The Stereoselective Dehydrative α-Glucosylation Using 6-*O*-Acetyl- and 6-*O*-*p*-Nitrobenzoyl-2,3,4-tri-*O*-benzyl-D-glucopyranoses

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The stereoselective synthesis of α-linked glucobiose derivatives using 6-*O*-acetyl- or 6-*O*-*p*-nitrobenzoyl-2,3,4-tri-*O*-benzyl-D-glucopyranose and a ternary mixture of *p*-nitrobenzenesulfonyl chloride, silver trifluoromethanesulfonate, and triethylamine in dichloromethane is described.

Many methods for systematic oligosaccharide synthesis have been reported.[1] Except for one unique approach,[2] all use the Koenigs-Knorr reaction and relatives[3] to form an interglycosidic linkage. Our objective has been to develop a reagent which will activate the anomeric center of a protected glycose like 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (**1**) in the presence of the alcohol to be glycosylated, in order to simplify the glycosylation procedure as written by Eq. 1[4] (G denotes 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl residue and equivalents):[5a,b]

$$\mathrm{GOH} + \mathrm{ROH} \xrightarrow[-\mathrm{H_2O}]{} \mathrm{GOR}. \qquad (1)$$

Until recently, few attempts have been made to simplify the glycosylation procedure.[4,5] This paper will describe the effect of the acyl group of the modified benzylated glucopyranoses, *i.e.*, 6-*O*-acetyl- and 6-*O*-*p*-nitrobenzoyl-2,3,4-tri-*O*-benzyl-D-glucopyranoses (**2** and **3**), on the selectivity of the dehydrative glucosylation using a ternary mixture of *p*-nitrobenzenesulfonyl chloride (NsCl), silver trifluoromethanesulfonate (AgOTf), and triethylamine (Et_3N) (the NST mixture)[4b] in CH_2Cl_2.

Results and Discussion

The NST mixture was found to undergo the stereoselective β-glucosylation of simple alcohols with **1**.[4b] It was later found, however, that such selectivity was retained only for the glucosylation of a primary hydroxyl group and that the glucosylation of a secondary group proceeded with a poor selectivity in the di- and trisaccharide synthesis using **1** and the NST mixture.[6] Therefore, an additional prerequisite is necessary for the dehydrative glucosylation with **1** and the NST mixture to proceed stereoselectively, irrespective of the reactivity of the hydroxyl group of partially benzylated saccharides. This led us to study the dehydrative glucosylation using the NST mixture and such derivatives of D-glucopyranose as **2** and **3**, since the modified benzylated glucopyranosyl bromides with 6-*O*-acetyl- or 6-*O*-*p*-nitrobenzoyl group are good intermediates for the highly stereoselective α-glucosylation.[7,8]

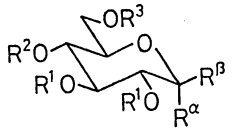
Compound **2** was prepared through the regioselective *O*-deacetylation of 1,6-di-*O*-acetyl-2,3,4-tri-*O*-benzyl-D-glucopyranose (**5**), which is readily available *via* the acetolysis of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (**6**),[9] by either of three reagents: (i) hot methanolic sodium acetate (NaOAc), (ii) benzylamine ($PhCH_2NH_2$) in $CHCl_3$,[10a] and (iii) N_2H_4 in pyridine.[10b] By the treatment of **6** with acetyl bromide (AcBr),[11] followed by hydrolysis in the presence of Ag_2CO_3, **2** was also prepared. The acylation of 2,3,4-tri-*O*-benzyl-β-D-glucopyranose (**7**)[9] with *N*-acetylimidazole[12] gave **2** with a poor regioselectivity, whereas that with *p*-nitrobenzoyl chloride afforded **3** in a good yield.

As expectedly, **2** was condensed with cyclohexanol by the NST mixture to afford the α-glucoside **8a** predominantly, although a similar glucosylation of the alcohol with **1** showed β-selectivity.[4b] The dehydrative glucosylation of the alcohol with **3** also showed α-selectivity. Judging from the temperature of the precipitation of AgCl, the glucosylation using **2** or **3** appears to proceed at a slightly higher temperature (>-10 °C) than that using **1** (<-20 °C), so that a part of such a simple alcohol as cyclohexanol may be sulfonated concurrently to depress the yield of the glucosides significantly.

The α-glucosylation of the primary hydroxyl group of the protected glucopyranoside **10**[8] with **2** proceeded well: the isomaltose derivative[8] **9a** was synthesized with ease *via* the treatment of a mixture of **2** and **10** with the NST mixture in CH_2Cl_2, followed by *O*-deacetylation, in a 54% yield, while the gentiobiose derivative **9b** was obtained as the by-product in a 21% yield. Compound **3** was similarly condensed with **10** to give the isomaltose derivative,[8] **16a**, and the gentiobiose one, **16b**, in 50 and 29% yields respectively. Thus, it is evident that the α-selectivity was caused by the 6-*O*-acyl group, because a similar glucosylation of benzyl 3-*O*-acetyl-2,4-di-*O*-benzyl-α-D-glucopyranoside with **1** was highly selective to form the gentiobiose derivative.[6] It was found that the glucosylation of the secondary hydroxyl group of the protected glucopyranoside **11**[13] with **2**, followed by *O*-deacetylation, gave the maltose derivative **12** exclusively in a 39% yield; no trace of the cellobiose derivative was found in the reaction mixture.

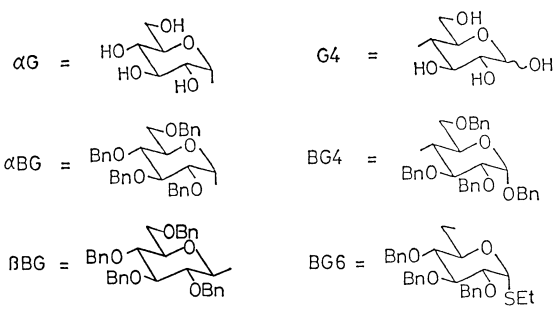
The present method is more efficient for the α-glucosylation of secondary hydroxyl groups than the method using a mixture of trimethylsilyl bromide (Me_3SiBr), $CoBr_2$, tetrabutylammonium bromide (*n*-Bu_4NBr), and Molecular Sieve (4A) (the TCTM mixture) in CH_2Cl_2,[4d] and may well be balanced with other selective α-glucosylation procedures[14] because of its simplicity and rapidity. For the α-glucosylation of primary hydroxyl groups, the method with the TCTM mixture, which does not need such a modified precursor as **2** or **3**, is more convenient than that with the NST mixture.

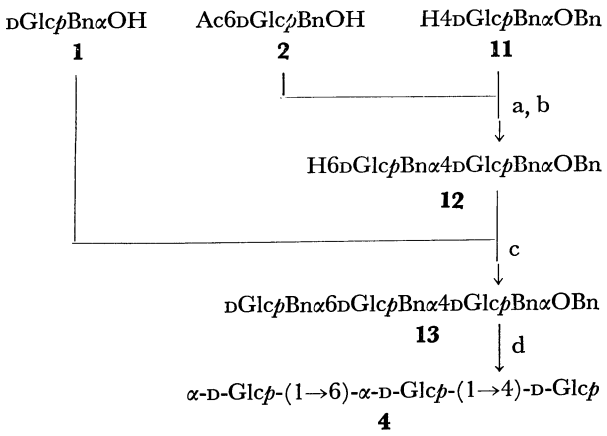
The combined use of both methods made it possible to perform the step-by-step synthesis of *O*-α-D-glucopyranosyl-(1→6)-*O*-α-D-glucopyranosyl-(1→4)-D-glucopyranose (panose, **4**),[15] formulated in Fig. 1. The maltose derivative **12**, synthesized through the condensation of **2** and **11** with the NST mixture as has been described above, was glucosylated with **1** using the TCTM mixture to furnish the fully benzylated α-panose (**13a**). The hydrogenolysis of **13a** afforded **4**, which has once been synthesized from maltose.[15c]



Code	R^{α}	R^{β}	R^1	R^2	R^3
1	OH	H	Bn	Bn	Bn
2	H,	OH	Bn	Bn	Ac
3	H,	OH	Bn	Bn	Pnb
4	OG4	H	H	H	αG
5	H,	OAc	Bn	Bn	Ac
7	H	OH	Bn	Bn	H
8a	OCh	H	Bn	Bn	Ac
8b	H	OCh	Bn	Bn	Ac
9a	OBG6	H	Bn	Bn	H
9b	H	OBG6	Bn	Bn	H
10	SEt	H	Bn	Bn	H
11	OBn	H	Bn	H	Bn
12	OBG4	H	Bn	Bn	H
13a	OBG4	H	Bn	Bn	αBG
13b	OBG4	H	Bn	Bn	βBG
14a	OBG6	H	Bn	Bn	Ac
14b	H	OBG6	Bn	Bn	Ac
15a	OCh	H	Bn	Bn	Pnb
15b	H	OCh	Bn	Bn	Pnb
16a	OBG6	H	Bn	Bn	Pnb
16b	H	OBG6	Bn	Bn	Pnb
17	H,	OAc	Bn	Bn	H
18	H	OPnb	Bn	Bn	H

Ac=Acetyl, Bn=benzyl, Ch=cyclohexyl, Et=ethyl, Pnb=*p*-nitrobenzoyl.





a (NsCl+TfOAg+Et_3N)/CH_2Cl_2
b NaOMe/(MeOH+1,4-Diox.)
c (Me_3SiBr+$CoBr_2$+*n*-Bu_4NBr+Mol. Sieve(4Å))/CH_2Cl_2
d Pd-C(10%)/AcOH(+H_2O)

Fig. 1. The scheme for a stepwise synthesis of panose, **4**.

Experimental

General. See Refs. 4b and 6.

6-O-Acetyl-2,3,4-tri-O-benzyl-D-glucopyranose (2). (1): A mixture of **5**[9] (106.4 mg, 0.20 mmol), NaOAc (46 mg), and MeOH (4.6 ml) was refluxed for 5 h. The solution was evaporated at 20 °C and then chromatographed using a mixture of toluene and 2-butanone (10:1). After the elution of **5** (35.2 mg, 33%) and a trace amount of **17**, there appeared **2** (45.2 mg, 69%). ^1H NMR($CDCl_3$, Me_4Si) δ 2.03 (3H, s, Ac), 5.19 (1H, d, J=4.0 Hz, HI), ^{13}C NMR ($CDCl_3$, Me_4Si) δ 20.9 (Ac), 91.1 (Clα), 97.4 (Clβ).

(2): $PhCH_2NH_2$ (Wako, 60 μl) was added to a cooled solution of **5** (94.5 mg, 0.18 mmol) in $(CH_2Cl)_2$ (0.9 ml). The solution was kept standing for 2 d at room temperature. Evaporation and subsequent chromatography gave **2** (71.1 mg, 80%).

(3): $N_2H_4 \cdot H_2O$ (Wako, ≈90%, 6.6 μl) was added to a cooled solution of **5** (96.6 mg, 0.18 mmol) in pyridine (0.9 ml). The solution was kept standing for 4 d at room temperature. Evaporation and subsequent chromatography gave **2** (63.3 mg, 71%).

(4): A mixture of **6**[9] (5.0 g, 11.6 mmol) and AcBr (5 ml) was stirred for 1.5 h at room temperature. The solution was then evaporated, and the residue was stirred into CH_2Cl_2 (5 ml) containing H_2O (2.05 ml) and Ag_2CO_3 (6.4 g). The mixture was chromatographed to give **2** (4.83 g, 75%).

(5): A mixture of **7**[9] (90 mg, 0.20 mmol), *N*-acetylimidazole (Tokyo Kasei, 30.6 mg), and $(CH_2Cl)_2$ (0.4 ml) was stirred for 16 h at room temperature. The mixture was then chromatographed to give **5** (14.5 mg, 14%, R_f 0.70 (toluene–2-butanone, 10:1)), **17** (27.8 mg, 28%, R_f 0.35), **2** (36.4 mg, 37%, R_f 0.30), and then **7** (8.8 mg, 10%, R_f 0.05); ^1H NMR($CDCl_3$, Me_4Si) δ (**17**) 2.02 (Ac-β), 2.13 (Ac-α), 5.62 (d, J=8.0 Hz, HI-β), 6.17 (d, J=3.5 Hz, HI-α).

2,3,4-Tri-O-benzyl-6-O-p-nitrobenzoyl-D-glucopyranose (3). A mixture of **7** (450 mg, 1.0 mmol), *p*-nitrobenzoyl chloride (Tokyo Kasei, 223 mg), and pyridine (10 ml) was stirred for 3 h at −10 °C and then for 16 h at room temperature. Usual processing and subsequent chromatography with benzene–2-butanone (10:1) gave 2,3,4-tri-*O*-benzyl-1,6-bis-*O*-(*p*-nitrobenzoyl)-β-D-glucopyranose (48 mg, 6%, R_f 0.84 (benzene–2-butanone, 10:1), mp 144.5—145.5 °C (lit,[7b] mp 144.5—145.5 °C), **18** (53 mg, 9%, R_f 0.60), **3** (310 mg, 52%, R_f 0.52), and **7** (129 mg, 29%); ^1H NMR($CDCl_3$, Me_4Si) δ (**3**) 5.24 (d, J=3.8 Hz, HI-α), 7.61—8.31 (4H, m, $-C_6H_4-$), (**18**) 5.71 (1H, d, J=8.0 Hz, HI), 8.05—8.33

Table 1. Physical and analytical data of compounds

Compound	Mp θ_m/°C	$[\alpha]_D^{20}$/° (*c*, Solv.)	Molecular formula	Calcd (%)			Found (%)			Lit
				C	H	N	C	H	N	
2	99.5—100	+32(1.0, $CHCl_3$)	$C_{29}H_{32}O_7$	70.71	6.55		70.44	6.50		
3	102.5—103.5	+65(0.4, $CHCl_3$)	$C_{34}H_{33}NO_9$	68.10	5.55	2.34	67.90	5.45	2.28	
4	195—198(decomp)	+147(0.1, H_2O)	$C_{18}H_{32}O_{16}$	42.86	6.39		42.78	6.60		a)
8a	—	+56(0.5, $CHCl_3$)	$C_{35}H_{42}O_7$	73.15	7.37		73.31	7.36		
8b	88—89	+15(0.2, $CHCl_3$)					72.90	7.36		
9b	120—121	+70(0.6, $CHCl_3$)	$C_{56}H_{62}O_{10}S$	72.54	6.74		72.58	6.78		
11	—	+48(2.0, $CHCl_3$)	$C_{34}H_{36}O_6$	75.53	6.71		75.30	6.81		b)
12	—	+64(0.8, $CHCl_3$)	$C_{61}H_{64}O_{11}$	75.29	6.63		74.95	6.60		
13a	—	+75(1.0, $CHCl_3$)	$C_{95}H_{98}O_{16}$	76.28	6.60		76.04	6.75		
13b	—	+57(1.0, $CHCl_3$)					76.17	6.61		
14a	—	+114(0.7, $CHCl_3$)	$C_{58}H_{64}O_{11}S$	71.88	6.60		71.20	6.58		
14b	89—91	+76(0.2, $CHCl_3$)					71.82	6.72		
15a	—	+65(0.9, $CHCl_3$)	$C_{41}H_{45}NO_9$	70.77	6.52	2.01	70.45	6.34	2.08	
15b	91—93	+45(0.2, $CHCl_3$)					70.33	6.34	2.17	
16b	—	+75(0.7, $CHCl_3$)	$C_{63}H_{65}NO_{13}S$	70.31	6.09	1.30	70.27	6.06	1.28	
17	—	+25(1.0, $CHCl_3$)	$C_{29}H_{32}O_7$	70.71	6.55		70.91	6.58		
18	166—167	−44(0.2, $CHCl_3$)	$C_{34}H_{33}NO_9$	68.10	5.55	2.34	68.07	5.49	2.34	
19	148—148.5	+115(0.3, $CHCl_3$)	$C_{42}H_{58}O_{28}$	49.90	5.78		50.27	5.88		c)

a) Ref. 6a; mp 213(decomp), $[\alpha]_D^{25}$ +154° (*c* 2.2, H_2O). b) Ref. 14b; $[\alpha]_D^{20}$ +43° (*c* 1.10, $CHCl_3$). c) Ref. 6b; mp 148.5—150 °C, $[\alpha]_D^{27}$ +120° (*c* 4.0, $CHCl_3$).

(4H, m, $-C_6H_4-$).

*Ethyl 2,3,4-Tri-*O*-benzyl-1-thio-α-*D*-glucopyranoside (**10**)*: A mixture of AcBr (5 ml) and **6** (5.0 g, 11.6 mmol) was stirred for 1.5 h at room temperature and then evaporated. The whole residue was treated with EtSH (Wako, 9.0 ml) in $MeNO_2$ (17 ml) containing 2,6-dimethylpyridine (4.2 ml). After evaporation, the residue was dissolved in MeOH (70 ml) containing methanolic NaOMe (2 M, 10 ml). After 20 h, AcOH (1.5 ml) was added to the mixture, which was evaporated and then chromatographed using benzene–2-butanone (10:1). This gave **10** (4.9 g, 75%), identified with the sample prepared previously through a different route.[8]

*Benzyl 2,3,6-Tri-*O*-benzyl-α-*D*-glucopyranoside (**11**)*: A mixture of benzyl 2,3-di-*O*-benzyl-α-D-glucopyranoside[13a] (0.65 g, 1.44 mmol), $PhCH_2Cl$ (6.5 ml), and NaH (≈50% disp., 70 mg) was vigorously stirred for 40 min at 80 °C. Usual processing and subsequent chromatography with hexane–EtOAc (4:1) gave benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (15 mg, 1.7%, R_f 0.75 (hexane–EtOAc, 4:1)), **11** (0.35 g, 45%, R_f 0.52), benzyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[13c] (0.10 g, 13%, R_f 0.30), and the unchanged starting material (0.18 g, 28%, R_f 0.08).

*Cyclohexyl 6-O-Acetyl-2,3,4-tri-*O*-benzyl-α- and -β-*D*-glucopyranoside (**8a** and **8b**)*: Et_3N (31 μl, 0.22 mmol) was added to a mixture of **2** (108 mg, 0.22 mmol), cyclohexanol (21 μl, 0.22 mmol), NsCl (49 mg, 0.22 mmol), and AgOTf (57 mg, 0.22 mmol) in CH_2Cl_2 (1.0 ml) at −35 °C under efficient stirring. The bath temperature was raised to 0 °C at a rate of ≈0.5 °C/min, and then the stirring was continued for 6 h. After the processing described previously,[4b] chromatography with hexane–EtOAc (5:1) gave **8b** (14.6 mg, 12%, R_f 0.66 (hexane–EtOAc, 3:1)), and **8a** (41.4 mg, 33%, R_f 0.60).

*Cyclohexyl 2,3,4-Tri-*O*-benzyl-6-*O*-p-nitrobenzoyl-α- and -β-*D*-glucopyranosides (**15a** and **15b**)*: A similar reaction using **3** (132 mg, 0.22 mmol), cyclohexanol (21 μl), NsCl (49 mg), AgOTf (57 mg), Et_3N (31 μl), and CH_2Cl_2 (1.0 ml) gave **15b** (11.8 mg, 8%, R_f 0.73 (hexane–EtOAc, 3:1)) and **15a** (55.6 mg, 37%, R_f 0.67).

*Ethyl O-(6-O-Acetyl-2,3,4-tri-*O*-benzyl-α- and -β-*D*-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-1-thio-α-*D*-glucopyranoside (**14a** and **14b**)*: Et_3N (156 μl, 1.1 mmol) was stirred into a mixture of **2** (492 mg, 1.0 mmol), **10** (494 mg, 1.0 mmol), NsCl (245.5 mg, 1.1 mmol), and AgOTf (283 mg, 1.1 mmol) in CH_2Cl_2 (5.0 ml) at −38 °C, after which the bath temperature was allowed to rise to 0 °C. After having been stirred for 16 h, the mixture was processed[4b] and then chromatographed (benzene–2-butanone, 100:1→3:1, gradient) to give **14a** (543.8 mg, 56%, R_f 0.44, benzene–2-butanone, 20:1)) and **14b** (244.5 mg, 25%, R_f 0.38); ^1H NMR(CCl_4, Me_4Si) δ (**14a**) 1.25 (3H, t, $C\underline{H}_3CH_2S$), 1.94 (3H, s, Ac), 2.57 (2H, m, $CH_3C\underline{H}_2S$), 5.35 (1H, d, J=5.0 Hz, Hl), 7.24 (30H, s, 6Ph); (**14b**) 1.23 (3H, t, $C\underline{H}_3CH_2S$), 1.96 (3H, s, Ac), 2.47 (2H, m, $CH_3C\underline{H}_2S$), 5.30 (1H, d, J=5.0 Hz, Hl), 7.20 (30H, s, 6Ph).

Compound **14a** (530 mg, 0.55 mmol) was treated with methanolic NaOMe (0.05 M, 20 ml) containing 1,4-dioxane (2 ml) to afford **9a** (485 mg, 96%), which was identified with the sample prepared previously.[8]

Compound **14b** (68 mg, 0.07 mmol) was treated with methanolic NaOMe (0.03 M, 3.5 ml) containing Me_2CO (1 ml) to give **9b** (55.2 mg, 85%).

*Ethyl O-(2,3,4-Tri-*O*-benzyl-6-*O*-p-nitrobenzoyl-α- and -β-*D*-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-1-thio-α-*D*-glucopyranoside (**16a** and **16b**)*: A similar reaction using **3** (100 mg, 0.17 mmol), **10** (84 mg, 0.17 mmol), NsCl (41 mg, 0.19 mmol), AgOTf (48 mg, 0.19 mmol), Et_3N (26 μl, 0.19 mmol), and CH_2Cl_2 (1.0 ml) and subsequent chromatography (benzene–2-butanone, 100:1→5:1, gradient) gave **16a** (90.2 mg, 50%, R_f 0.75 (benzene–2-butanone, 20:1)), identified with the sample synthesized previously[8] and then **16b** (52.0 mg, 29%, R_f 0.65); ^1H NMR(CCl_4, Me_4Si) δ (**16a**) 1.25 (3H, t, $C\underline{H}_3CH_2S$), 2.50 (2H, m, $CH_3C\underline{H}_2S$), 5.28 (1H, d, J= 5.0 Hz, Hl), 7.95—8.17 (4H, m, $-C_6H_4-$); (**16b**) 1.23 (3H, t, $C\underline{H}_3CH_2S$), 2.53 (2H, m, $CH_3C\underline{H}_2S$), 5.27 (1H, d, J=

5.0 Hz, Hl), 8.03—8.12 (4H, m, $-C_6H_4-$).

Benzyl O-*(2,3,4-Tri*-O-*benzyl*-α-D-*glucopyranosyl)-(1→4)-2,3,6-tri*-O-*benzyl*-α-D-*glucopyranoside (**12**)*: A similar glucosylation reaction using **2** (180 mg, 0.37 mmol), **11** (197.4 mg, 0.37 mmol), NsCl (97.5 mg, 0.44 mmol), AgOTf (113 mg, 0.44 mmol), Et_3N (61.5 μl, 0.44 mmol), and CH_2Cl_2 (1.8 ml) and subsequent chromatography (benzene–2-butanone) gave a sirup (173.5 mg, R_f 0.60 (benzene–2-butanone, 10:1), this being the sole spot in the region where $R_f > 0.43$). This was then treated with methanolic NaOMe (0.05 M, 11 ml) containing 1,4-dioxane (2 ml) to give a sirup which showed a single spot. ^{13}C NMR of this sirup, composed of **12** (135.6 mg, 39% for **11**), showed no signal of the anomeric carbons corresponding to the β-glucopyranoside; ^{13}C NMR($CDCl_3$, Me_4Si) δ 95.1 (Cl), 96.3 (Cl′).

Benzyl O-*(2,3,4,6-Tetra*-O-*benzyl*-α- *and* -β-D-*glucopyranosyl)-(1→6)*-O-*(2,3,4-tri*-O-*benzyl*-α-D-*glucopyranosyl)-(1→4)-2,3,6-tri*-O-*benzyl*-α-D-*glucopyranoside (**13a** and **13b**)*. A mixture of **1** (151 mg, 0.28 mmol), **12** (209 mg, 0.125 mmol), $CoBr_2$ (62 mg, 0.28 mmol), *n*-Bu_4NBr (90 mg, 0.28 mmol), Molecular Sieve (Linde-4A, 230 mg), and Me_3SiBr (37 μl, 0.28 mmol) in CH_2Cl_2 (0.7 ml) was stirred for 48 h at room temperature. The subsequent chromatography (hexane–2-butanone, 100:1→3:1, gradient) of the reaction mixture gave **13a** (93.2 mg, 29%, R_f 0.58 (hexane–2-butanone, 20:1)) and then **13b** (27.2 mg, 9%, R_f 0.55). ^{13}C NMR ($CDCl_3$, Me_4Si) δ (**13a**) 95.0 (Cl), 96.2 (Cl′), 97.1 (Cl″); (**13b**) 95.1 (Cl), 96.3 (Cl′), 103.7 (Cl″).

O-α-D-*Glucopyranosyl-(1→6)*-O-α-D-*glucopyranosyl-(1→4)*-D-*glucopyranose (Panose, **4**)*: Two hydrogenations of **13a** (73.8 mg, 0.062 mmol) over Pd–C (10%, 73 mg) in AcOH (7 ml) containing H_2O (0.03 ml) gave a glass, which was then triturated with MeOH to give **4** (19.3 mg, 61%). The ^{13}C NMR (D_2O, Me_4Si (ext.)) of this agreed well with that previously reported;[15d] 61.6 (C6″), 61.8 (C6), 67.0 (C6′), 70.5 (C4″), 70.6 (C4′), 71.1 (C5α), 72.4 (C5′), 72.6 (C2α and C2″), 72.7 (C2′), 72.9 (C5″), 74.2 (C3α, C3′, and C3″). 75.1 (C2β). 75.7 (C3β), 77.2 (C5β), 78.2 (C4β), 78.5 (C4α), 93.0 (C1α), 96.8 (C1β), 99.2 (C1″), 100.8 (C1′).

A sample of **4** (6.8 mg) was treated with aq $NaBH_4$ (0.2%, 4 ml) at room temperature overnight. After the addition of AcOH (1 drop), the mixture was evaporated and coevaporated with MeOH. The residue was stirred in Ac_2O (1 ml)c ontaining NaOAc (14 mg) at 100 °C for 6 h. Subsequent chromatography (benzene–2-butanone) gave a homogeneous glass. This was crystallized with MeOH to give *O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-1,2,3,5,6-penta-*O*-acetyl-D-glucitol (**19**) (10.0 mg, 74%).

References

1) N. K. Mathur, O. K. Narang, and R. E. Williams, "Polymers as Aids in Organic Chemistry," Academic Press (1981), Chap. 6.

2) S. David, A. Lubineau, and J.-M. Vatèle, *Nouv. J. Chim.*, **4**, 547 (1980).

3) A. F. Bochkov and G. E. Zaikov, "Chemistry of the *O*-Glycosidic Bond, Formation and Cleavage," Engl. ed by C. Schuerch, Pergamon Press, London (1979), Chap. 3.

4) a) S. Koto, N. Morishima, and S. Zen, *Bull. Chem. Soc. Jpn.*, **52**, 784 (1979); b) S. Koto, T. Sato, N. Morishima, and S. Zen, *ibid.*, **53**, 1761 (1980); c) S. Koto, N. Morishima, and S. Zen, *ibid.*, **55**, 1543 (1982); d) N. Morishima, S. Koto, C. Kusuhara, and S. Zen, *Chem. Lett.*, **1981**, 427; S. Koto, N. Morishima, C. Kusuhara, S. Sekido, T. Yoshida, and S. Zen, *Bull. Chem. Soc. Jpn.*, **55**, 2995 (1982); e) S. Koto, N. Morishima, S. Sato, and S. Zen, The 26th International Congress of IUPAC, Tokyo, 1977.

5) a) A. A. Pavia, J.-M. Rocheville, and S. Z. Ung, *Carbohydr. Res.*, **79**, 79 (1980); G. Grynkiewicz, *Pol. J. Chem.*, **53**, 1571 (1979); b) Seemingly, a dehydrative glycosylation has been studied by Russian chemists (*e.g.*, A. M. Gakhokidze, *Zhur. Obsh. Khim.*, **11**, 117 (1941); A. M. Gakhokidze and N. D. Kutidze, *ibid.*, **22**, 247 (1952), *etc.*); c) J. Leroux and A. S. Perlin, *Carbohydr. Res.*, **67**, 163 (1978).

6) S. Koto, S. Inada, T. Yoshida, M. Toyama, and S. Zen, *Can. J. Chem.*, **59**, 255 (1981).

7) a) P. J. Pfaffli, S. H. Hixon, and L. Anderson, *Carbohydr. Res.*, **23**, 195 (1972); b) T. Ishikawa and H. G. Fletcher, Jr., *J. Org. Chem.*, **34**, 563 (1969).

8) S. Koto, T. Uchida, and S. Zen, *Bull. Chem. Soc. Jpn.*, **46**, 2520 (1973).

9) G. Zemplén, Z. Csürös, and S. Angyal, *Chem. Ber.*, **70**, 1848 (1937).

10) a) C. Ferrer Salat, P. Axero Agneseti, and M. Bemporad Caniato, Span. Patent, No. 430636 (*Chem. Abstr.*, **87**, 23683k (1977)); b) Y. Ishido, N. Sakairi, M. Sekiya, and N. Nakazaki, *Carbohydr. Res.*, **97**, 51 (1981).

11) A. R. Jeanes, C. A. Wilham, and G. E. Hilbert, *J. Am. Chem. Soc.*, **75**, 3667 (1953).

12) J. M. McLaren, R. V. Stick, and S. Webb, *Aust. J. Chem.*, **30**, 2689 (1977).

13) a) A. Lubineau, A. Thieffry, and A. Veyriérs, *Carbohydr. Res.*, **46**, 143 (1976); b) S. David, A. Lubineau, and A. Thieffry, *Tetrahedron*, **34**, 299 (1978); c) P. A. Adams, R. Harrison, T. D. Inch, and P. Rich, *Biochem. J.*, **155**, 1 (1976).

14) J. R. Pougny, M. A. A. Nassr, N. Naulet, and P. Sinaÿ, *Nouv. J. Chim.*, **2**, 389 (1978); T. Mukaiyama, T. Nakatsuka, and S. Shoda, *Chem. Lett.*, **1979**, 487; T. Mukaiyama, Y. Murai, and S. Shoda, *ibid.*, **1981**, 431.

15) a) S. C. Pan, L. W. Nicholson, and P. Kolachov, *J. Am. Chem. Soc.*, **73**, 2547 (1951); b) M. L. Wolfrom, A. Thompson, and J. T. Galkowski, *ibid.*, **73**, 4093 (1951); c) M. L. Wolfrom and K. Koizumi, *J. Org. Chem.*, **32**, 656 (1967); d) T. Usui, N. Yamaoka, K. Matsuda, K. Tuzimura, H. Sugiyama, and S. Sato, *J. Chem. Soc., Perkin Trans. 1*, **1973**, 2425.