*O*-Isopropylidene-α-L-arabinopyranoside (**136**). To a stirring solution of **134** (2.70 g) in acetone containing 2,2-dimethoxypropane[34] (DMP, 2.5 ml) was added H_2SO_4 (10 μl) at room temp. After 6 h, the solution was treated with $NaHCO_3$ (0.35 g), concentrated, and chromatographed (TB system) to yield **136** (1.80 g, 56%), $[\alpha]_D$ +40° (*c* 2.2, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.34, 1.52 (2s, CMe_2), 3.37 (s, OMe), 3.63 (t, $J_{1,2}$=$J_{2,3}$=7.5 Hz, H-2), 4.06 (dd, $J_{3,4}$=6 Hz, H-3), 4.21 (d, H-1).

Found: C, 52.61; H, 8.19%. Calcd for $C_{11}H_{20}O_6$: C, 53.21; H, 8.12%.

Similar reactions of **161** and **179** afforded **163** (92%) and **195** (84%), respectively.

2-Methoxyethyl 3,4-*O*-Isopropylidene-β-L-fucopyranoside (**163**). $[\alpha]_D$ −30° (*c* 0.9, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.35, 1.52 (2s, CMe_2), 1.41 (d, $J_{5,6}$=6.5 Hz, H-6), 3.38 (s, OMe) 3.55 (dd, $J_{1,2}$=8 Hz, $J_{2,3}$=7 Hz, H-2), 3.86 (m, $J_{4,5}$=2 Hz, H-5), 3.99 (dd, $J_{3,4}$=5 Hz, H-4), 4.04 (dd, H-3), 4.19 (d, H-1).

Found: C, 54.52; H, 8.41%. Calcd for $C_{12}H_{22}O_6$: C, 54.95; H, 8.45%.

2-Methoxyethyl 2,3-*O*-Isopropropylidene-α-L-rhamnopyranoside (**195**). $[\alpha]_D$ −29° (*c* 0.7, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.34, 1.51 (2s, CMe_2), 1.29 (d, $J_{5,6}$=6.5 Hz, H-6), 3.38 (s, OMe), 4.11 (t, $J_{2,3}$=$J_{3,4}$=6 Hz, H-3), 4.19 (d, $J_{1,2}$=0 Hz, H-2), 4.98 (s, H-1).

Anal. ($C_{12}H_{22}O_6$) C, H.

2-Methoxyethyl 3,4-*O*-Isopropylidene-β-D-galactopyranoside (**45**). To a stirring mixture of **43** (1.87 g), acetone (50 ml), DMP (7 ml) and *N*,*N*-dimethylformamide[35] (4 ml) was added H_2SO_4 (80 μl) at room temp; the mixture was then stirred for 4 h at a reflux temperature. After processing, chromatography (CM system) afforded **45** (1.21 g, 55%), $[\alpha]_D$ −16° (*c* 0.9, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.33, 1.50 (2s, CMe_2), 3.38 (s, OMe), 3.56 (dd, $J_{1,2}$=8 Hz, $J_{2,3}$=7 Hz, H-2), 3.82 (dd, $J_{5,6b}$=4 Hz, $J_{6a,6b}$=11 Hz, H-6b), 3.86 (m, $J_{4,5}$=2 Hz, $J_{5,6a}$=6 Hz, H-5), 3.96 (dd, H-6a), 4.08 (dd, $J_{3,4}$=6 Hz, H-3), 4.14 (dd, H-4), 4.22 (d, H-1).

Found: C, 51.42; H, 8.06%. Calcd for $C_{12}H_{22}O_7$: C, 51.79; H, 7.97%.

2-Methoxyethyl 4,6-*O*-Benzylidene-β-D-galactopyranoside (**53**). A mixture of **43** (1.06 g), benzaldehyde (7 ml), and $ZnCl_2$ (0.3 g) was stirred overnight, followed by the usual processing and chromatography (CM system), to furnish **53** (1.03 g, 71%), mp 139—140 °C (from IPE), $[\alpha]_D$ −18° (*c* 0.4, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.36 (s, OMe), 3.43 (m, $J_{4,5}$=1 Hz, $J_{5,6eq}$=1.5 Hz, $J_{5,6ax}$=2 Hz, H-5), 3.78 (dd, $J_{1,2}$=8 Hz, $J_{2,3}$=10 Hz, H-2), 4.04 (dd, $J_{6eq,6ax}$=12.5 Hz, H-6ax), 4.16 (dd, $J_{3,4}$=4 Hz, H-4), 4.29 (dd, H-6eq), 4.32 (d, H-1), 5.52 (s, benzylidene).

Found: C, 59.51; H, 6.74%. Calcd for $C_{16}H_{21}O_7$: C, 59.07; H, 6.51%.

2-Methoxyethyl 4,6-*O*-Benzylidene-α-D-mannopyranoside (**86**). A solution of **71** (643 mg) in *N*,*N*-dimethylformamide (13 ml) containing benzaldehyde dimethyl acetal (0.53 ml) was treated with pyridinium tosylate[36] (13 mg) for 6.5 h at 80 °C. Processing and chromatography (CM system) provided **86** (314 mg, 36%), mp 93—95 °C, $[\alpha]_D$ +51° (*c* 0.8, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.56 (s, OMe), 4.86 (d, $J_{1,2}$=1 Hz, H-1), 5.58 (s, benzylidene).

Found: C, 58.67; H, 6.77%. Calcd for $C_{16}HO_7$: C, 59.07; H, 6.51%.

After the elution of **86**, another acetal (46 mg, 5%) was obtained. That was acetylated with Ac_2O and pyridine, followed by chromatography (TB system), to yield 2-methoxyethyl 4,6-di-*O*-acetyl-2,3-*O*-benzylidene-α-D-mannopyranoside (**87**), mp 52—53 °C, $[\alpha]_D$ −28° (*c* 0.5, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=2.06, 2.09 (2s, OAc), 3.40 (s, OMe), 3.97 (m, $J_{4,5}$=10.5 Hz, $J_{5,6a}$=5.5 Hz, $J_{5,6b}$=2.5 Hz, H-5), 4.10 (dd, $J_{6a,6b}$=12 Hz, H-6b), 4.24 (dd, H-6a), 4.31 (dd, $J_{1,2}$=1 Hz, $J_{2,3}$=6.5 Hz, H-2), 4.42 (dd, $J_{3,4}$=7 Hz, H-3), 5.12 (dd, H-4), 5.23 (d, H-1), 5.90 (s, benzylidene) (Found: C, 58.60; H, 6.42%).

2-Methoxyethyl 6-*O*-Trityl-β-D-glucopyranoside (**27**). A mixture of **7**[12] (2.40 g), trityl chloride (7.72 g), and pyridine 12 ml) was stirred at 70 °C overnight. The processed mixture was chromatoraphed (CM system) to give forth **27** (2.53 g, 53%), mp 72—73°C (from IPE), $[\alpha]_D$ −32° (*c* 3.3, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.35 (s, OMe), 4.02 (m, $J_{4,5}$=11 Hz, $J_{5,6}$=3 and 5 Hz, H-5), 4.31 (d, $J_{1,2}$=8 Hz, H-1),

Anal. ($C_{28}H_{32}O_7$) C, H.

Similar tritylations of **43** and **71** afforded (**65**) (50%) and **97** (61%).

2-Methoxyethyl 6-*O*-Trityl-β-D-galactopyranoside (**65**). $[\alpha]_D$ −29° (*c* 3.0, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.32 (s, OMe), 3.65 (dd, $J_{1,2}$=7.5 Hz, $J_{2,3}$=10 Hz, H-2), 4.23 (d, H-1).

Anal. ($C_{28}H_{32}O_7$), C, H.

2-Methoxyethyl 6-*O*-Trityl-α-D-mannopyranoside (**97**). Mp 65—67 °C, $[\alpha]_D$ +11° (*c* 0.9, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.37 (s, OMe), 3.94 (dd, $J_{1,2}$=1.5 Hz, $J_{2,3}$=3.5 Hz, H-2), 4.85 (d, H-1).

Found: C, 69.39; H, 6.55%. Calcd for $C_{28}H_{32}O_7$: C, 69.98; H, 6.71%.

2-Methoxyethyl 4-*O*-Trityl-β-D-xylopyranoside (**115**). A mixture of **114** (631 mg), trityl chloride (1.27 g), and pyridine (3 ml) was stirred at 70 °C overnight, followed by processing and chromatography (TB system), to give a mixture of the monotrityl ethers (301 mg) and then **115** (338 mg, 25%), mp 43—45 °C (from hexane containing IPE), $[\alpha]_D$ −58° (*c* 1.1, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.32 (s, OMe), 4.66 (d, $J_{1,2}$=4 Hz, H-1).

Anal. ($C_{27}H_{30}O_6$) C, H.

The whole mixture (301 mg) of the faster-moving monotrityl ethers was acetylated with Ac_2O and pyridine, followed by chromatography (TB system), to yield 2-methoxyethyl 3,4-di-*O*-acetyl-2-*O*-trityl-β-D-xylopyranoside (**116**) (77 mg, 5% from **115**), $[\alpha]_D$ −5° (*c* 0.5, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.78, 2.11 (2s, OAc), 3.26 (s, OMe), 3.45 (dd, $J_{1,2}$=4.5 Hz, $J_{2,3}$=6.5 Hz, H-2), 3.45 (dd, $J_{4,5b}$=6.5 Hz, $J_{5a,5b}$=12.5 Hz, H-5b), 3.95 (dd, $J_{4,5a}$=4.5 Hz), 4.02 (d, H-1), 4.67 (dd, $J_{3,4}$=6.5 Hz, H-4), 5.25 (t, H-3) (Found: C, 69.62; H, 6.26%), and then 2-methoxyethyl-2,4-di-*O*-acetyl-3-*O*-trityl-β-D-xylopyranoside (**117**) (142 mg, 9%), mp 147—148 °C (from IPE), $[\alpha]_D$ −28° (*c* 1.2, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.63, 1.78 (2s, OAc), 3.14 (dd, $J_{4,5b}$=6.5 Hz, $J_{5a,5b}$=12 Hz, H-5b), 3.37 (s, OMe), 4.15 (dd, $J_{4,5a}$=4 Hz, H-5a), 4.34 (dd, $J_{1,2}$=5 Hz, H-1), 4.57 (dd, $J_{3,4}$=6.5 Hz, H-4), 4.87 (dd, $J_{2,3}$=7 Hz, H-2) (Found: C, 70.17; H, 6.42%).

2-Methoxyethyl 3-*O*-Trityl-α-L-rhamnopyranoside (**188**). A similar tritylation of **179** (0.88 g) with trityl chloride (2.2 g)

in pyridine (2.6 ml), followed by chromatography (TB system), produced **188** (0.93 g, 51%), mp 45—47 °C (from hexane containing IPE), $[\alpha]_D$ −48 ° (*c* 0.7, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.26 (d, $J_{5,6}$=6.5 Hz, H-6), 3.31 (s, OMe), 3.07 (dd, $J_{1,2}$=2 Hz, $J_{2,3}$=3 Hz, H-2), 3.79 (dd, $J_{3,4}$=9 Hz, H-3), 4.57 (d, H-1).

Found: C, 72.87; H, 6.83%. Calcd for $C_{28}H_{32}O_6$: C, 72.39; H, 6.94%.

After the elution of **188**, there appeared another trityl ether (0.18 g, 10%), which was acetylated with Ac_2O and pyridine to furnish, after chromatography (TB system), 2-methoxyethyl 2,3-di-*O*-acetyl-4-*O*-trityl-α-L-rhamnopyranoside (**189**), $[\alpha]_D$ −84° (*c* 0.4, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.08 (d, $J_{5,6}$=6 Hz, H-6), 1.18, 1.88 (2s, OAc), 3.18 (t, $J_{3,4}$=$J_{4,5}$=10 Hz, H-4), 3.43 (s, OMe), 4.07 (m, H-5), 4.59 (d, $J_{1,2}$=2 Hz, H-1), 5.22 (dd, $J_{2,3}$=3.5 Hz, H-2), 5.28 (dd, H-3) (Found: C, 70.13; H, 6.74%).

2-Methoxyethyl 2,6-Di-*O*-benzyl-β-D-galactopyranoside (**46**). Amixture of **45** (1.20 g), crushed KOH (3.4 g), and $PhCH_2Cl$ (14 ml) was stirred for 2 h at 120 °C, cooled, and then diluted with toluene. After washing with H_2O thoroughly, the organic layer was concentrated under reduced pressure at 95 °C to give an oily product, which was successively heated in aq AcOH (80%, 20 ml) at 95 °C for 1 h. Concentration and chromatography (TB system) provided **46** (1.36 g, 75%), $[\alpha]_D$ +9° (*c* 3.5, $CHCl_3$), ^1H NMR ($CDCl_3$), δ=3.38 (s, OMe), 3.52 (dd, $J_{1,2}$=7.5 Hz, $J_{2,3}$=9.5 Hz, H-2), 3.60 (dd, $J_{3,4}$=3 Hz, $J_{4,5}$=1 Hz, H-4), 3.99 (dd, H-3), 4.42 (d, H-1).

Anal. ($C_{23}H_{30}O_7$) C, H.

Compounds **53** and **86** were similarly transformed into **57** (84%) and **91** (87%), respectively.

2-Methoxyethyl 2,3-Di-*O*-benzyl-β-D-galactopyranoside (**57**). $[\alpha]_D$ −0.4° (*c* 2.9, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.38 (s, OMe), 3.45 (dd, $J_{4,5}$=0 Hz, $J_{5,6a}$=6 Hz, $J_{5,6b}$=5 Hz, H-5), 3.50 (dd, $J_{3,4}$=9 Hz, $J_{3,4}$=3.5 Hz, H-3), 3.68 (dd, $J_{1,2}$=8 Hz, H-2), 3.77 (dd, $J_{6a,6b}$=11.5 Hz, H-6b), 3.94 (dd, H-6a), 3.99 (d, H-4), 4.42 (d, H-1).

Anal. ($C_{23}H_{30}O_7$) C, H.

2-Methoxyethyl 2,3-Di-*O*-benzyl-α-D-mannopyranoside (**91**). $[\alpha]_D$ +22 ° (*c* 0.9, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.36 (s, OMe), 3.74 (dd, $J_{2,3}$=3 Hz, $J_{3,4}$=9.5 Hz, H-3), 3.87 (dd, $J_{1,2}$=1.5 Hz, H-2), 4.04 (t, $J_{4,5}$=9.5 Hz, H-4), 4.90 (d, H-1).

Anal. ($C_{23}H_{30}O_7$) C, H.

2-Methoxyethyl 2-*O*-Benzyl-α-L-arabinopyranoside (**138**). Benzylation of **136** (1.59 g) with $PhCH_2Cl$ (10 ml) and KOH (2.5 g) at 120 °C for 2 H and subsequent processing and chromatography (HE system) afforded a sirup. That was treated with trifluoroacetic acid (TFA, 6 ml) in $CHCl_3$ (20 ml) containing MeOH (20 ml) for 2.5 h at room temp. After quick concentration with an efficient pump at 25 °C and co-evaporation with toluene, chromatography (TB system) afforded **138** (0.86 g, 58%), mp 47—48 °C, $[\alpha]_D$ −13° (*c* 0.9, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.37 (s, OMe), 4.60 (d, $J_{1,2}$=4.5 Hz, H-1).

Anal. ($C_{15}H_{22}O_6$) C, H.

Compounds **163** and **195** were similarly converted into **165** (71%) and **202** (88%), respectively.

2-Methoxyethyl 2-*O*-Benzyl-β-L-fucopyranoside (**165**). $[\alpha]_D$ −18° (*c* 1.8, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.33 (d, $J_{5,6}$=6.5 Hz, H-6), 3.38 (s, OMe), 3.46 (dd, $J_{1,2}$=7.5 Hz, $J_{2,3}$=9.5 Hz, H-2), 4.38 (d, H-1).

Anal. ($C_{16}H_{24}O_6$) C, H.

2-Methoxyethyl 4-*O*-Benzyl-α-L-rhamnopyranoside (**202**). $[\alpha]_D$ −53° (*c* 0.8, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.34 (d, $J_{5,6}$=6.5 Hz, H-6), 3.34 (t, $J_{3,4}$=$J_{4,5}$=9.5 H, H-4), 3.36 (s, OMe), 3.94 (dd, $J_{2,3}$=3.5 Hz, H-3), 3.98 (dd, $J_{1,2}$=1.5 Hz, H-2), 4.80 (d, H-1).

Anal. ($C_{16}H_{24}O_6$) C, H.

2-Methoxyethyl 3-*O*-Allyl-2-*O*-benzyl-β-D-galactopyranoside (**56**). Benzylation of **54** (380 mg) with $PhCH_2Cl$ (1.6 ml) and KOH (0.41 g) took place for 2 h at 120 °C, followed by a subsequent hydrolysis of the product mixture, processed as described for **46**, with aq AcOH (80%, 15 ml) for 1 h at 95 °C. Chromatography (TB system) gave **56** (295 mg, 77%), $[\alpha]_D$ −0.5° (*c* 3.0, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.36 (s, OMe), 3.40 (dd, $J_{2,3}$=9 Hz, $J_{3,4}$=4 Hz, H-3), 3.45 (m, $J_{4,5}$=1 Hz, $J_{5,6a}$= 7 Hz, $J_{5,6b}$=5 Hz, H-5), 3.60 (dd, $J_{1,2}$=7.5 Hz, H-2), 3.79 (dd, $J_{6a,6b}$=11.5 Hz, H-6b), 3.90 (dd, H-6a), 4.40 (d, H-1).

Found: C, 61.55; H, 7.73%. Calcd for $C_{19}H_{28}O_7$: C, 61.94; H, 7.66%.

2-Methoxyethyl 3-*O*-Allyl-2-*O*-benzyl-α-D-mannopyranoside (**90**). A similar process for **88** (332 mg) afforded **90** (271 mg, 81%), $[\alpha]_D$ +18° (*c* 1.1, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.36 (s, OMe), 4.90 (d, $J_{1,2}$=1.5 Hz, H-1).

Found: C, 61.38; H, 7.66%. Calcd for $C_{19}H_{28}O_7$: C, 61.94; H, 7.66%.

2-Methoxyethyl 2,3,4-Tri-*O*-benzyl-β-D-glucopyranoside (**22**). A mixture of **27** (2.3 g), $PhCH_2Cl$ (23 ml), and KOH (5.6 g) was stirred for 2 h at 120 °C, processed as described for **46**, and then hydrolyzed with aq AcOH (80%, 40 ml) for 1 h at 95 °C to deliver, after chromatography (TB system), **22** (1.1 g, 45%), mp 63—65 °C (from hexane containing IPE), $[\alpha]_D$ −3° (*c* 5.1, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.41 (s, OMe), 3.49 (dd, $J_{1,2}$=7.5 Hz, $J_{2,3}$=9 Hz, H-2), 4.51 (d, H-1).

Anal. ($C_{30}H_{36}O_7$) C, H.

A similar process was applied to **65** and **97** to produce **58** (69%) and **93** (46%), respectively.

2-Methoxyethyl 2,3,4-Tri-*O*-benzyl-β-D-galactopyranoside (**58**). Mp 58—59 °C, $[\alpha]_D$ −22° (*c* 1.0, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.38 (s, OMe), 3.54 (dd, $J_{2,3}$=9.5 Hz, $J_{3,4}$=3 Hz, H-3). 3.86 (dd, $J_{1,2}$=8 Hz, H-2), 4.42 (d, H-1).

Anal. ($C_{30}H_{36}O_7$) C, H.

2-Methoxyethyl 2,3,4-Tri-*O*-benzyl-α-D-mannopyranoside (**93**). $[\alpha]_D$ +27° (*c* 1.2, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.35 (s, OMe), 3.89 (dd, $J_{1,2}$=2 Hz, $J_{2,3}$=3 Hz, H-2), 3.99 (t, $J_{3,4}$=$J_{4,5}$= 9.5 Hz, H-4), 4.88 (d, H-1).

Anal. ($C_{30}H_{36}O_7$) C, H.

2-Methoxyethyl 2,3-Di-*O*-benzyl-β-D-xylopyranoside (**118**). Compound **115** (102 mg) was benzylated with $PhCH_2Cl$ (1.4 ml) and KOH (0.36 g) for 2 h at 120 °C. After processing, as described for **46**, the residue was treated with TFA (0.12 ml) in $CHCl_3$ (2 ml) containing MeOH (2 ml) for 1 h at room temp. After removing the volatile substances, as described for **138**, chromatogrphy (TB system) gave **118** (46 mg, 52%), mp 63—64 °C (from hexane), $[\alpha]_D$ −29° (*c* 0.6, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.26 (dd, $J_{4,5ax}$=9 Hz, $J_{5eq,5ax}$=11 Hz, H-5ax), 3.38 (s, OMe), 3.45 (dd, $J_{1.2}$=7 Hz, $J_{2,3}$=5 Hz, H-2), 4.00 (dd, $J_{4,5eq}$=4.5 Hz, H-5eq), 4.48 (d, H-1).

Anal. ($C_{22}H_{28}O_6$) C, H.

2-Methoxyethyl 2,4-Di-*O*-benzyl-α-L-rhamnopyranoside (**190**). Compound **188** (510 mg) was converted similarly into **190** (242 mg, 55%), $[\alpha]_D$ −21° (*c* 0.9, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.33 (d, $J_{5,6}$=6.5 Hz, H-6), 3.32 (t, $J_{3,4}$=$J_{4,5}$=9.5 Hz, H-4), 3.36 (s, OMe), 3.96 (m. H-5), 3.79 (dd, $J_{1,2}$=1.5 Hz,

$J_{2,3}$=4 Hz, H-2), 4.86 (d, H-1).

Found: C, 68.10; H, 7.47%. Calcd for $C_{23}H_{30}O_6$: C, 68.64; H, 7.51%.

2-Methoxyethyl 2-*O*-Allyl-α-L-arabinopyranoside (**137**). A mixture of **136** (147 mg), allyl bromide (1.7 ml), and NaH (60%, 0.17 g, 7 equiv of OH) was stirred for 2 h at a reflux temperature. The mixture was cooled, diluted with toluene and treated carefully with H_2O to destroy NaH. The organic layer was washed well with H_2O, concentrated, and then treated with TFA (1 ml) in $CHCl_3$ (3 ml) containing MeOH (3 ml) for 5 h at room temp. After removing the excess reagents, as described for **138**, chromatography (TB system) furnished **137** (91 mg, 62%), $[\alpha]_D$ −32° (*c* 0.6, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.38 (s, OMe), 4.59 (d, $J_{1,2}$=4.5 Hz, H-1).

Found: C, 52.65; H, 7.85%. Calcd for $C_{11}H_{20}O_6$: C, 53.21; H, 8.12%.

Compounds **163** and **195** were similarly transformed into **164** (49%) and **196** (85%), respectively.

2-Methoxyethyl 2-*O*-Allyl-β-L-fucopyranoside (**164**). Mp 52—54 °C, (from hexane containing IPE), $[\alpha]_D$ −57° (*c* 1.1, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.33 (d, $J_{5,6}$=6.5 Hz, H-6), 3.36 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=2.5 Hz, H-3), 3.37 (dd, $J_{1,2}$=7.5 Hz, H-2), 3.38 (s, OMe), 3.61 (m, $J_{4,5}$=1 Hz, H-5), 4.32 (d, H-1).

Anal. ($C_{12}H_{22}O_6$) C, H.

2-Methoxyethyl 4-*O*-Allyl-α-L-rhamnopyranoside (**196**). $[\alpha]_D$ −64° (*c*, 0.7. $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.31 (d, $J_{5,6}$=6.5 Hz, H-6), 3.23 (t, $J_{3,4}$=$_{4,5}$=9.5 Hz, H-4), 3.37 (s, OMe), 3.67 (m, H-5), 3.89 (dd, $J_{2,3}$=4 Hz, H-3), 3.98 (dd, *J*=1.5 Hz, H-2), 4.79 (d, H-1).

Anal. ($C_{12}H_{22}O_6$) C, H.

2-Methoxyethyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**10**). To a solution of **9** (1.00 g) in $CHCl_3$ (3.0 ml) containing AcBr (1.00 ml) was added H_2O (0.20 ml) at 0 °C; the mixture was then stirred for 1.5 h at 20 °C. After concentration and co-evaporation with toluene at 30 °C in vacuo, the residue was dissolved in chilled $MeNO_2$ (2.4 ml) and 2,6-dimethylpyridine (0.98 ml) and then MEOH (0.61 ml) were added into the solution under stirring. After standing overnight, the solution was diluted with toluene and washed with aq $NaHCO_3$ (5%) thoroughly. The organic layer was concentrated and then stirred in $PhCH_2Cl$ (20 ml) containing KOH (10 g) for 2 h at 120 °C. The mixture was cooled, diluted with toluene and cold H_2O, and then washed well with H_2O. The concentration and subsequent chromatogrphy on alumina (Woelm, 02084), developed with hexane, IPE, and then 2-butanone, afforded an oily benzylated orthoester. That was then treated with $BF_3 \cdot Et_2O$ (12 μl) in CH_2Cl_2 (15 ml) for 5 min at room temp. Processing and chromatography (HE system) gave **10** (0.68 g, 48%), $[\alpha]_D$ +0.8° (*c* 1.0, $CHCl_3$).

Anal. ($C_{32}H_{38}O_8$) C, H.

The acetates **37**, **74**, **105**, and **126** were similarly converted into the 2-acetates **38** (44%), **75** (49%), **106** (50%), and **129** (43%), respectively.

2-Methoxyethyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranoside (**38**). $[\alpha]_D$ +2° (*c* 6.5, $CHCl_3$).

Anal. ($C_{32}H_{38}O_8$) C, H.

2-Methoxyethyl 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (**75**). $[\alpha]_D$ +27° (*c* 3.8, $CHCl_3$).

Anal. ($C_{32}H_{38}O_8$) C, H.

2-Methoxyethyl 2-*O*-Acetyl-3,4-di-*O*-benzyl-β-D-xylopyranoside (**106**). $[\alpha]_D$ −13° (*c* 5.6, $CHCl_3$).

Anal. ($C_{24}H_{30}O_7$) C, H.

2-Methoxyethyl 2-*O*-Acetyl-3,4-di-*O*-benzyl-α-L-arabinopyranoside (**129**). Mp 60—62 °C (from hexane), $[\alpha]_D$ −9° (*c* 0.9, $CHCl_3$).

Anal. ($C_{24}H_{30}O_7$) C, H.

2-Methoxyethyl 2-*O*-Acetyl-3,4-di-*O*-benzyl-β-L-fucopyranoside (**156**). A mixture of **151** (572 mg) and AcBr (2.9 ml) was stirred for 1 h at 25 °C. After quick concentration and co-evaporation with toluene at 30 °C in vacuo, the residue was dissolved in chilled $MeNO_2$ (3 ml) and the treated with 2,6-dimethylpyridine (2.4 ml) and MEOH (1.5 ml) at room temp overnight. Subsequent processing, benzylation, and rearrangement were carried out as described for **10** to give **156** (383 mg, 25%), mp 84—85 °C (from hexane), $[\alpha]_D$ +1° (*c* 1.1, $CHCl_3$).

Anal. ($C_{25}H_{32}O_7$) C, H.

2-Methoxyethyl 2-*O*-Acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (**183**). Similarly, **178** (monohydrate, 572 mg) was converted into **183** (645.8 mg, 46%), $[\alpha]_D$ −17° (*c* 5.2, $CHCl_3$).

Anal. ($C_{25}H_{32}O_7$) C, H.

2-Methoxyethyl 3-*O*-Allyl-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (**51**). Benzylation of **56** (172 mg) with $PhCH_2Cl$ (1.5 ml) and KOH (0.37 g) for 2 h at 120 °C and chromatography (HE system) delivered **51** (208 mg, 81%), $[\alpha]_D$ −14° (*c* 2.3, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.40 (s, OMe), 3.46 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=3 Hz, H-3), 3.82 (dd, $J_{1,2}$=8 Hz, H-2), 3.90 (d, $J_{4,5}$=0 Hz, H-4), 4.43 (d, H-1), 5.98 (m, allyl).

Anal. ($C_{33}H_{40}O_7$) C, H.

The diols **90**, **137**, **164**, and **196** were similarly converted into **84** (78%), **132** (75%), **159** (74%), and **197** (83%), respectively.

2-Methoxyethyl 3-*O*-Allyl-2,4,6-tri-*O*-benzyl-α-D-mannopyranoside (**84**). $[\alpha]_D$ +31° (*c* 1.1, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.33 (s, OMe), 4.91 (d, $J_{1,2}$=1.5 Hz, H-1), 5.95 (m, allyl).

Found: C, 71.82; H, 7.33%. Calcd for $C_{33}H_{40}O_7$: C, 72.24; H, 7.35%.

2-Methoxyethyl 2-*O*-Allyl-3,4-di-*O*-benzyl-α-L-arabinopyranoside (**132**). $[\alpha]_D$ −1.2° (*c* 1.4, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.25 (dd, $J_{4,5ax}$=1.5 Hz, $J_{5eq,5ax}$=13 Hz, H-5ax), 3.38 (s, OMe), 3.46 (dd, $J_{2,3}$=9 Hz, $J_{3,4}$=3.5 Hz, H-3), 3.70 (dd, $J_{1,2}$=7.5 Hz, H-2), 4.01 (dd, $J_{4,5eq}$=3 Hz, H-5eq), 4.30 (d, H-1), 5.97 (m, allyl).

Anal. ($C_{25}H_{32}O_6$) C, H.

2-Methoxyethyl 2-*O*-Allyl-3,4-di-*O*-benzyl-β-L-fucopyranoside (**159**). $[\alpha]_D$ +24° (*c* 0.7, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.15 (d, $J_{5,6}$=6.5 Hz, H-6), 3.37 (s, OMe), 3.43 (m, $J_{4,5}$=1.5 Hz, H-5), 3.45 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=3.5 Hz, H-3), 3.52 (dd, H-4), 3.68 (dd, $J_{1,2}$=7.5 Hz, H-1), 4.29 (d, H-1), 5.99 (m, allyl).

Anal. ($C_{26}H_{34}O_6$) C, H.

2-Methoxyethyl 4-*O*-Allyl-2,3-di-*O*-benzyl-α-L-rhamnopyranoside (**197**). $[\alpha]_D$ −44° (*c* 1.0, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.32 (d, 6.5 Hz, H-6), 3.34 (s, OMe), 3.66 (m, $J_{5,6}$=10 Hz, H-5), 4.79 (d, $J_{1,2}$=1.5 Hz, H-1), 5.94 (m, allyl).

Anal. ($C_{26}H_{34}O_6$) C, H.

2-Methoxyethyl 4-*O*-Allyl-2,3,6-tri-*O*-benzyl-α-D-galactopyranoside (**61**). The monohydroxy compound **63** (163 mg) was stirred in $PhCH_2Cl$ (1.0 ml) containing NaH (60%, 100 mg, 7 equiv) for 2 h at 120 °C. Processing and chromatography (HE system) furnished **61** (148 mg, 76%), $[\alpha]_D$ −2.5° (*c* 0.8, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.37 (s, OMe), 3.47 (dd, $J_{2,3}$=10.5 Hz, $J_{3,4}$=3 Hz, H-3), 3.73 (dd, $J_{1,2}$=7.5 Hz, H-1), 3.81

(d, $J_{4,5}$=0 Hz, H-4), 4.39 (d, H-1), 5.90 (m, allyl).

Anal. ($C_{33}H_{40}O_7$) C, H.

Similar benzylations of **149**, **176**, and **203** afforded **147** (79%), **174** (93%), and **186** (85%).

2-Methoxyethyl 4-*O*-Allyl-2,3-di-*O*-benzyl-α-L-arabinopyranoside (**147**). $[\alpha]_D$ +0.8° (*c* 0.5, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.29 (dd, $J_{4,5ax}$=1.5 Hz, $J_{5eq,5ax}$=13 Hz, H-5ax), 3.38 (s, OMe), 3.51 (dd, $J_{2,3}$=9 Hz, $J_{3,4}$=4 Hz, H-3), 3.77 (dd, $J_{1,2}$=7 Hz, H-2), 4.16 (d, H-1), 5.95 (m, allyl).

Found: C, 70.29; H, 7.02%. Calcd for $C_{25}H_{32}O_6$: C, 70.07; H, 7.53%.

2-Methoxyethyl 4-*O*-Allyl-2,3-di-*O*-benzyl-α-L-fucopyranoside (**174**). $[\alpha]_D$ +1.4° (*c* 0.5, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.28 (d, $J_{5,6}$=6.5 Hz, H-6), 3.37 (dd, OMe), 3.75 (dd, $J_{1,2}$=7.4 Hz, $J_{2,3}$=9 Hz, H-2), 4.36 (d, H-1), 5.95 (m, allyl).

Anal. ($C_{26}H_{34}O_6$) C, H.

2-Methoxyethyl 2-*O*-Allyl-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (**186**). $[\alpha]_D$ −42° (*c* 1.1, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.32 (d, $J_{5,6}$=6 Hz, H-6), 3.36 (s, OMe), 3.83 (dd, $J_{1,2}$= 1.5 Hz, $J_{2,3}$=3 Hz, H-2), 3.87 (dd, $J_{3,4}$=9.5 Hz, H-3), 4.80 (d, H-1), 5.94 (m, allyl).

Found: C, 70.25; H, 7.67%. Calcd for $C_{23}H_{34}O_6$: C, 70.56; H, 7.74%.

2-Methoxyethyl 2,4,6-Tri-*O*-benzyl-β-D-glucopyranoside (**15**). To a stirring solution of **2**[12] (2.03 g) in $PhCH_2Cl$ (40 ml) was added crushed NaOH (1.7 g) and the mixture was vigorously stirred for 2.5 h at 100 °C. Processing and chromatography (TB system) gave **3** (0.15 g, 5%) and **15** (1.00 g, 39%), $[\alpha]_D$ +6° (*c* 3.3, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.31 (dd, $J_{1,2}$=8 Hz, $J_{2,3}$=9 Hz, H-2), 3.39 (s, OMe), 4.44 (d, H-1).

Anal. ($C_{30}H_{36}O_7$) C, H.

Further elution gave **21** (0.18 mg, 7%) and **12** (0.20 g, 8%).

2-Methoxyethyl 3,4,6-Tri-*O*-benzyl-β-D-galactopyranoside (**40**). A reaction of **33** (180 mg) with $PhCH_2Cl$ (1.8 ml) and crushed KOH (220 mg) in DME (1.8 ml) was conducted under stirring for 2.5 h at 85 °C. The processed mixture of products was chromatographed (TB system) to deliver **35** (34 mg, 13%), **47** (38 mg, 17%), **48** (29 mg, 13%), and then **40** (61 mg, 27%), $[\alpha]_D$ −9° (*c* 3.5, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.37 (s, OMe), 3.46 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=3 Hz, H-3), 3.90 (d, $J_{4,5}$=0 Hz, H-4), 4.00 (dd, $J_{1,2}$=8 Hz, H-2), 4.30 (d, H-1).

Anal. ($C_{30}H_{36}O_7$) C, H.

2-Methoxyethyl 3-*O*-Acetyl-2,4,6-tri-*O*-benzyl- and 4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-α-D-mannopyranosides (**80** and **81**). A mixture of **71** (0.98 g), $PhCH_2Cl$ (19 ml), and crushed KOH (1.08 g) was stirred efficiently for 4 h at 110 °C. Processing and chromatography (TB system) afforded **72** (0.18 g, 7%) and then a mixture of **83** and **92**, which was acetylated with Ac_2O (5 ml) and pyridine (1 ml). After concentration and co-evaporation with toluene, the residue was chromatographed (TB system) to deliver **81** (0.46 g, 20%), $[\alpha]_D$ +19° (*c* 2.6, $CHCl_3$) and then **80** (0.80 g, 35%), $[\alpha]_D$ +11° (*c* 1.4, $CHCl_3$).

Anal. ($C_{32}H_{38}O_8$) **80**, C, H. **81**, C, H.

When benzylation of **71** (2.0 g) was carried out using $PhCH_2Cl$ (40 ml) and LiOH (2.7 g) for 6.5 h at 130 °C, followed by the sequential process described above, to give **81** (1.21 g, 26%), **80** (0.10 g, 2%) were obtained.

2-Methoxyethyl 2,3,6-Tri-*O*-benzyl-β-D-glucopyranoside (**21**). Benzylation of **20**[7] (2.47 g) with $PhCH_2Cl$ (25 ml) and NaH (60%, 0.30 g, 1.3 equiv) under stirring for 1 h at 100 °C and chromatography (TB system) furnished **3** (0.23 g, 7%) and **21** (1.99 g, 66%), $[\alpha]_D$ −18° (*c* 2.3, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.39 (s, OMe), 4.47 (d, $J_{1,2}$=7.5 Hz, H-1).

Found: C, 70.34; H, 7.23%. Calcd for $C_{30}H_{34}O_7$: C, 70.84; H, 7.13%.

Further elution gave **22** (0.54 g, 18%).

The diols **57** and **91** were similarly benzylated to afford **48** (77%) and **58** (5%), and **92** (61%) and **93** (7%), respectively.

2-Methxyethyl 2,3,6-Tri-*O*-benzyl-β-D-galactopyranoside (**48**). $[\alpha]_D$ −4° (*c* 1.1, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.38 (s, OMe), 3.50 (dd, $J_{2,3}$=9.5 Hz, $J_{3,4}$=4 Hz, H-3), 3.56 (m, $J_{4,5}$=1 Hz, $J_{5,6a}$=$J_{5,6b}$=5.5 Hz, H-5), 3.67 (dd, $J_{1,2}$=7.5 Hz, H-2), 3.72 (dd, $J_{6a,6b}$=10 Hz, H-6b), 3.80 (dd, H-6a), 4.02 (dd, H-4), 4.41 (d, H-1).

Anal. ($C_{30}H_{36}O_7$) C, H.

2-Methoxyethyl 2,3,6-Tri-*O*-benzyl-α-D-mannopyranoside (**92**). $[\alpha]_D$ +1.3° (*c* 1.4, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.36 (s, OMe), 3.89 (dd, $J_{1,2}$=2 Hz, $J_{2,3}$=3.5 Hz, H-2), 4.07 (t, $J_{3,4}$=$J_{4,5}$= 10 Hz, H-4), 4.96 (d, H-1).

Found: C, 70.32; H, 7.20%. Calcd for $C_{30}H_{36}O_7$: C, 70.84; H, 7.17%.

2-Methoxyethyl 2,3-Di-*O*-benzyl-α-L-arabinopyranoside (**140**). Benzylation of the diol **138** (150 mg) with $PhCH_2Cl$ (3 ml) and LiOH (60 mg, 5 equiv) for 2 h at 130 °C and chromatography (TB system) delivered **127** (45 mg, 19%), **139** (9 mg, 5%), and then **140** (56 mg, 29%), $[\alpha]_D$ +6° (*c* 1.0) ^1H NMR ($CDCl_3$) δ=3.38 (s, OMe), 3.43 (dd, $J_{4,5ax}$=1.5 Hz, $J_{5eq,5ax}$=13 Hz, H-5ax), 3.54 (dd, $J_{2,3}$=8.5 Hz, $J_{3,4}$=4 Hz, H-3), 3.67 (dd, $J_{1,2}$=7 Hz, H-1), 3.92 (m, $J_{4,5eq}$=3.5 Hz, H-4), 4.00 (dd, H-5eq), 4.37 (d, H-1).

Anal. ($C_{22}H_{28}O_6$) C, H.

The diols **46** (7 equiv of LiOH, 7 h) and **165** (7 equiv of LiOH, 7 h) similarly yielded **47** (20%, the faster-moving) and **48** (32%, the slower-moving), as well as **166** (14%, the faster-moving) and **167** (32%, the slower-moving), respectively.

2-Methoxyethy 2,3-Di-*O*-benzyl-β-L-fucopyranoside (**167**). $[\alpha]_D$ −3° (*c* 0.8, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.34 (d, $J_{5,6}$=6.5 Hz, H-6), 3.38 (s, OMe), 3.49 (dd, $J_{2,3}$=9.5 Hz, $J_{3,4}$=2.5 Hz, H-3), 3.52 (m, $J_{4,5}$=1 Hz, H-5), 3.62 (dd, $J_{1,2}$=7.5 Hz, H-2), 4.37 (d, H-1).

Anal. ($C_{23}H_{30}O_6$) C, H.

2-Methoxyethyl 2,4,6-Tri-*O*-benzyl-β-D-galactopyranoside (**47**). A mixture of **46** (188 mg), $PhCH_2Cl$ (1.5 ml), KOH (53 mg, 2.1 equiv), and DME (1.5 ml) was stirred for 1.5 h at 70 °C, followed by processing and chromatography (TB system), to give **35** (42 mg, 16%) and then **47** (131 mg, 57%), $[\alpha]_D$ −1° (*c*1.3, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.38 (s, OMe), 3.61 (dd, $J_{1,2}$=7 Hz, $J_{2,3}$=9.5 Hz, H-2), 3.67 (dd, $J_{3,4}$=3 Hz, H-3), 3.87 (d, $J_{4,5}$=0 Hz, H-4), 4.41 (d, H-1).

Found: C, 70.42; H, 7.08%. Calcd for $C_{30}H_{36}O_7$: C, 70.84; H, 7.13%.

Further elution gave **48** (42 mg, 8%).

The diols **138**, **165**, and **202** were similarly benzylated to give **139** (50%) and **140** (22%), and **166** (65%) and **167** (16%), and **190**, (73%, the faster-moving) and **185** (9%, the slower-moving), respectively.

2-Methoxyethyl 2,4-Di-*O*-benzyl-α-L-arabinopyranoside (**139**). Mp 65—66 °C, $[\alpha]_D$ −10° (*c* 0.7, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.37 (s, OMe), 3.47 (dd, $J_{4,5b}$=3 Hz, $J_{5a,5b}$=11 Hz, H-5b), 3.63 (dd, $J_{1,2}$=4.5 Hz, $J_{2,3}$=2 Hz, H-2), 3.80 (m, $J_{3,4}$=3 Hz, $J_{4,5a}$=6 Hz, H-4), 3.97 (dd, H-5a), 4.55 (d, H-1).

Anal. ($C_{22}H_{28}O_6$) C, H.

2-Methoxyethyl 2,4-Di-*O*-benzyl-β-L-fucopyranoside (**166**). $[\alpha]_D$ −12° (*c* 0.9, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.24 (d, $J_{5,6}$=6.5 Hz, H-6), 3.38 (s, OMe), 4.37 (d, $J_{1,2}$=7.5 Hz, H-1).

Anal. ($C_{23}H_{30}O_6$) C, H.

2-Methoxyethyl 3-*O*-Allyl-2,4,6-tri-*O*-benzyl- and 2-*O*-Allyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosides (**53** and **55**). A mixture of **53** (1.00 g), allyl bromide (9 ml), KOH (0.28 g, 1.6 equiv), and DME (9 ml) was stirred for 1.5 h at 70 °C. Processing and chromatography (TB system) gave the diallyl ether (0.25 g, 20%) and then **55** (0.25 g, 22%), $[\alpha]_D$ −8° (*c* 4.4, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.38 (s, OMe), 3.40 (m, $J_{4,5}$=$J_{5,6a}$=1.5 Hz, $J_{5,6b}$=2 Hz, H-5), 3.51 (dd, $J_{1,2}$=8 Hz, $J_{2,3}$=9.5 Hz, H-2), 3.67 (dd, $J_{3,4}$=4 Hz, H-3), 4.04 (dd, $J_{6a,6b}$=12.5 Hz, H-6b), 4.19 (dd, H-4), 4.29 (dd, H-6a), 4.38 (d, H-1), 5.53 (s, benzylidene).

Further elution afforded **54** (0.52 g, 46%), mp 147—149 °C (from IPE), $[\alpha]_D$ +38° (*c* 0.7, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.39 (s, OMe), 3.48 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=4 Hz, H-3), 3.99 (dd, $J_{1,2}$=8 Hz, H-2), 4.07 (dd, $J_{5,6b}$=2 Hz, $J_{6a,6b}$=12 Hz, H-6b), 4.22 (dd, $J_{5,6a}$=1.5 Hz, H-6a), 4.39 (d, H-1), 5.53 (s, benzylidene).

Found: **54**, C, 61.92; H, 7.07%. **55**, C, 61.93; H, 7.18%. Calcd for $C_{19}H_{25}O_7$: C, 62.45; H, 6.90%.

The diols **46** (3 equiv of KOH, 1 h), **86** (3 equiv of KOH, 2 h), **138** (1.7 equiv of KOH, 45 min), **165** (2 equiv of KOH, 45 min), and **202** (3 equiv of KOH, 1.5 h) were similarly allylated to yield **63** (50%, the faster-moving) and **64** (9%, the slower-moving), **88** (40%, the slower-moving) and **89** (11%, the faster-moving), **149** (56%, the faster-moving) and **150** (21%, the slower-moving), **176** (66%, the faster-moving) and **177** (26%, the slower-moving), as well as **203** (51%, the faster-moving) and **204** (29%, the solwer-moving), respectively.

2-Methoxyethyl 4- and 3-*O*-Allyl-2,6-di-*O*-benzyl-β-D-galactopyranosides (**63** and **64**). **63**, $[\alpha]_D$ −4° (*c* 1.0, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.37 (s, OMe), 3.53 (dd, $J_{1,2}$=7.5 Hz, $J_{2,3}$=9.5 Hz, H-2), 4.38 (d, H-1), 5.88 (m, allyl). **64**, $[\alpha]_D$ +7° (*c* 0.7, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.38 (s, OMe), 3.40 (dd, $J_{2,3}$=9.5 Hz, $J_{3,4}$=3.5 Hz, H-3), 3.60 (dd, $J_{1,2}$=8 Hz, H-2), 4.40 (d, H-1), 5.93 (m, allyl).

Anal. ($C_{26}H_{34}O_6$) **63**, C, H. **64**, C, H.

2-Methoxyethyl 3- and 2-*O*-Allyl-4,6-*O*-benzylidene-α-D-mannopyranosides (**88** and **89**). **88**, $[\alpha]_D$ +40° (*c* 0.6, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.39 (s, OMe), 4.13 (dd, $J_{1,2}$=1.5 Hz, $J_{2,3}$=4 Hz, H-2), 4.20 (t, $J_{3,4}$=$J_{4,5}$=9 Hz, H-4), 4.93 (d, H-1), 5.59 (m, allyl). **89**, $[\alpha]_D$ +23° (*c* 0.9, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.40 (s, OMe), 4.92 (d, $J_{1,2}$=1.5 Hz, H-1), 5.57 (s, benzylidene).

Found: **88**, C, 62.42; H, 7.17%. **89**, C, 62.49; H, 7.32%. Calcd for $C_{19}H_{25}O_7$: C, 62.45; H, 6.90%.

2-Methoxyethyl 4- and 3-*O*-Allyl-2-*O*-benzyl-α-L-arabinopyranosides (**149** and **150**). **149**, $[\alpha]_D$ −7° (*c* 0.6, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.36 (s, OMe), 3.48 ($J_{4,5b}$=3 Hz, $J_{5a,5b}$=12 Hz, H-5b), 2.61 (dd, $J_{1,2}$=5 Hz, $J_{2,3}$=7 Hz, H-2), 3.73 (dd, $J_{3,4}$=3 Hz, $J_{4,5a}$=6 Hz, H-4), 3.86 (dd, H-3), 3.95 (dd, H-5a), 4.54 (d, H-1), **150**, $[\alpha]_D$ +15° (*c* 0.8, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.38 (s, OMe), 3.60 (dd, $J_{1,2}$=7 Hz, $J_{2,3}$=9 Hz, H-2), 4.35 (d, H-1), 5.92 (m, allyl).

Anal. ($C_{18}H_{26}O_6$) **149**, C, H. **150**, C, H.

2-Methoxyethyl 4- and 3-*O*-Allyl-2-*O*-benzyl-β-L-fucopyranosides (**176** and **177**). **176**, $[\alpha]_D$ −13° (*c* 0.6, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.30 (d, $J_{5,6}$=6.5 Hz, H-6), 3.37 (s, OMe), 3.55 (m, $J_{4,5}$=1 Hz, H-5), 4.36 (d, $J_{1,2}$=7.5 Hz, H-1), 5.93 (m, allyl). **177**, $[\alpha]_D$ −1.4° (*c* 0.7, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.35 (d, $J_{5,6}$=6.5 Hz, H-6), 3.38 (s, OMe), 3.40 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=4 Hz, H-3), 3.54 (m, $J_{4,5}$=1 Hz, H-5), 3.55 (dd, $J_{1,2}$=7.5 Hz, H-2), 3.76 (dd, H-4), 4.37 (d, H-1), 5.93 (m, allyl).

Anal, ($C_{19}H_{28}O_6$) **176**, C, H. **177**, C, H.

2-Methoxyethyl 2- and 3-*O*-Allyl-4-*O*-benzyl-α-L-rhamnopyranosides (**203** and **204**). **203**, $[\alpha]_D$ −32° (*c* 0.9, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.32 (d, $J_{5,6}$=6.5 Hz, H-6), 3.28 (t, $J_{3,4}$=$J_{4,5}$=10 Hz, H-4), 3.37 (s, OMe), 3.68 (m, H-5), 3.70 (dd, $J_{1,2}$=1.5 Hz, $J_{2,3}$=4 Hz, H-2), 3.96 (dd, H-3), 4.84 (d, H-1), 5.93 (m, allyl). **204**, $[\alpha]_D$ −59° (*c* 0.6, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.30 (d, $J_{5,6}$=6.5 Hz, H-6), 3.37 (s, OMe), 3.41 (t, $J_{3,4}$=$J_{4,5}$=10 Hz, H-4), 3.72 (m, H-5), 3.75 (dd, $J_{2,3}$=4 Hz, H-3), 4.07 (dd, $J_{1,2}$=1.5 Hz, H-2), 4.84 (d, H-1), 5.95 (m, allyl).

Anal. ($C_{19}H_{28}O_6$) **203**, C, H. **204**, C, H.

The alcohols, **15**, **21**, **22**, **47**, **48**, **58**, **92**, **93**, **118**, **139**, **140**, **166**, **167**, **190**, and **199** were acetylated with excess Ac_2O in pyridine, followed by chromatographical purification (HE system), to yield the corresponding acetates, **16**, **23**, **28**, **49**, **59**, **66**, **81**, **98**, **119**, **141**, **145**, **168**, **172**, **191**, and **200**.

2-Methoxyethyl 3-*O*-Acetyl-2,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**16**). Mp 64—65 °C (from hexane), $[\alpha]_D$ +17° (*c* 1.0, $CHCl_3$).

Anal. ($C_{32}H_{38}O_8$) C, H.

2-Methoxyethyl 4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**23**). $[\alpha]_D$ −13° (*c* 2.3, $CHCl_3$).

Anal. ($C_{32}H_{38}O_8$) C, H.

2-Methoxyethyl 6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (**28**). Mp 80—81 °C (from hexane), $[\alpha]_D$ −32° (*c* 0.9, $CHCl_3$).

Anal. ($C_{32}H_{38}O_8$) C, H.

2-Methoxyethyl 3-*O*-Acetyl-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (**49**). $[\alpha]_D$ +29° (*c* 1.0, $CHCl_3$).

Anal. ($C_{32}H_{38}O_8$) C, H.

2-Methoxyethyl 4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (**59**). $[\alpha]_D$ +11° (*c* 2.0, $CHCl_3$).

Anal. ($C_{32}H_{38}O_8$) C, H.

2-Methoxyethyl 6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-β-D-galactopyranoside (**66**). $[\alpha]_D$ −17° (*c* 2.6, $CHCl_3$).

Anal. ($C_{32}H_{38}O_8$) C, H.

2-Methoxyethyl 6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (**98**). $[\alpha]_D$ +30° (*c* 0.9, $CHCl_3$).

Anal. ($C_{32}H_{38}O_8$) C, H.

2-Methoxyethyl 4-*O*-Acetyl-2,3-di-*O*-benzyl-β-D-xylopyranoside (**119**). $[\alpha]_D$ −28° (*c* 0.9, $CHCl_3$).

Anal. ($C_{24}H_{30}O_7$) C, H.

2-Methoxyethyl 3-*O*-Acetyl-2,4-di-*O*-benzyl-α-L-arabinopyranoside (**141**). $[\alpha]_D$ +29° (*c* 0.7, $CHCl_3$).

Anal. ($C_{24}H_{30}O_7$) C, H.

2-Methoxyethyl 4-*O*-Acetyl-2,3-di-*O*-benzyl-α-L-arabinopyranoside (**145**). $[\alpha]_D$ +33° (*c* 0.8, $CHCl_3$).

Found: C, 66.57; H, 7.07%. Calcd for $C_{24}H_{30}O_7$: C, 66.96; H, 7.05%.

2-Methoxyethyl 3-*O*-Acetyl-2,4-di-*O*-benzyl-β-L-fucopyranoside (**168**). $[\alpha]_D$ −41° (*c* 0.6, $CHCl_3$).

Anal. ($C_{25}H_{32}O_7$) C, H.

2-Methoxyethyl 4-*O*-Actyl-2,3-di-*O*-benzyl-β-L-fucopyranoside (**172**). $[\alpha]_D$ −29° (*c* 0.6, $CHCl_3$).

Anal. ($C_{25}H_{32}O_7$) C, H.

2-Methoxyethyl 3-*O*-Acetyl-2,4-di-*O*-benzyl-α-L-rhamonopyranoside (**191**). $[\alpha]_D$ −7° (*c* 0.8, $CHCl_3$).

Anal. ($C_{25}H_{32}O_7$) C, H.

2-Methoxyethyl 4-*O*-Acetyl-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (**200**). $[\alpha]_D$ −39° (*c* 0.5, $CHCl_3$)

Anal. ($C_{25}H_{32}O_7$) C, H.

Deacetylation of **10**, **38**, **75**, **80**, **106**, **129**, **156**, and **183** with dil NaOMe (0.6%) at room temp, followed by chromatography (TB system), furnished the corresponding alcohols, **12**, **40**, **77**, **83**, **108**, **131**, **158**, and **185**.

2-Methoxyethyl 3,4,6-Tri-*O*-benzyl-β-D-glucopyranoside (**12**). $[\alpha]_D$ −6° (*c* 7.4, $CHCl_3$). ^1H NMR ($CDCl_3$) δ=3.40 (s, OMe), 4.32 (d, $J_{1,2}$=7 Hz, H-1).

Anal. ($C_{30}H_{36}O_7$).

2-Methoxyethyl 3,4,6-Tri-*O*-benzyl-α-D-mannopyranoside (**77**). $[\alpha]_D$ +44° (*c* 1.0, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.37 (s, OMe), 3.88 (t, $J_{3,4}=J_{4,5}$=8.5 Hz, H-4), 3.95 (dd, $J_{2,3}$=3.5 Hz, H-3), 4.14 (dd, $J_{1,2}$=2 Hz, H-2), 4.97 (d, H-1).

Found: C, 70.29; H, 7.12%. Calcd for $C_{30}H_{36}O_7$: C, 70.84; H, 7.13%.

2-Methoxyethyl 2,4,6-Tri-*O*-benzyl-α-D-mannopyranoside (**83**). $[\alpha]_D$ +16° (*c* 1.1, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.35 (s, OMe), 4.99 (d, $J_{1,2}$=1.5 Hz, H-1).

Anal. ($C_{30}H_{36}O_7$) C, H.

2-Methoxyethyl 3,4-Di-*O*-benzyl-β-D-xylopyranoside (**108**). $[\alpha]_D$ −27° (*c* 2.2, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.28 (dd, $J_{4,5ax}$=9 Hz, $J_{5eq,5ax}$=12 Hz, H-5ax), 3.39 (s, OMe), 3.98 (dd, $J_{4,5eq}$=4.5 Hz, H-5eq), 4.33 (d, $J_{1,2}$=8 Hz, H-1).

Anal. ($C_{22}H_{28}O_6$) C, H.

2-Methoxyethyl 3,4-Di-*O*-benzyl-α-L-arabinopyranoside (**131**). $[\alpha]_D$ +23° (*c* 0.4, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.29 (d, $J_{4,5ax}$=0 Hz, $J_{5eq,5ax}$=13 Hz, H-5ax), 3.39 (s, OMe), 3.41 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=3 Hz, H-3), 3.69 (dd, $J_{4,5eq}$=2.5 Hz, H-4), 4.00 (dd, $J_{1,2}$=7.5 Hz, H-2), 4.07 (dd, H-5eq), 4.22 (d, H-1).

Anal. ($C_{22}H_{28}O_6$) C, H.

2-Methoxyethyl 3,4-Di-*O*-benzyl-β-L-fucopyranoside (**158**). $[\alpha]_D$ +13° (*c* 0.8, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.21 (d, $J_{5,6}$=6.5 Hz, H-6), 3.38 (s, OMe), 3.45 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=3 Hz, H-3), 3.50 (m, $J_{4,5}$=1.5 Hz, H-5), 3.98 (dd, $J_{1,2}$=7.5 Hz, H-1), 4.26 (d, H-1).

Found: C, 68.25; H, 7.50%. Calcd for $C_{23}H_{30}O_6$: C, 68.64; H, 7.15%.

2-Methoxyethyl 3,4-Di-*O*-benzyl-α-L-rhamnopyranoside (**185**). $[\alpha]_D$ −31° (*c* 1.3, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.33 (d, $J_{5,6}$=6 Hz, H-6), 3.38 (s, OMe), 3.47 (t, $J_{3,4}=J_{4,5}$=10 Hz, H-4), 3.89 (dd, $J_{2,3}$=4 Hz, H-3), 4.12 (dd, $J_{1,2}$=1.5 Hz, H-2), 4.86 (d, H-1).

Anal. ($C_{23}H_{30}O_6$) C, H.

2-Methoxyethyl 2,3-Di-*O*-benzyl-α-L-rhamnopyranoside (**199**). The allyl ether **197** (417 mg) was deallylated through the published method,[21] followed by chromatography (TB system), to produce **199** (202 mg, 53%), $[\alpha]_D$ −2° (*c* 1.1, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.32 (d, $J_{5,6}$=6 Hz, H-6), 3.37 (s, OMe), 3.88 (dd, $J_{1,2}$=1.5 Hz, $J_{2,3}$=2.5 Hz, H-2), 4 87 (d, H-1).

Anal. ($C_{23}H_{30}O_6$) C, H.

The monohydroxy alcohols **12**, **15**, **21**, **22**, **40**, **47**, **48**, **58**, **77**, **83**, **92**, **93**, **108**, **111**,[6] **118**, **131**, **139**, **140**, **158**, **166**, **167**, **185**, and **190** were allylated by refluxing in neat allyl bromide containing excess NaH, followed by chromatographical purification (HE system), to furnished the corresponding allyl ethers **13**, **18**, **25**, **30**, **41**, **51**, **61**, **68**, **78**, **84**, **95**, **100**, **109**, **112**, **121**, **132**, **143**, **147**, **159**, **170**, **174**, **186**, and **193**.

2-Methoxyethyl 2-*O*-Allyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**13**). $[\alpha]_D$ −13° (*c* 2.9, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.33 (dd, $J_{1,2}$=8 Hz, $J_{2,3}$=9 Hz, H-2), 3.37 (s, OMe), 3.53 (t, $J_{3,4}=J_{4,5}$=9 Hz, H-4), 3.59 (t, H-3), 4.35 (d, H-1), 5.94 (m, allyl).

Anal. ($C_{33}H_{40}O_7$) C, H.

2-Methoxyethyl 3-*O*-Allyl-2,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**18**). Mp 58—59 °C (from hexane), $[\alpha]_D$ +7.3° (*c* 0.4, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.39 (s, OMe), 4.40 (d, $J_{1,2}$=7.5 Hz, H-1), 5.96 (m, allyl).

Anal. ($C_{33}H_{40}O_7$) C, H.

2-Methoxyethyl 4-*O*-Allyl-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**25**). Mp 118—119 °C (from IPE), $[\alpha]_D$ +20° (*c* 2.8, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.39 (s, OMe), 3.44 (dd, $J_{1,2}$=8 Hz, $J_{2,3}$=9 Hz, H-2), 4.44 (d, H-1), 5.82 (m, allyl).

Anal. ($C_{33}H_{40}O_7$) C, H.

2-Methoxyethyl 6-*O*-Allyl-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (**30**). Mp 59—60 °C (from hexane), $[\alpha]_D$ +2° (*c* 0.3, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.39 (s, OMe), 3.46 (m, $J_{4,5}$=9 Hz, $J_{5,6}$=2 and 5 Hz, H-5), 3.49 (dd, $J_{1,2}$=7.5 Hz, $J_{2,3}$=9 Hz, H-2), 3.59 (t, $J_{3,4}$=9 Hz, H-3), 3.68 (t, H-3), 4.45 (d, H-1).

Anal. ($C_{33}H_{40}O_7$) C, H.

2-Methoxyethyl 2-*O*-Allyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranoside (**41**). $[\alpha]_D$ −22° (*c* 1.0, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.37 (s, OMe), 3.46 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=3 Hz, H-3), 3.70 (dd, $J_{1,2}$=7.5 Hz, H-2), 3.86 (d, $J_{4,5}$=0 Hz, H-4), 4.33 (d, H-1), 5.91 (m, allyl).

Anal. ($C_{33}H_{40}O_7$) C, H.

2-Methoxyethyl 6-*O*-Allyl-2,3,4-tri-*O*-benzyl-β-D-galactopyranoside (**68**). $[\alpha]_D$ −1° (*c* 3.5, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.37 (s, OMe), 3.84 (dd, $J_{1,2}$=7.5 Hz, $J_{2,3}$=10 Hz, H-2), 4.41 (d, H-1), 5.89 (m, allyl).

Anal. ($C_{33}H_{40}O_7$) C, H.

2-Methoxyethyl 2-*O*-Allyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (**78**). $[\alpha]_D$ +38° (*c* 3.0, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.36 (s, OMe), 3.85 (dd, $J_{1,2}$=2 Hz, $J_{2,3}$=1.5 Hz, H-2), 4.92 (d, H-1), 5.94 (m, allyl).

Anal. ($C_{33}H_{40}O_7$) C, H.

2-Methoxyethyl 4-*O*-Allyl-2,3,6-tri-*O*-benzyl-α-D-mannopyranoside (**95**). $[\alpha]_D$ +31° (*c* 1.0, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.34 (s, OMe), 4.92 (d, $J_{1,2}$=1.5 Hz, H-1), 5.84 (m, allyl).

Found: C, 71.60; H, 7.47%. Calcd for $C_{33}H_{40}O_7$: C, 72.24; H, 7.45%.

2-Methoxyethyl 6-*O*-Allyl-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (**100**). $[\alpha]_D$ +27° (*c* 2.2, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.34 (s, OMe), 3.88 (dd, $J_{1,2}$=2 Hz, $J_{2,3}$=3 Hz, H-2), 4.92 (d, H-1), 5.93 (m, allyl).

Found: C, 71.84; H, 7.41%. Calcd for $C_{33}H_{40}O_7$: C, 72.24; H, 7.35%.

2-Methoxyethyl 2-*O*-Allyl-3,4-di-*O*-benzyl-β-D-xylopyranoside (**109**). $[\alpha]_D$ −18° (*c* 2.0, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.18 (dd, $J_{4,5ax}$=10 Hz, $J_{5eq,5ax}$=11.5 Hz, H-5ax), 3.27 ($J_{1,2}$= 7.5 Hz, $J_{2,3}$=9 Hz, H-2), 3.38 (s, OMe), 3.51 (t, $J_{3,4}$=9 Hz, H-3), 3.91 (dd, $J_{4,5eq}$=5 Hz, H-5eq), 4.31 (d, H-1), 5.95 (m, allyl).

Anal. ($C_{25}H_{32}O_6$) C, H.

2-Methoxyethel 3-*O*-Allyl-2,4-di-*O*-benzyl-β-D-xylopyranoside (**112**). $[\alpha]_D$ −4 ° (*c* 1.5, $CHDCl_3$), ^1H NMR ($CDCl_3$) δ=3.17 (dd, $J_{4,5ax}$=10 Hz, $J_{5eq,5ax}$=11.5 Hz, H-5ax), 3.33 (dd, $J_{1,2}$=7.5 Hz, $J_{2,3}$=9 Hz, H-2), 3.38 (s, OMe), 3.43 (t, $J_{3,4}$=9 Hz, H-3), 3.55 (m, $J_{4,5eq}$=5 Hz, H-4), 3.90 (dd, H-5eq), 4.34 (d, H-1), 5.97 (m, allyl).

Anal. ($C_{25}H_{32}O_6$). C, H.

2-Methoxyethyl 4-*O*-Allyl-2,3-di-*O*-benzyl-β-D-xylopyranoside (**121**). $[\alpha]_D$ +2° (*c* 0.8, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.18

(dd, $J_{4,5ax}$=10 Hz, $J_{5eq,5ax}$=11.5 Hz, H-5ax), 3.39 (s, OMe), 4.38 (d, $J_{1,2}$=8 Hz, H-1), 5.89 (m, allyl).

Anal. ($C_{25}H_{32}O_6$) C, H.

2-Methoxyethyl 3-*O*-Allyl-2,4-di-*O*-benzyl-α-L-arabinopyranoside (**143**). $[\alpha]_D$ +11° (*c* 0.7, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=3.39 (dd, $J_{4,5ax}$=1.5 Hz, $J_{5eq,5ax}$=13 Hz, H-5ax), 3.48 (s, OMe), 3.53 (dd, $J_{2,3}$=9.5 Hz, $J_{3,4}$=4 Hz, H-3), 3.87 (dd, $J_{1,2}$=7 Hz, H-2), 4.13 (dd, $J_{4,5eq}$=3 Hz, H-5eq), 4.46 (d, H-1), 6.01 (m, allyl).

Found: C, 69.58; H, 7.49%. Calcd for $C_{25}H_{32}O_6$: C, 70.07; 7.53%.

2-Methoxyethyl 3-*O*-Allyl-2,4-di-*O*-benzyl-β-L-fucopyranoside (**170**). $[\alpha]_D$ +15° (*c* 0.8, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.18 (d, $J_{5,6}$=6.5 Hz, H-6), 3.37 (s, OMe), 3.41 (dd, $J_{2,3}$=10 Hz, $J_{3,4}$=3 Hz, H-3), 3.45 (m, $J_{4,5}$=1 Hz, H-5), 3.54 (dd, H-4), 3.75 (dd, $J_{1,2}$=7.5 Hz, H-2), 4.35 (d, H-1), 5.95 (m, allyl).

Found: C, 70.25; H, 7.85%. Calcd for $C_{26}H_{34}O_6$: C, 70.56; H, 7.74%.

2-Methoxyethyl 3-*O*-Allyl-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (**193**). $[\alpha]_D$ −44° (*c* 0.4, $CHCl_3$), ^1H NMR ($CDCl_3$) δ=1.32 (d, $J_{5,6}$=6 Hz, H-6), 3.34 (s, OMe), 3.57 (t, $J_{3,4}$=$J_{4,5}$=10 Hz, H-4), 3.68 (m, H-5), 3.76 (dd, $J_{2,3}$=3.5 Hz, H-3), 3.82 (dd, $J_{1,2}$=2 Hz, H-2), 4.79 (d, H-1), 5.95 (m, allyl).

Found: C, 70.24; H, 7.67%. Calcd for $C_{25}H_{34}O_6$: C, 70.56; H, 7.74%.

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