Stereoselective α-Glucosylation with Tetra-*O*-benzyl-α-D-glucose and a Mixture of Trimethylsilyl Bromide, Cobalt(II) Bromide, Tetrabutylammonium Bromide, and a Molecular Sieve. A Synthesis of 3,6-Di-*O*-(α-D-glucopyranosyl)-D-glucose

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A mixture of trimethylsilyl bromide, cobalt(II) bromide, tetrabutylammonium bromide, and a molecular sieve (4A) is effective for the stereoselective, one-stage α-glucosylation of alcohol with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose in dichloromethane. Using this procedure, several disaccharide derivatives as well as *O*-α-D-glucopyranosyl-(1→3)-*O*-[α-D-glucopyranosyl-(1→6)]-D-glucopyranose are synthesized.

A variety of procedure for stereoselective α-glucosylation have recently been reported.[1] However, they all use moisture-sensitive compounds such as glycosyl halides.[1a,b] We are now developing a glycosylation procedure in which the anomeric center of 2,3,4,6-tetra-*O*-benzyl-α-D-gluopyranose (αGOH, **1**) is activated in the presence of an alcohol.[2] The treatment of the mixture of **1** and an alcohol (ROH) in CH_2Cl_2 containing methanesulfonic acid ($MeSO_3H$) and $CoBr_2$ has been found to give an anomeric mixture of the corresponding gucosides.[2c] In this reaction, HBr, generated *in situ* by the reaction of $MeSO_3H$ and $CoBr_2$, cooperates with $CoBr_2$ to convert **1** into the glucosyl bromide (**2**) in the presence of an alcohol, and **2** reacts with alcohol to afford the glucosides (Eq. 1, Q=H).[2c]

$$\alpha\text{GOH} + \text{ROH} \xrightarrow{\text{QBr/CoBr}_2} \alpha\text{GOR} + \beta\text{GOR} \quad (1)$$

A glucosylation reaction (Eq. 1, Q=Me_3Si) was then provisionally set up by replacing the HBr acid with trimethylsilyl bromide (Me_3SiBr).[3a] This paper will report a handy stereoselective α-glucosylation procedure[4] developed by modifying this reaction and its use in the synthesis of several disaccharide derivatives and the first synthesis of *O*-α-D-glucopyranosyl-(1→3)-*O*-[α-D-glucopyranosyl-(1→6)]-D-glucopyranose (**23**), the trisaccharide constituting the branching poing of the dextrans from *Leuconostic mesenteroides*.[5]

Results and Discussion

α-Glucosylation of Simple Alcohols. Table 1 contains the results regarding the glucosylation of cyclohexylmethanol (Runs 1—9) (Eq. 1, Q=Me_3Si, R=cyclohexylmethyl). Compared to the previously used method, which uses $MeSO_3H$ and $CoBr_2$,[2c] the efficiency was greatly improved (Runs 2 and 3). The use of the molecular sieve, 4A (MS-4A), was essential (Runs 1 and 3), because it scavenges HBr, which causes an undesirable debenzylation reaction.[2c] The use of the mixture of Me_3SiCl[3b] and $CoBr_2$ also gave good results, but the efficiency was less satisfactory (Run 4).

It was found that the reaction of **1** with Me_3SiBr and $CoBr_2$ efficiently produced the glucosyl bromide **2**.[3c] However, trace amounts of the silylated compounds of **1** and alcohol were isolated from the product mixture of the glucosylation reaction. Hence, the silylation of the starting materials is considered to occur concurrently during the glucosylation reaction. Nevertheless, the experiments using 5α-cholestan-3β-ol as the alcohol confirmed that: (1) the trimethylsilyl compound (**3**) smoothly reacted with the mixture of Me_3SiBr and $CoBr_2$ to generate **2**,[3d] which then underwent the glucosylation of the alcohol in the presence of $CoBr_2$,[2c] and (2) the trimethylsilyl derivative of the alcohol readily reacted with **2** in the presence of $CoBr_2$ to furnish the corresponding glucosides. Therefore, the silylation reactions, if any, seem not to interfere with the glucosylation reaction (Eq. 1, Q=Me_3Si).

Because the glucosylation reaction proceeds *via* **2**, tetrabutylammonium bromide (*n*-Bu_4NBr) was then added to the reaction mixture, for the salt was expected to cause bromide ion-catalyzed stereoselective α-glucosylation (Eq. 2).[1b] Table 1 shows that the addition of *n*-Bu_4NBr gave rise to the predominant formation of the α-glucosides, though the reaction was slowed[2c] (Runs 3, 5—7). Slightly excess amounts (30%) of **1** and the reagent mixture in relation to the alcohol achieved a quantative glucosylation (Run 9). Other simple alcohols, such as cyclohexanol and 6-(2,4-dinitroanilino)-1-hexanol, furnished the corresponding α-glucosides in good yields (Runs 10 and 11). Thus, the replacement of HBr with Me_3SiBr and MS-4A makes it possible to carry out a longer glucosylation reaction (Runs 7—12) than before.[2c]

$$\alpha\text{GOH} + \text{ROH} \xrightarrow{\text{Me}_3\text{SiBr/CoBr}_2\text{/}n\text{-Bu}_4\text{NBr}} \alpha\text{GOR} \ (+\beta\text{GOR}) \quad (2)$$

The Oligosaccharide Synthesis Using the Quarternary Mixture. The α-glucosylation procedure was then used for a systematized oligosaccharide synthesis using the benzyl as the persistent protecting group.[6] Table 1 shows that the reagent mixture was effective for the stereoselective α-glucosylation of the primary hydroxyl group of partially benzylated monosaccharides, such as **9**, **10**, and **11** (Runs 13—15). The reagent mixture performed the α-glucosylation of the secondary hydroxyl group of the xylopyranoside derivatives (**5** and **6**) with acceptable yields (Runs 16 and 17).

The reagent mixture was then applied to the step-by-step synthesis of the branched-chain trisaccharide (**23**) to establish the scope of the applicability of the present procedure, as is summarized in Fig. 1, the symbolism for monosaccharide derivatives exemplified in Table 5 is used. The first glucosylation step for

Table 1. Glucosylation with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (αGOH, **1**) in CH_2Cl_2 at 25±3 °C[a]

Run	**1** (equiv.)	Alcohol[b]	Me_3SiX X	Me_3SiX (equiv.)	$CoBr_2$ (equiv.)	MS-4A w/w of **1**	*n*-Bu_4NBr (equiv.)	Time h	Yield[c] (α/β) %	Recov. of **1**/%
1	1.0	CmOH	Br	1.0	1.0	—	—	2	63 (55/45)	12
2	1.0	CmOH	Br	1.0	1.0	1.5	—	0.5	79 (41/59)	11
3	1.0	CmOH	Br	1.0	1.0	1.5	—	2	81 (40/60)	3
4	1.0	CmOH	Cl	1.0	1.0	1.5	—	2	59 (52/48)	37
5	1.0	CmOH	Br	1.0	1.0	1.5	1.0	2	54 (72/28)	40
6	1.0	CmOH	Br	1.0	1.0	1.5	1.0	6	65 (72/28)	34
7	1.0	CmOH	Br	1.0	1.0	1.5	1.0	16	82 (75/25)	4
8	1.3	CmOH	Br	1.0	1.0	1.5	1.0	16	94 (74/26)	—[d]
9	1.3	CmOH	Br	1.3	1.3	2.0	1.3	16	100 (76/24)	—[d]
10	1.3	ChOH	Br	1.3	1.3	2.0	1.3	16	90 (80/20)	—[d]
11	1.3	DhOH	Br	1.3	1.3	2.0	1.3	16	94 (73/27)	—[d]
12	1.3	CtOH	Br	1.3	1.3	2.0	1.3	24	87 (72/28)	—[d]
13	1.3	**9**	Br	1.3	1.3	2.0	1.3	16	69 (85/15)	—[d]
14	1.3	**10**	Br	1.3	1.3	2.0	1.3	18	61 (78/15)	—[d]
15	1.3	**11**	Br	1.3	1.3	2.0	1.3	20	73 (86/14)	—[d]
16	1.3	**5**[e]	Br	1.3	1.3	2.0	1.3	42	35 (82/18)	—[d]
17	1.3	**6**[e]	Br	1.3	1.3	2.0	1.3	42	49 (86/14)	—[d]
18	1.3	**7**	Br	1.3	1.3	2.0	1.3	42	32 (74/26)	—[d]
19	1.3	**17a**	Br	1.3	1.3	2.0	1.3	42	19 (86/14)	—[d]

a) Mole ratios are based on the amount of alcohol. b) CmOH=cyclohexylmethanol, ChOH=cyclohexanol, CtOH=5α-cholestan-3β-ol, DhOH=6-(2,4-dinitroanilino)-1-hexanol. The glucosides obtained are: Runs 1—9, αGOCm and βGOCm; Run 10, αGOCh and βGOCh; Run 11, αGODh and βGODh; Run 12, **4a** and **4b**; Run 13, **15a** and **15b**; Run 14, **14a** and **14b**; Run 15, **17a** and **17b** after de-*O*-acetylation; Run 16, **12a** and **12b**; Run 17, **13a** and **13b**; Run 18; **16a** and **16b**; Run 19, **22a** and **22b**. c) Yields are based on the amount of the alcohol charged. d) Not determined. e) N. Morishima, S. Koto, C. Kusuhara, and S. Zen, *Bull. Chem. Soc. Jpn.*, **55**, 631 (1982).

Table 2. ^{13}C NMR data of the anomeric carbons of the protected di- and trisaccharides[a]

Compound		C-1	C-1′→3	C-1″→6
Benzylates				
14a		95.1	97.3	
14b		95.1	102.5	
16a		94.9		97.5
16b		95.4		104.0
22a		95.2	97.4	97.4
22b		94.0	102.8	97.5
Acetates				
19	α	89.2	96.2	
	β	91.8	96.2	
21	α	89.1		96.0
	β	91.8		96.3
24	α	88.8	96.1	95.8
	β	91.7	96.1	95.8

a) The spectra were recorded by means of a JEOL-PS-100 spectrometer equipped with a JEOL-EC-100 computer and using a 8 mmφ tube at 37 °C (noise decoupled; pulse width, 13 μs (45°), repetition, 2 s frequency range, 5000 Hz; 8 K data points).

the monosaccharide derivative (**11**) was carried out well (Table 1). After the deacetylation, however, the second glucosylation step for the disaccharide derivative (**17a**) (Run 19) was carried out only with difficulty to furnish the fully benzylated trisaccharide (**22a**). The chemical shift of the anomeric carbons of **22a** (Table 2) closely resembles that of the α(1→3), α(1→6)-trisaccharide derivatives.[7] The hydrogenolysis of **22a** gave **23**. The chemical shift of the anomeric and aglyconic carbons of **23** and its per-*O*-acetate (**24**) corresponds well with those of nigerose (**18**)[8] and isomaltose (**20**)[8] and their acetates (**19** and **21**). It should be noted, however, that the low yield of the glucosylation of the disaccharide derivative (**17a**) with **1** shows the limitations of the present method in a multistep glucosylation.

Experimental

General. The instruments used were identical with those described previously.[2,6] Such compounds as **1**, $CoBr_2$, *n*-Bu_4NBr, and solid glycosyl acceptors were stored *in vacuo* over P_2O_5. Me_3SiBr (PCR) was used without any pretreatments. MS-4A (Linde, 60—80 mesh) was dried at 450 °C in an electric furnace. Column chromatography was performed on silica gel (Kanto Kagaku, 100 mesh), using the gradient eluent system of benzene and 2-butanone (100:1→10:1), unless otherwise stated, each fraction was examined by TLC on silica gel (Merck, 7731).

The fully benzylated oligosaccharides (**14a**, **16a**, and **22a**) was hydrogenated twice over an equal amount of Pd on C (Kawaken, 10%) in AcOH (6 ml) containing H_2O (0.03 ml) at 410 kPa overnight. The oligosaccharides (**18**, **20**, and **23**) were acetylated with Ac_2O and AcONa at 100 °C.

The ^{13}C NMR data of di- and trisaccharides and their

Table 3. ^{13}C NMR data of 3,6-di-*O*-(α-D-glucopyranosyl)-D-glucopyranose and related disaccharides[a)]

Carbon	**18**	**20**	**23**	Carbon	**18**	**20**	**23**
1α	93.3 (93.1)	93.5 (93.8)	93.7	1′	100.1 (99.8)		100.6
1β	97.0 (97.0)	97.4 (97.7)	97.5	2′	72.8 (72.8)		73.1
2α	71.1 (71.3)	72.8 (73.3)	72.9	3′	74.0 (74.1)		74.4[b)]
2β	74.0 (74.1)	75.6 (75.9)	75.3	4′	71.1 (71.3)		70.9
3α	80.7 (80.8)	74.4 (75.0)	81.9	5′	72.8 (72.8)		73.1
3β	83.2 (83.2)	77.3 (77.7)	84.3	6′	61.5 (61.8)		61.8
4α	70.5 (70.6)	70.8 (71.3)	70.9	1″		99.3 (99.4)	99.4
4β	70.4 (70.6)	70.8 (71.3)	70.9	2″		72.8 (73.3)	73.1
5α	72.3 (72.2)	71.3 (71.3)	72.9	3″		74.4 (75.0)	74.2[b)]
5β	76.7 (76.6)	75.4 (75.9)	77.0	4″		70.8 (71.3)	70.9
6α	61.4 (61.8)	67.0 (67.4)	66.9	5″		73.1 (73.8)	73.1
6β	61.6 (61.8)	67.0 (67.4)	66.9	6″		61.7 (62.5)	61.8

a) The measurement conditions are described in Table 2. The values in parentheses are those reported previously (Ref. 8). b) Interexchangeable.

Table 4. Physical and analytical data of oligosaccharide derivatives

Compound	Mp θ_m/°C	$[\alpha]_D^{20}$/° (*c*, $CHCl_3$)	Found (%) C	Found (%) H	Formula	Calcd (%) C	Calcd (%) H
12a	—	+58 (1.0)	74.04	6.93	$C_{54}H_{58}O_{10}$	74.81	6.74
12b	—	+38 (1.5)	73.87	6.94			
13a	—	+40 (1.0)	74.79	6.94			
13b	91—92	+10 (1.0)	74.65	6.67			
14a	—	+72 (2.0)	76.88	6.70	$C_{68}H_{70}O_{11}$	76.81	6.64
14b	—	+57 (1.0)	76.18	6.79			
16a	102—105	+64 (0.6)	75.69	6.63			
16b	128—130	+39 (0.4)	75.99	6.60			
22a	—	+79 (1.0)	75.98	6.73	$C_{95}H_{98}O_{16}$	76.28	6.60
22b	—	+66 (0.7)	75.99	6.56			
24	—	+82 (0.3)	49.33	5.68	$C_{40}H_{54}O_{28}$	49.69	5.63
25	77—79	+97 (0.2)	49.85	5.69	$C_{42}H_{58}O_{28}$	49.90	5.78

Table 5. Symbolism of some monosaccharide derivatives[a)]

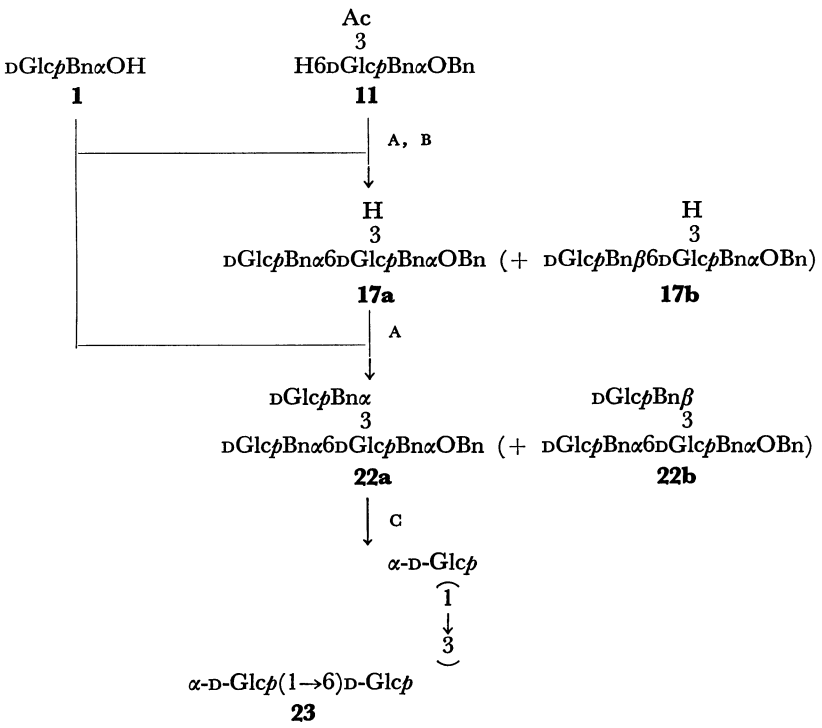
	1	**5**	**11**
Unprotected hydroxyl group[b)]	None	OH-3	OH-6
Temporary protecting group	None	None	Ac-3
Persistent protecting group	Bn	Bn	Bn
Anomeric configuration	α	α	α
Substituent at C-1	OH	OMe	OBn
Monosaccharide involved	D-Glc*p*	D-Xyl*p*	D-Glc*p*
Symbolism	DGlc*p*BnαOH	H3DXyl*p*BnαOMe	Ac 3 H6DGlc*p*BnαOBn

a) Ac=Acetyl, Bn=benzyl, Me=methyl. b) The hydroxyl group at C-1 is not taken into account.

derivatives are listed in Tables 2 and 3, while the physical and analytical data of new compounds are listed in Table 4.

Procedure for the Glucosylation Using the Benzylated Glucose (1). Me_3SiBr (22 μl, 0.17 mmol) was stirred into a mixture of **1** (90 mg, 0.17 mmol), the respective alcohol (0.13 mmol), $CoBr_2$ (37 mg, 0.17 mmol), *n*-Bu_4NBr (54 mg, 0.17 mmol), and MS-4A (180 mg) in CH_2Cl_2 (0.45 ml), and the resulting mixture was agitated at room temperature (22—28 °C). The filtrate of the reaction mixture was then evaporated and chromatographed. The glucosides thus obtained, the yields of which are listed in Table 1, were identified with those prepared before,[2,6)] except for ten compounds, **12a**, **12b**, **13a**, **13b**, **14a**, **14b**, **16a**, **16b**, **22a**, and **22b**.

*Benzyl 2,4,6-Tri-*O*-benzyl-α-D-glucopyranoside (7).* Benzyl α-D-glucopyranoside[6b,c)] (1.0 g, 3.7 mmol) was heated in $PhCH_2Cl$ (Tokyo Kasei, 10 ml) and powdered KOH (Wako, 0.95 g, 17 mmol) at 90—95 °C for 2 h under vigorous stirring. The filtrate of the reaction mixture was then evaporated and chromatographed. Benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside appeared first, and then the main fraction of **7** was obtained as a syrup (1.3 g). This was purified through acetylation with Ac_2O and pyridine, follow-



A : $Me_3SiBr/CoBr_2/n\text{-}Bu_4NBr$/MS-4A/$CH_2Cl_2$,
B : NaOMe/MeOH/1,4-dioxane, C : H_2/Pd/C/AcOH.

Fig. 1. Synthetic scheme of the glucotriose, **23**.

ed by chromatography of furnish the acetate (**8**) (1.1 g, 55%), mp 93—95 °C, $[\alpha]_D^{20}$ +81° (*c* 1.0, $CHCl_3$) (lit,[9] mp 76—78 °C, $[\alpha]_D^{20}$ +53.0 (*c* 1, $CHCl_3$)] (Found: C, 74.10, H, 6.63%).

The treatment of **8** with a dil. solution of NaOMe in MeOH gave **7** quantitatively; $[\alpha]_D^{20}$ +88° (*c* 2.3, $CHCl_3$). Found: C, 75.47, H, 6.58%. Calcd for $C_{34}H_{36}O_6$: C, 75.53; H, 6.71%.

Reaction of ***1*** *with* Me_3SiBr *and* $CoBr_2$. Me_3SiBr (11 μl, 0.083 mmol) was stirred into a mixture of **1** (45 mg, 0.083 mmol) and $CoBr_2$ (18.3 mg, 0.083 mmol) in CH_2Cl_2 (0.3 ml). After stirring for 0.5 h at room temperature, the mixture was filtered quickly. The ^1H NMR of the filtrate was essentially identical with that of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl bromide (**2**)[10] in CH_2Cl_2 (δ=6.59, J= 4 Hz).[2c]

*Reaction of 2,3,4,6-Tetra-*O*-benzyl-α-*D*-glucopyranosyloxytrimethylsilane (****3****) with* Me_3SiBr *and* $CoBr_2$. Compound **3**[11] (62.7 mg, 0.010 mmol) was treated with Me_3SiBr (13 μl, 0.010 mmol) and $CoBr_2$ (22.4 mg, 0.010 mmol) in CH_2Cl_2 for 15 min at room temperature. The filtrate showed a ^1H NMR spectrum almost identical with that of **2** in CH_2Cl_2.

Reaction of the Bromide ***2*** *with (5α-Cholestan-3β-yloxy)trimethylsilane in the Presence of* $CoBr_2$. A mixture of **2**[10] (42 mg, 0.07 mmol), and trimethylsilyl compound[12] (32 mg, 0.07 mmol), and $CoBr_2$ (15 mg, 0.07 mmol) in CH_2Cl_2 (0.4 ml) was stirred for 2 h at room temperature. The filtrate of the reaction mixture was then chromatographed[2b] to give **4a** (19 mg, 30%) and **4b** (11 mg, 17%).

Without $CoBr_2$, the glucosylation did not proceed.

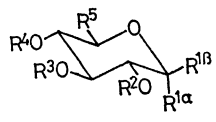
Reaction of the Trimethylsilyl Glucose ***3*** *with 5α-Cholestan-3β-ol,* $CoBr_2$, Me_3SiBr, *and MS-4A.* A mixture of **2a** (55 mg, 0.090 mmol), the alcohol (26.3 mg, 0.068 mmol), $CoBr_2$ (21 mg, 0.095 mmol), MS-4A (72 mg), and Me_3SiBr (12 μl, 0.090 mmol) in CH_2Cl_2 (0.24 ml) was agitated for 6 h at room temperature. The subsequent chromatography of the mixture gave **4a** (15 mg, 24%) and **4b** (24 mg, 38%).

*Benzyl O-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-*D*-glucopyranosyl)-(1→6)-2,4,6-tri-*O*-benzyl-α-*D*-glucopyranosides (****17a*** *and* ***17b****).* A mixture of **1** (570 mg, 1.06 mmol), **11** (400 mg, 0.81 mmol), $CoBr_2$ (232 mg, 1.06 mmol), $n\text{-}Bu_4NBr$ (340 mg, 1.06 mmol), MS-4A (855 mg), and Me_3SiBr (138 μl, 1.06 mmol) in CH_2Cl_2 (2.45 ml) was stirred for 20 h at room temperature. The filtrate of the reaction mixture was then briefly chromatographed to give a sirupy mixture of the products (602 mg). This was de-*O*-acetylated and then chromatographed in the manner described before[6b] to give **17a** (475 mg, 60%) and **17b** (85 mg, 11%). They were identified with the respective samples synthesized previously.[6b]

*O-α-*D*-Glucopyranosyl-(1→3)-*O*-[α-*D*-glucopyranosyl-(1→6)]-*D*-glucopyranose (****29****).* Me_3SiBr (78 μl, 0.60 mmol) was stirred into a mixture of **1** (322 mg, 0.60 mmol), the disaccharide **17a** (445 mg, 0.46 mmol), $CoBr_2$ (1313 mg, 0.60 mmol), $n\text{-}Bu_4NBr$ (191 mg, 0.60 mmol), and MS-4A (485 mg) in CH_2Cl_2 (1.6 ml), after which the stirring was continued for 40 h at room temperature. The filtrate of the reaction mixture was then evaporated and chromatographed to give a syrupy product mixture (266 mg) with three spots [R_f 0.58 (**22b**), 0.55 (**22a**), and 0.50 (the benzylate of α,α-trehalose[2a]), benzene–2-butanone (20:1)]. This was carefully separated through three chromatographies to give **22a** and **22b** (Table 1).

The hydrogenation of **22a** (90 mg) gave **23** (26 mg) as a foam, $[\alpha]_D^{20}$ +126° (*c* 0.4, H_2O) [lit,[5] $[\alpha]_D^{14}$ +133° (*c* 0.7, H_2O)]. Found: C, 40.37; 6.23%. Calcd for $C_{18}H_{32}O_{16}\cdot 1.5H_2O$: C, 40.67; H, 6.64%.

The reduction of **23** (10 mg, 0.010 mmol) with $NaBH_4$ (Wako, 30 mg) in H_2O (3 ml) for 48 h at room temperature, followed by the usual work-up and acetylation, furnished crystalline *O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→3)-*O*-[(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→6)]-1,2,4,5-tetra-*O*-acetyl-D-glucitol (**25**) (8.4 mg, 42%).



Bn = Benzyl,
Ct = 5α-cholestan-3β-yl,
G = 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl,
AcG = 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl,
Glc = D-glucopyranosyl.

Code	$R^{1\alpha}$	$R^{1\beta}$	R^2	R^3	R^4	R^5
1	OH	H	Bn	Bn	Bn	CH_2OBn
2	Br	H	Bn	Bn	Bn	CH_2OBn
3	$OSiMe_3$	H	Bn	Bn	Bn	CH_2OBn
4a	OCt	H	Bn	Bn	Bn	CH_2OBn
4b	H	OCt	Bn	Bn	Bn	CH_2OBn
5	OMe	H	Bn	H	Bn	H
6	OMe	H	Bn	Bn	H	H
7	OBn	H	Bn	H	Bn	CH_2OBn
8	OBn	H	Bn	Ac	Bn	CH_2OBn
9	OMe	H	Bn	Bn	Bn	CH_2OH
10	OBn	H	Bn	Bn	Bn	CH_2OH
11	OBn	H	Bn	Ac	Bn	CH_2OH
12a	OMe	H	Bn	αG	Bn	H
12b	OMe	H	Bn	βG	Bn	H
13a	OMe	H	Bn	Bn	αG	H
13b	OMe	H	Bn	Bn	βG	H
14a	OBn	H	Bn	αG	Bn	CH_2OBn
14b	OBn	H	Bn	βG	Bn	CH_2OBn
15a	OMe	H	Bn	Bn	Bn	$CH_2O\alpha G$
15b	OMe	H	Bn	Bn	Bn	$CH_2O\beta G$
16a	OBn	H	Bn	Bn	Bn	$CH_2O\alpha G$
16b	OBn	H	Bn	Bn	Bn	$CH_2O\beta G$
17a	OBn	H	Bn	H	Bn	$CH_2O\alpha G$
17b	OBn	H	Bn	H	Bn	$CH_2O\beta G$
18	H,	OH	H	αGlc	H	CH_2OH
19	H,	OAc	Ac	αAcG	Ac	CH_2OAc
20	H,	OH	H	H	H	$CH_2O\alpha Glc$
21	H,	OAc	Ac	Ac	Ac	$CH_2O\alpha AcG$
22a	OBn	H	Bn	αG	Bn	$CH_2O\alpha G$
22b	OBn	H	Bn	βG	Bn	$CH_2O\alpha G$
23	H,	OH	H	αGlc	H	$CH_2O\alpha Glc$
24	H,	OAc	Ac	αAcG	Ac	$CH_2O\alpha AcG$

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