# α-D-Glucosylation by 6-O-Acetyl-2,3,4-tri-O-benzyl-D-glucopyranose Using Trimethylsilyl Triflate and Pyridine. Synthesis of α-Maltosyl and α-Isomaltosyl α-D-Glucosides[1]

Shinkiti KOTO,* Kazuo YAGO,† Shonosuke ZEN, Fumiya TOMONAGA,† and Shigehiko SHIMADA†
School of Pharmaceutical Sciences, Kitasato University, Shirokane, Minato-ku, Tokyo 108
†Department of Pharmacy, Kitasato University Hospital, Kitasato, Sagamihara 228
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The D-glucosylation of methyl 2,3,4-tri-O-benzyl-α-D-glucopyranoside and methyl 2,3,6-tri-O-benzyl-β-D-glucopyranoside by 2,3,4,6-tetra-O-benzyl-α-D-glucopyranose using pyridine and excess trimethylsilyl triflate was carried out in dichloromethane, 1,2-dimethoxyethane, and acetonitrile. In a given solvent, the selectivity of the reaction varied depending on the type of hydroxyl group of the glucosyl acceptors. The D-glucosylation of these acceptors with 6-O-acetyl-2,3,4-tri-O-benzyl-D-glucopyranose employing this reagent system in dichloromethane proceeded with good α-selectivity irrespective of the type of the hydroxyl group. This α-D-glucosylation was applied for the synthesis of O-α-D-glucopyranosyl-(1→4)- and -(1→6)-α-D-glucopyranosyl α-D-glucopyranosides from α,α-trehalose.

Traditional glycosylation is performed with the aid of various heavy-metal compounds.[2] Several methods are, however, free from the use of such materials.[3,4] The desiloxane-promoted condensation between a 1-O-silyl derivative of 2,3,4,6-tetra-O-benzyl-α-D-glucopyranose (**1**) as a D-glucosyl donor and a silylated alcohol as its acceptor is catalyzed by strong acids such as sulfonic acids,[5] as well as a Lewis acid like trimethylsilyl triflate (TMSOTf).[6,7] Since trimethylsilyl triflate[8] is a powerful silylation reagent for a hydroxy compound, a mixture of excess trimethylsilyl triflate and a base such as pyridine (Py) was expected to bring about a condensation between **1** and an alcohol (Eq. 1) in which G denotes a 2,3,4,6-tetra-O-benzyl-D-glucosyl residue or appropriate equivalents.

$$\mathrm{GOH} + \mathrm{ROH} \xrightarrow[-2\mathrm{TfOH}\cdot\mathrm{Py}]{(2+x)\mathrm{TMSOTf}+2\mathrm{Py}} (\mathrm{GOTMS} + \mathrm{ROTMS}) \xrightarrow[-\mathrm{TMS_2O}]{x\mathrm{TMSOTf}} \mathrm{GOR} \qquad (1)$$

The results of the D-glucosylation of the protected glucosides **2** and **3** with **1** (prescribed by Eq. 1) is summarized in Table 1. The value of $x$, the excess of trimethylsilyl triflate (Eq. 1), was sufficient at 1.5 for the primary alcohol **2** (Entry 1) and at 2 for the secondary alcohol **3** (Entry 4) to react in dichloromethane at 0°C. Glucosylation in this solvent, however, showed poor selectivity. On the other hand, the glucosylation of **3** (Entry 5) in 1,2-dimethoxyethane exhibited a good α-selectivity but the reaction was slow. The reaction of **2** (Entry 2) in 1,2-dimethoxyethane, however, did not show any selectivity. The glucosylation of **2** (Entry 3) in acetonitrile[4] showed only moderate β-selectivity. A similar selectivity, however, was not observed in the reaction of **3** (Entry 6) in acetonitrile. Such a weak solvent-dependency of the selectivity is in contrast to the remarkable dependence of the selectivity observed in a coupling reaction between glucosyl fluoride and silylated alcohol in the presence of trimethylsilyl triflate.[4]

Expectedly,[7] in the absence of an acceptor, **1** underwent self-condensation[5] to give **9** and **10** (Entry 7).

6-O-Acetyl-2,3,4-tri-O-benzyl-D-glucopyranose (**4**), readily derived from 1,6-anhydro-β-D-glucopyranose (levoglucosan), has been used as an α-D-glucosyl donor in dehydrative glucosylation.[9] This compound was again effective for α-D-glucosylation in the glucosylation of **2** and **3** using the above-described reagent mixture (Entries 8 and 9). The α-selectivity (86%) of the glucosylation of the primary alcohol was improved

Table 1. Results of D-Glucosylation by Protected D-Glucoses Using Pyridine and Excess Trimethylsilyl Triflate

| Entry | Donor GOH (equiv) | Acceptor ROH (0.1 mmol) | Solv. (0.5 ml) | Py (equiv) | TMSOTf (equiv) | $x$[a] | Temp °C | Time h | Glucosides GOR %(α/β) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **1** (1.0) | **2** | $CH_2Cl_2$ | 2.5 | 4.0 | 1.5 | 0 | 4.5 | **5+6** 90(43/57) |
| 2 | **1** (1.1) | **2** | $(CH_2OMe)_2$ | 2.6 | 4.6 | 2.0 | 0 | 4.5 | **5+6** 48(48/52) |
| 3 | **1** (1.1) | **2** | MeCN | 2.6 | 4.6 | 2.0 | 0 | 4.5 | **5+6** 81(32/68) |
| 4 | **1** (1.3) | **3** | $CH_2Cl_2$ | 2.8 | 4.9 | 2.1 | 0 | 4.5 | **7+8** 78(57/43) |
| 5 | **1** (1.3) | **3** | $(CH_2OMe)_2$ | 2.8 | 4.9 | 2.1 | 0 | 6 | **7+8** 31(82/18) |
| 6 | **1** (1.3) | **3** | MeCN | 2.8 | 4.9 | 2.1 | 5 | 3 | **7+8** 68(42/58) |
| 7 | **1** (1.0) | **1** | $CH_2Cl_2$ | 2.4 | 4.3 | 1.9 | 0 | 6 | **9+10** 79(45/55) |
| 8 | **4** (1.1) | **2** | $CH_2Cl_2$ | 2.6 | 4.1 | 1.5 | 0 | 4.5 | **11+12** 89(86/14) |
| 9 | **4** (1.3) | **3** | $CH_2Cl_2$ | 2.8 | 4.9 | 2.1 | 0 | 4.5 | **13+14** 72(86/14) |

a) $x$=TMSOTf(equiv)−Py(equiv) (cf. Eq. 1).

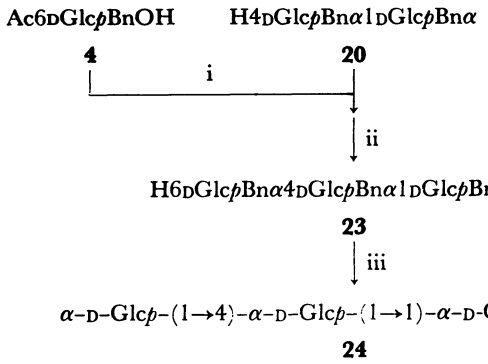



Fig. 1. Synthetic Scheme of α-Maltosyl α-D-Glucoside (**24**); Bn=—$CH_2Ph$ (cf. Ref. 19 for the code-expression of the protected carbohydrates).

compared to the previously reported method (69%).[9]

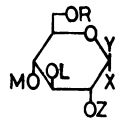
The α-D-glucosylation described so far was then applied to the synthesis of *O*-α-D-glucopyranosyl-(1→4)- and -(1→6)-α-D-glucopyranosyl α-D-glucopyranosides (**24** and **28**) as illustrated in Fig. 1 for the case of **24**. Various kinds of unsymmetrical α,α-trehaloses have been synthesized in view of biological interests.[10–12] A short-time treatment of a solution of α,α-trehalose (**15**) in dimethyl sulfoxide with 2,2-dimethoxypropane in the presence of *p*-toluenesulfonic acid, followed by acetylation, gave the monoisopropylidene derivative **17** in a 57% yield. This compound was transformed into the hexabenzyl derivative **19**, which was then converted into a heptabenzyl derivative **20** via controlled benzylation. The heptabenzyl derivative **21** was prepared via tritylation of **19**. Glucosylation of **20** and **21** with **4** gave the corresponding α-glucosides **22** and **26** with good selectivity. A deprotection of these compounds afforded the unsymmetrical derivatives, **24** and **28**, of trehalose, and their C-13 were consistent with their proposed structure.

## Experimental[13,14]

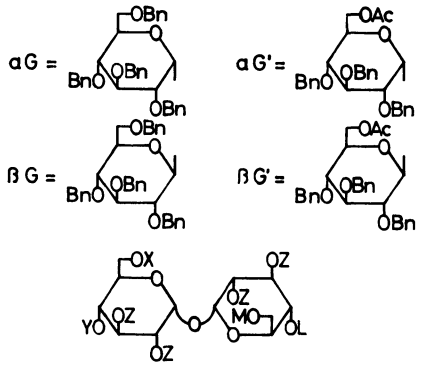
Compounds **5**,[15] **6**,[16] **7**,[13] **8**,[13] **9**,[5] and **10**[5] were identified with those prepared before.

**Procedure for Glucosylation.** Pyridine and trimethylsilyl triflate (Aldrich) were successively injected into a stirring mixture of a donor and an acceptor in a solvent at −45 °C. The temperature was allowed to increase to the temperature specified in Table 1 and below. The reaction was continued for an appropriate duration. After the addition of triethylamine equimolar to trimethylsilyl trilfate, the mixture was concentrated and chromatographed using toluene–2-butanone system (gradient elution).

**Methyl *O*-(6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranosides (11 and 12).** Compound **11**, mp 80—82°C, $[\alpha]_D^{20}$ +56° (*c* 2.1, $CHCl_3$), $R_f$=0.35 (toluene/2-butanone=10/1), $\delta_C$($CDCl_3$, TMS) 97.3 and 98.2 (the anomeric carbons). Compound **12**, $[\alpha]_D^{20}$ +29° (*c* 0.5, $CHCl_3$), $R_f$=0.33, $\delta_C$($CDCl_3$, TMS) 98.2

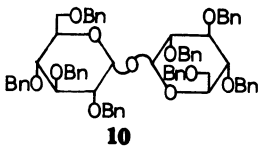


| Cpd. | X | Y | Z | L | M | R |
|---|---|---|---|---|---|---|
| **1** | OH | H | Bn | Bn | Bn | Bn |
| **2** | OMe | H | Bn | Bn | Bn | H |
| **3** | H | OMe | Bn | Bn | H | Bn |
| **4** | OH, | H | Bn | Bn | Bn | Ac |
| **5** | OMe | H | Bn | Bn | Bn | αG |
| **6** | OMe | H | Bn | Bn | Bn | βG |
| **7** | H | OMe | Bn | Bn | αG | Bn |
| **8** | H | OMe | Bn | Bn | βG | Bn |
| **11** | OMe | H | Bn | Bn | Bn | αG′ |
| **12** | OMe | H | Bn | Bn | Bn | βG′ |
| **13** | H | OMe | Bn | Bn | αG′ | Bn |
| **14** | H | OMe | Bn | Bn | βG′ | Bn |

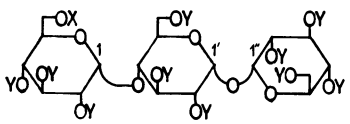





| Cpd. | X | Y | Z | L | M |
|---|---|---|---|---|---|
| **9** | Bn | Bn | Bn | Bn | Bn |
| **15** | H | H | H | H | H |
| **16** | Me | Me | Ac | Me | Me |
| **17** | Me | Me | Ac | Ac | Ac |
| **18** | Ac | Ac | Ac | Ac | Ac |
| **19** | H | H | Bn | Bn | Bn |
| **20** | Bn | H | Bn | Bn | Bn |
| **21** | H | Bn | Bn | Bn | Bn |

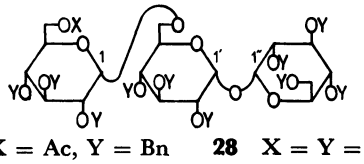


**10**



**22** X = Ac, Y = Bn **24** X = Y = H

**23** X = H, Y = Bn **25** X = Y = Bz



**26** X = Ac, Y = Bn **28** X = Y = H

**27** X = H, Y = Bn

and 104.1 (the anomeric carbons).

Found: **11**, C, 72.79, H, 6.64%. **12**, 72.81, H, 6.64%. Calcd for $C_{57}H_{62}O_{12}$: C, 72.90, H, 6.65%.

**Methyl O-(6-O-Acetyl-2,3,4-tri-O-benzyl-α- and -β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside(13 and 14).** Compound **13**, $[\alpha]_D^{20}$ +33° (*c* 1.3, $CHCl_3$), $R_f$= 0.38 (toluene/2-butanone=10/1), $\delta_C$($CDCl_3$, TMS) 96.8 and 104.9 (the anomeric carbons). Compound **14**, $[\alpha]_D^{20}$ +10° (*c* 0.6, $CHCl_3$), $R_f$=0.33, $\delta_C$($CDCl_3$, TMS) 102.5 and 104.9 (the anomeric carbons).

Found: **13**, C, 73.17, H, 6.69%. **14**, C, 73.15, H, 6.75%. Calcd for $C_{57}H_{62}O_{12}$: C, 72.90, H, 6.65%.

**2,3-Di-O-benzyl-α-D-glucopyranosyl 2,3,4,6-Tetra-O-benzyl-α-D-glucopyranoside (19).** A solution of **15** (Tokyo Kasei, 1.0 g, 2.9 mmol), *p*-toluenesulfonic acid monohydrate (100 mg) in dimethyl sulfoxide (19 ml) was treated with 2,2-dimethoxypropane (1.0 ml) at room temperature for 55 min. After the addition of triethylamine (1.5 ml), the mixture was evaporated at 85°C to give a syrup which was then treated with acetic anhydride (12 ml) and pyridine (24 ml) at room temperature. Chromatography using toluene–2-butanone system (gradient) afforded **16** (0.21 g, 12%), **17** (1.06 g, 57%), mp 80—81°C, $[\alpha]_D^{20}$ +141° (*c* 0.6, $CHCl_3$) (lit,[11] mp 79—80°C, $[\alpha]_D$ +150.5° (*c* 1.1, $CHCl_3$)), and **18** (0.61 g, 31%).

The monoisopropylidene derivative **17** (530 mg, 0.84 mmol) was heated in benzyl chloride (10.5 ml) containing potassium hydroxide (2.5 g) at 130°C for 1.0 h. Filtration and evaporation at 95°C gave a yellow oil, which was heated in 80% aq acetic acid (40 ml) at 90°C for 15 min. Evaporation and chromatography using toluene–2-butanone system (gradient) gave **19** (484 mg, 66% from **17**), $[\alpha]_D^{20}$ +92° (*c* 0.6, $CHCl_3$) (lit,[11] [α]+90° (*c* 3.09, $CHCl_3$)).

**2,3,6-Tri-O-benzyl-α-D-glucopyranosyl 2,3,4,6-Tetra-O-benzyl-α-D-glucopyranoside (20).** A mixture of **19** (484 mg, 0.55 mmol), silver oxide (1.66 g), anhydrous calcium sulfate (1.66 g), and benzyl bromide (0.66 ml) in chloroform (7.2 ml) was stirred at room temperature overnight.[17] Chromatography using hexane–acetone system (gradient) gave **9** (33.7 mg), **20** (387 mg, 73%), $[\alpha]_D^{20}$ +89° (*c* 1.2, $CHCl_3$), $\delta_C$($CDCl_3$, TMS) 94.5 (2C, the anomeric carbons), **21** (72 mg, 14%), $[\alpha]_D^{20}$ +96° (*c* 1.4, $CHCl_3$), $\delta_C$($CDCl_3$, TMS) 94.3 and 94.5 (the anomeric carbons).

Found: **20**, C, 74.42, H, 6.42%. **21**, C, 74.76, H, 6.49%. Calcd for $C_{61}H_{64}O_{11}$: C, 75.29, H, 6.63%.

**2,3,4-Tri-O-benzyl-α-D-glucopyranosyl 2,3,4,6-Tetra-O-benzyl-α-D-glucopyranoside (21).** A solution of **19** (70.2 mg, 0.080 mmol), and trityl chloride (120 mg) in pyridine (0.7 ml) was kept standing for 3 h at 65°C. After the addition of triethylamine (1 ml) and toluene (1 ml), the mixture was evaporated to dryness. The residue was heated in benzyl chloride (2.8 ml) containing potassium hydroxide (1.0 g) at 130°C for 2 h. After filtration and evaporation, the residue obtained was heated in aq acetic acid (80%, 4 ml) at 95°C for 0.5 h. Chromatography (toluene–2-butanone) gave **21** (60.0 mg, 78%).

**O-(6-O-Acetyl-2,3,4-tri-O-benzyl-α-D-glucopyranosyl)(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranosyl 2,3,4,6-Tetra-O-benzyl-α-D-glucopyranoside (22).** D-Glucosylation of **20** (143.2 mg, 0.15 mmol) with **4** (94.2 mg, 0.19 mmol) in the presence of pyridine (33.4 μl) and trimethylsilyl triflate (156.4 μl) in dichloromethane (1.4 ml) was conducted at 5 °C for 6 h. Chromatography (toluene–2-butanone, gradient) gave the impure β-anomer (ca. 20 mg, $R_f$=0.53 (toluene/2-butanone=10/1), $\delta_C$($CDCl_3$, TMS) 103.2) and **22** (161.0 mg, 76%), $[\alpha]_D^{20}$ +81° (*c* 0.4, $CHCl_3$), $R_f$=0.49, $\delta_C$($CDCl_3$, TMS) 94.0, 94.6, and 97.3 (the anomeric carbons). Found: C, 75.25, H, 6.57%. Calcd for $C_{90}H_{94}O_{17}$: C, 74.67, H, 6.54%.

**O-(6-O-Acetyl-2,3,4-tri-O-benzyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranosyl 2,3,4,6-Tetra-O-benzyl-α-D-glucopyranoside (26).** Condensation between **4** (55.6 mg, 0.11 mmol) and **21** (100.0 mg, 0.10 mmol) in the presence of pyridine (21.6 μl) and trimethylsilyl triflate (91.4 μl) in dichloromethane (1.0 ml) at 5°C for 6 h, followed by chromatography (toluene–2-butanone, gradient) gave the impure β-anomer (ca. 10 mg, $R_f$=0.47 (toluene/2-butanone=10/1), $\delta_C$($CDCl_3$, TMS) 103.2) and **26** (118 mg, 79%), $[\alpha]_D^{20}$ +93° (*c* 0.7, $CHCl_3$), $R_f$=0.43, $\delta_C$($CDCl_3$, TMS) 94.3 (2C), and 97.4 (the anomeric carbons). Found: C, 75.13, H, 6.51%. Calcd for $C_{90}H_{94}O_{17}$: C, 74.67, H, 6.54%.

**O-(2,3,4-Tri-O-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranosyl 2,3,4,6-Tetra-O-benzyl-α-D-glucopyranoside (23).** A solution of **22** (50.3 mg, 0.035 mmol) in methanol (2 ml) and acetone (1 ml) was treated with 1.5M (1M=1 mol $dm^{-3}$) sodium methoxide in methanol (0.3 ml) at room temperature overnight. After neutralization with acetic acid, evaporation and chromatography (toluene–2-butanone) furnished **23** (30.2 mg, 62%), $[\alpha]_D^{20}$ +95° (*c* 1.6, $CHCl_3$), $\delta_C$($CDCl_3$, TMS) 94.1, 94.7, and 97.1 (the anomeric carbons). Found: C, 75.19, H, 6.63%. Calcd for $C_{88}H_{92}O_{16}$: C, 75.19, H, 6.60%.

**O-(2,3,4-Tri-O-benzyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-O-D-glucopyranosyl 2,3,4,6-Tetra-O-benzyl-α-D-glucopyranoside (27).** Similar deacetylation of **26** (58.2 mg, 0.04 mmol) gave **27** (55 mg, 97%), $[\alpha]_D^{20}$+101° (*c* 1.5, $CHCl_3$), $\delta_C$($CDCl_3$, TMS) 94.4 (2C) and 97.5 (the anomeric carbons). Found: C, 75.01, H, 6.50%. Calcd for $C_{88}H_{92}O_{16}$: C, 75.19, H, 6.60%.

**O-α-D-Glucopyranosyl-(1→4)-α-D-glucopyranosyl α-D-Glucopyranoside (24).** Hydrogenation of **23** (53.6 mg, 0.038 mmol) over palladized charcoal (10%, 40 mg) in acetic acid (6 ml) under 340 kPa of hydrogen at room temperature overnight, followed by chromatography (chloroform/methanol=1/1), gave **24** (17 mg, 81%), $[\alpha]_D^{20}$+169° (*c* 0.4, $H_2O$), $\delta_H$($D_2O$, TMS(ext.)) 5.61 (2H, d, *J*=3.6 Hz, H-1, H-1′), 5.85 (1H, d, *J*=3.0 Hz, H-1″), $\delta_C$($D_2O$, TMS(ext.))[18] 61.7 (3C, C-6, -6′, and -6″), 70.6 (C-4), 70.9 (C-4″), 72.0 (C-2′), 72.1 (C-2″), 72.3 (C-2), 73.0 (C-5), 73.4 (C-5″), 73.8 (C-5′), 73.9 (C-3″), 74.1 (C-3′), 74.3 (C-3), 78.2 (C-4′), 94.5 (C-1″), 94.7 (C-1′), and 101.0 (C-1). Found: C, 42.59, H, 6.19%. Calcd for $C_{18}H_{32}O_{16}$: C, 42.86, H, 6.39%.

Benzoylation of **24** (5.1 mg, 0.01 mmol) with benzoyl chloride (1 ml) and pyridine (2 ml) gave the perbenzoate **26** (13.7 mg, 82%), mp 118—119°C, $[\alpha]_D^{20}$ +202° (*c* 0.8, $CHCl_3$) (Found: C, 69.06, H, 4.64%); lit,[12] mp 121—122°, $[\alpha]_D^{21}$+217° (*c* 0.7, $CHCl_3$).

**O-α-D-Glucopyranosyl-(1→6)-α-D-glucopyranosyl α-D-Glucopyranoside (28).** Similar hydrogenation of **27** (70.6 mg, 0.05 mmol) gave **28** (15.2 mg, 60%), $[\alpha]_D^{20}$+144° (*c* 0.6, $H_2O$), $\delta_H$($D_2O$, TMS(ext.)) 5.41 (1H, d, *J*=3.6 Hz, H-1″), 5.61 (2H, d, *J*=3.5 Hz, H-1, H-1′), $\delta_C$($CDCl_3$TMS(ext.))[18] 61.7 (2C, C-6 and C-6″), 66.6 (C-6′), 70.8 (C-4), 70.9 (2C, C-4′ and -4″), 71.8 (C-2′), 72.2 (2C, C-2 and -2″), 72.7 (C-5), 73.1 (C-5′), 73.4 (C-5″), 73.8 (C-3″), 74.1 (C-3′), 74.4 (C-3), 94.6 (2C, C-1′ and -1″), and 99.0 (C-1). Found: C, 42.76, H, 6.13%. Calcd for $C_{18}H_{32}O_{16}$: C, 42.86, H, 6.39%.

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