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Dehydrative Glycosylation by Diethylaminosulfur Trifluoride (DAST) –Tin(II) Trifluoromethanesulfonate–Tetrabutylammonium Perchlorate –Triethylamine System

Motoko Hirooka* **and Shinkiti Koto***

School of Pharmaceutical Sciences, Kitasato University, Shirokane, Minato-ku, Tokyo 108-8641

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Dehydrative glycosylation using 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose was carried out by the use of a condensing reagent system composed of diethylaminosulfur trifluoride (DAST), tin(II) triflate, tetrabutylammonium perchlorate, and triethylamine. Using this system, two tetrasaccharides, *O*-*α*-D-glucopyranosyl-(1→4)-*O*-*α*-D-glucopyranosyl-(1→3)-*O*-*α*-D-glucopyranosyl-(1→4)-D-glucopyranose and *O*-*α*-D-glucopyranosyl-(1→3)-*O*-*α*-D-glucopyranosyl-(1→4)-*O*-*α*-D-glucopyranosyl-(1→4)-D-glucopyranose, were synthesized.

Simplification of the procedure of glycosylation[1] is beneficial to glycosylation technology.[2] Dehydrative glycosylation[3] (Eq. 1; DOH denotes glycosyl donors

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

such as 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**1**, Fig. 1) and AOH expresses glycosyl acceptors) has an attractive point that it is free from glycosylation using moisture-sensitive donors.[2] The glycosylations using a dehydrating reagent system also have nothing to do with preparation of a donor having a latent leaving group[2] from a 1-OH derivative like **1**. However, little attention has been paid to such kind of glycosylation.[4]

Diethylaminosulfur trifluoride (DAST)[5] converts a 1-OH sugar derivative like **1** into the corresponding protected glycosyl fluorides[6] such as 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl fluorides (**2** and **3**). The fluorides are, in turn, activated in situ with Lewis acid[7] in the presence of glycosyl acceptors to undergo glycosylation. This led us to search for any Lewis acid which can *activate the fluorides but not inhibit DAST* from converting **1** into the fluorides. We wish to report our experimental results concerning the combined use of DAST and Lewis acid for dehydrative glycosylation (Eq. 1). We here describe for the first time how the reagent system composed of DAST (Et_2NSF_3), tin(II) trifluoromethanesulfonate ($Sn(OTf)_2$), tetrabutylammonium perchlorate (Bu_4NClO_4), and triethylamine (Et_3N), performs dehydrative glycosylation (Eq. 2).

$$\mathrm{DOH + AOH} \xrightarrow{\mathrm{Et_2NSF_3+Sn(OTf)_2+Bu_4NClO_4+Et_3N}} \mathrm{DOA} \qquad (2)$$

When DAST was added into a solution of **1** (α/β = 75/25) in dichloromethane (CH_2Cl_2) at −60 °C and the reaction temperature was allowed to rise to 0 °C,[5,8] the glucosyl fluorides **2** and **3** (95%, **2/3** = 26/74) (Table 1, Run 1) was obtained after chromatography. It was confirmed that DAST converted **1** into a mixture of the fluorides **2** and **3** (Run 2, 51%, **2/3** = 24/76) when cyclohexanol was included. DAST was then reacted with an equimolar mixture of **1** and cyclohexanol in the presence of various Lewis acids[7] at −60 °C and then the reaction temperature was allowed to rise to 0 °C. It was found that $Sn(OTf)_2$ performed the glycosylation to give the cross-condensates **6** and **7** (Run 3, 28%, **6/7** = 75/25) but with severe concurrent formation (58%) of the self-condensates: **8**, **9**, and **10** (Fig. 1). Unreacted **1** could be recovered almost quantitatively through chromatography. The combined use of a base[9] such as Et_3N with $Sn(OTf)_2$ increased the yields of the desired cross-condensates **6** and **7** (Run 4, 43%, **6/7** = 23/77). Based on the results of Run 1 and Run 4, the present glycosylation may be considered to proceed through the pathways illustrated in Scheme 1. DAST reacts with **1** below 0 °C to form the glycosyl fluorides **2** and **3**, which immediately coordinate with $Sn(OTf)_2$. The complexes of the glycosyl fluorides with $Sn(OTf)_2$ will form reactive glycosyl triflates with a rapid anomeric equilibrium in which αDOTf predominates due to anomeric effect. The use of two molar amounts of the acceptor and the reagents diminished the yield of the self-condensates from 43% (Run 4) to 24% (Run 5). The cross-condensates **6** and **7** were obtained as major products (Run 5, 53%). However, a notable amount of the stable α-fluoride **2** remained unreacted (Run 5, 20%). The solvents such as propionitrile (EtCN) (Run 7) and diethyl ether (Et_2O) (Runs 8 and 9) worked to exhaust **2**, but such an effect of toluene (Run 6) was not sufficient. The solvent Et_2O, which forms the β-onium intermediate giving α-glycosides[10] (Scheme 1), increased the yield of the α-anomer **6**, as predicted. To exhaust the fluorides **2** and **3**, Bu_4NClO_4 was also used to give **6** and **7** with an unexpectedly enhanced β-selectivity (Run 10, 62%, **6/7** = 5/95). These results may be explained by assuming the in situ generation of the perchlorate having α-configuration such as $[\alpha D]^{\oplus}[ClO_4]^{\ominus}$, via a rapid equilibrium favoring the

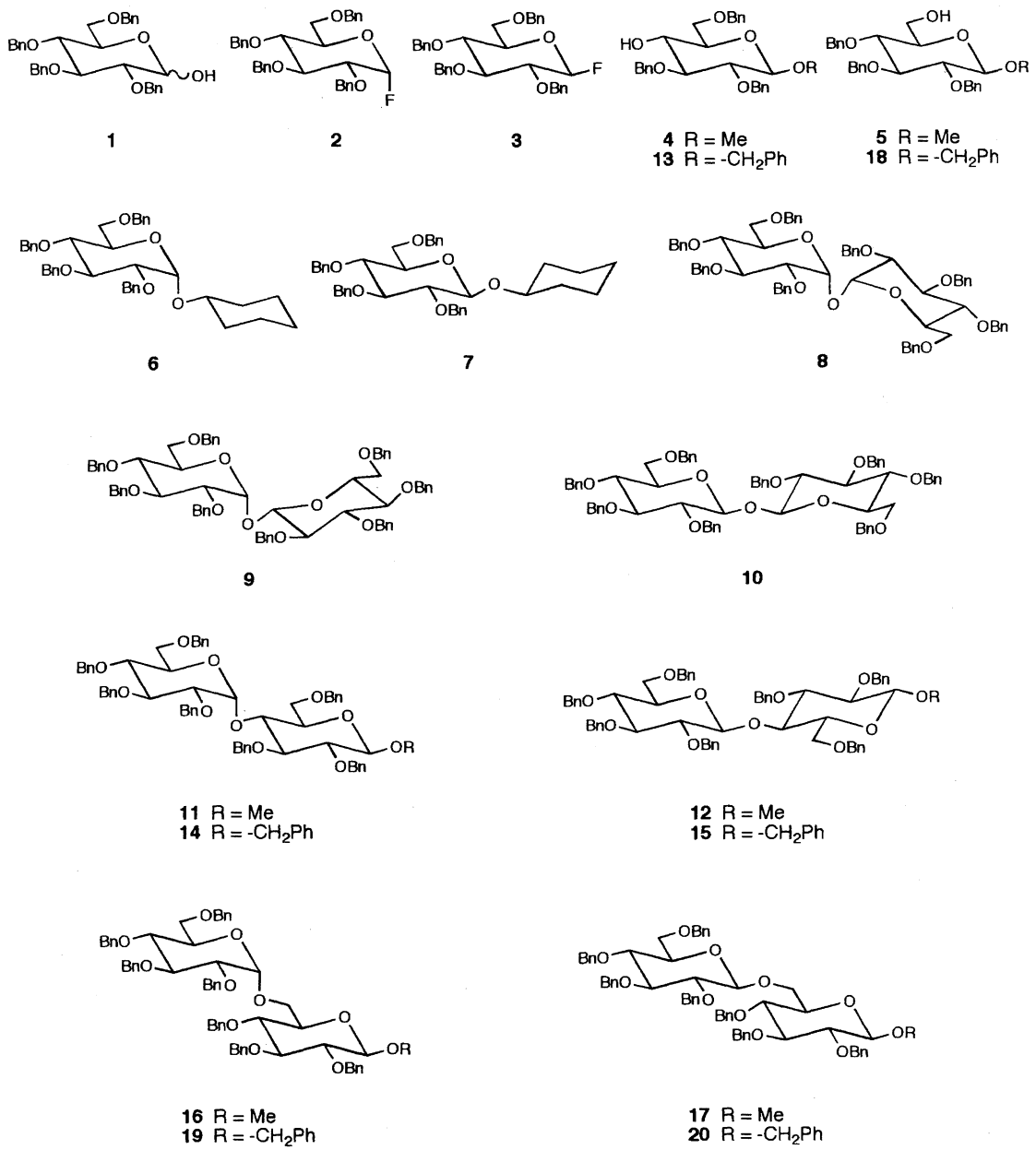


Fig. 1.

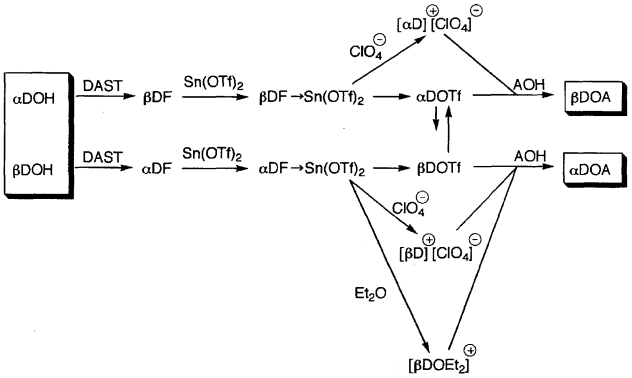
α-anomer, to afford more of the precursor of the β-glycoside **7** (Scheme 1). Such behavior of the additive Bu_4NClO_4 was not exhibited in CH_2Cl_2–Et_2O (1 : 1, v/v) to afford a significant amount of the α-anomer **6** (Run 12, **6/7** = 31/69). Although the present system contains toxic DAST, the β-selectivity (α/β = 5/95) which resulted in the condensation between **1** and cyclohexanol was much higher than that observed in the earlier case using *p*-nitrobenzenesulfonyl chloride–silver trifluoromethanesulfonate–triethylamine (α/β = 28/72).[11] This is in a marked contrast to α-selective dehydrative glycosylation using cobalt(II) bromide–methanesulfonic acid–tetraethylammonium perchlorate[12] or with *p*-nitrobenzenesulfonyl chloride–silvertrifluoromethanesulfonate–*N*,*N*-dimethylacetamide–triethylamine.[13]

The conditions of Runs 9, 10, and 12 which gave promising results were then applied to the condensation of the donor **1** and the acceptor **4** to give the corresponding condensates **11** and **12** (Runs 14, 15, and 16; Table 2). Unreacted **1** and **4** were recovered. The β-selectivity shown by Run 10 was barely retained in Run 15 (**11/12** = 35/65). Run 16 using Bu_4NClO_4 in CH_2Cl_2–Et_2O (1 : 1, v/v) furnished the α-anomer **11** (**11/12** = 58/42). The conditions of the β-selective Run 10 were applied to the condensations of the donor **1** with the other acceptors: **5**, **13**, and **18**. In every case, the β-selectivity was significantly diminished (Runs 17, 19, and 21). The conditions of Run 12 using the solvent CH_2Cl_2–Et_2O (1 : 1, v/v) was also examined (Runs 18, 20, and 22). Similar to Run 16, the acceptor **13** with a secondary hydroxy group afforded the corresponding α-linked condensate **14** preferentially (Run 18, **14/15** = 65/35). In all cases from Run 14 to Run 22, we did not obtain the fluorides obtainable by replacing the hydroxy group of the

Table 1. Results of Experiments Using 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranose (**1**) (0.1 mmol) and Cyclohexanol (ChOH)

Run	**1**	ChOH	DAST	$Sn(OTf)_2$	Bu_4NClO_4	Et_3N Solv.[a]		**2+3**	**6+7**	**8+9+10**	**1**[b]
	equiv	equiv	equiv	equiv	equiv	equiv		%(**2**/**3**)	%(**6**/**7**)	%	%
1	1	0	1	0	0	0	D	95 (26/74)	0	2	1
2	1	1	1	0	0	0	D	51 (24/76)	0	0	44
3	1	1	1	1	0	0	D	0	28 (75/25)	58	5
4	1	1	1	1	0	1	D	0	43 (23/77)	43	14
5	1	2	2	2	0	2	D	20 (100/0)	53 (11/89)	24	3
6	1	2	2	2	0	2	T	8	33 (30/70)	12	39
7	1	2	2	2	0	2	P	0	62 (23/77)	18	20
8	1	2	2	2	0	2	E	0	58 (41/59)	3	35
9	1	2	2	2	0	2	DE	2	73 (26/74)	17	7
10	1	2	2	2	2	2	D	2	62 (5/95)	14	18
11	1	2	2	2	2[c]	2	D	10	55 (15/85)	15	17
12	1	2	2	2	2	2	DE	0	64 (31/69)	23	13
13	2	1	2	2	2	2	DE	0	60 (33/67)[d]	19	24

a) D = CH_2Cl_2, DE = CH_2Cl_2–Et_2O (1 : 1, v/v), E = Et_2O, P = EtCN, T = PhMe. b) Recovery of **1**. c) Instead of Bu_4NClO_4, Bu_4NOTf was used. d) Based on cyclohexanol charged.



Scheme 1. Plausible pathways for dehydrative glycosylation using DAST–$Sn(OTf)_2$–Bu_4NClO_4–Et_3N system.

acceptors: **4**, **5**, **13**, and **18**, with the fluoride group.[5,8]

The conditions of Run 12, mainly affording the α-glycosides in the condensation of **1** and the acceptors **4** (Run 16) and **13** (Run 18), were applied to the glycosylations (Runs 23, 24, and 25, Table 2) of the acceptors **13** and **21**[13] with the biosyl donors,[14] **22**, **23**, and **24** (Fig. 2). In every case, the corresponding α-anomers were selectively produced. Throughout the experiments summarized in Table 2, we did not isolate the fluorides that would be formed via displacement of the hydroxy group in the acceptors, AOH, with fluoride group.

Finally, using the conditions of Run 12, we synthesized two tetrasaccharides *O*-α-D-glucopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→4)-D-glucopyranose[15] (**31**) (Scheme 2) and *O*-α-D-glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→4)-D-glucopyranose[16] (**32**) (Scheme 3). The former is the tetrasaccharide unit of the intracellular glucan (nigeran) produced by *Aspergillus niger* 152 and also is pro-

Table 2. Results of Glycosylation Using DAST–$Sn(OTf)_2$–Bu_4NClO_4–Et_3N[a]

Run	DOH	AOH[a]	Solvent[b]	DOA	% (product ratio)	DOH[c]/%	AOH[d]/%
14	**1**	**4**	DE[e]	**11+12**	58 (**11**/**12** = 40/60)	1	34
15	**1**	**4**	D	**11+12**	62 (**11**/**12** = 35/65)	4	30
16	**1**	**4**	DE	**11+12**	50 (**11**/**12** = 58/42)	31	28
17	**1**	**13**	D	**14+15**	65 (**14**/**15** = 42/58)	10	34
18	**1**	**13**	DE	**14+15**	48 (**14**/**15** = 65/35)	25	32
19	**1**	**5**	D	**16+17**	50 (**16**/**17** = 36/64)	5	6
20	**1**	**5**	DE	**16+17**	46 (**16**/**17** = 43/57)	1	20
21	**1**	**18**	D	**19+20**	42 (**19**/**20** = 33/67)	50	20
22	**1**	**18**	DE	**19+20**	25 (**19**/**20** = 40/60)	67	20
23	**22**	**21**	DE	**25+26**	45 (**25**/**26** = 78/22)	12	28
24	**23**	**13**	DE	**27+28**	49 (**27**/**28** = 80/20)	10	41
25	**24**	**13**	DE	**29+30**	50 (**29**/**30** = 84/16)	10	28
26	**33**	**13**	DE	**34+35**	64 (**34**/**35** = 66/34)	11	17
27	**22**	**36**	DE	**37+38**	57 (**37**/**38** = 67/33)	12	17
28	**33**	**43**	DE	**44+45**	45 (**44**/**45** = 58/42)	2	30
29	**1**	**46**	DE	**47+48**	52 (**47**/**48** = 90/10)	2	51

a) Two molar amounts to DOH (0.1 mmol) were used. b) D = CH_2Cl_2, DE = CH_2Cl_2–Et_2O (1 : 1, v/v). c) Recovery of DOH. d) Recovery of AOH. e) Without Bu_4NClO_4.

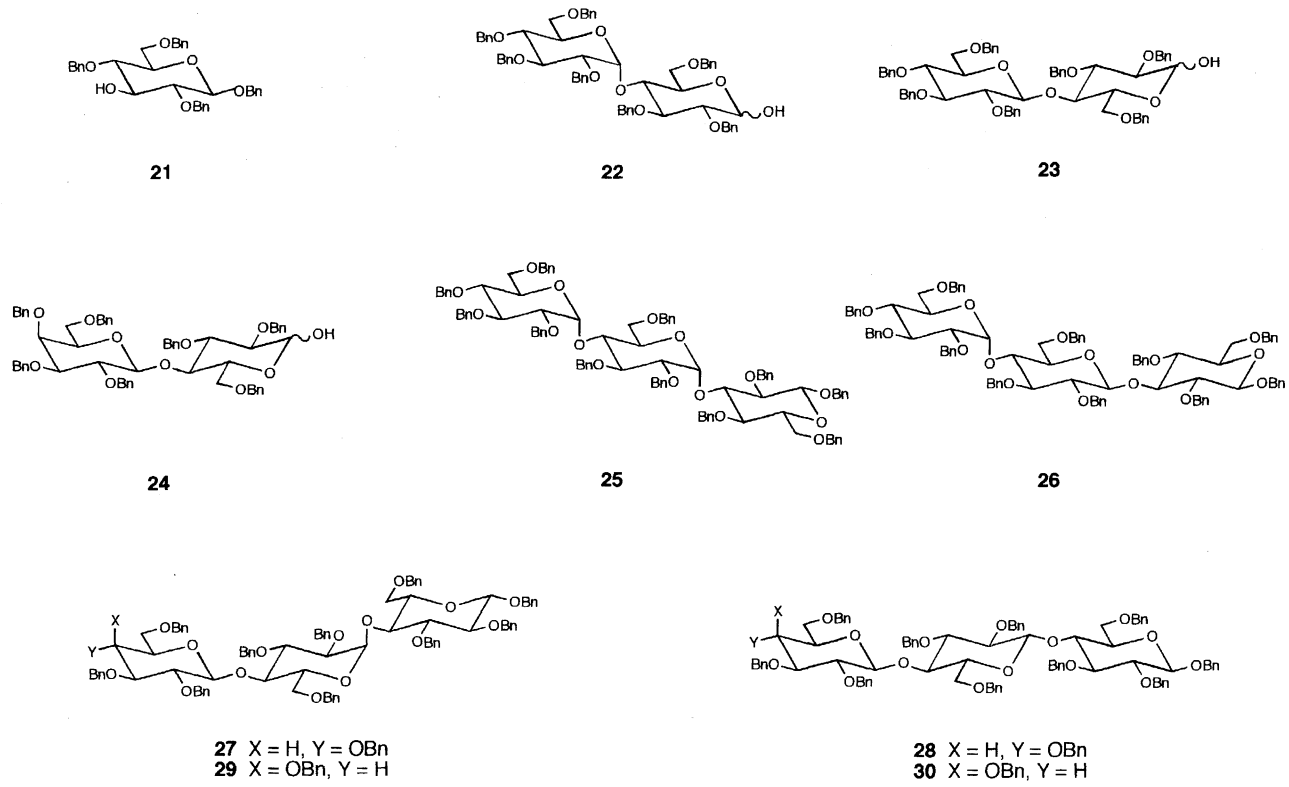


Fig. 2.

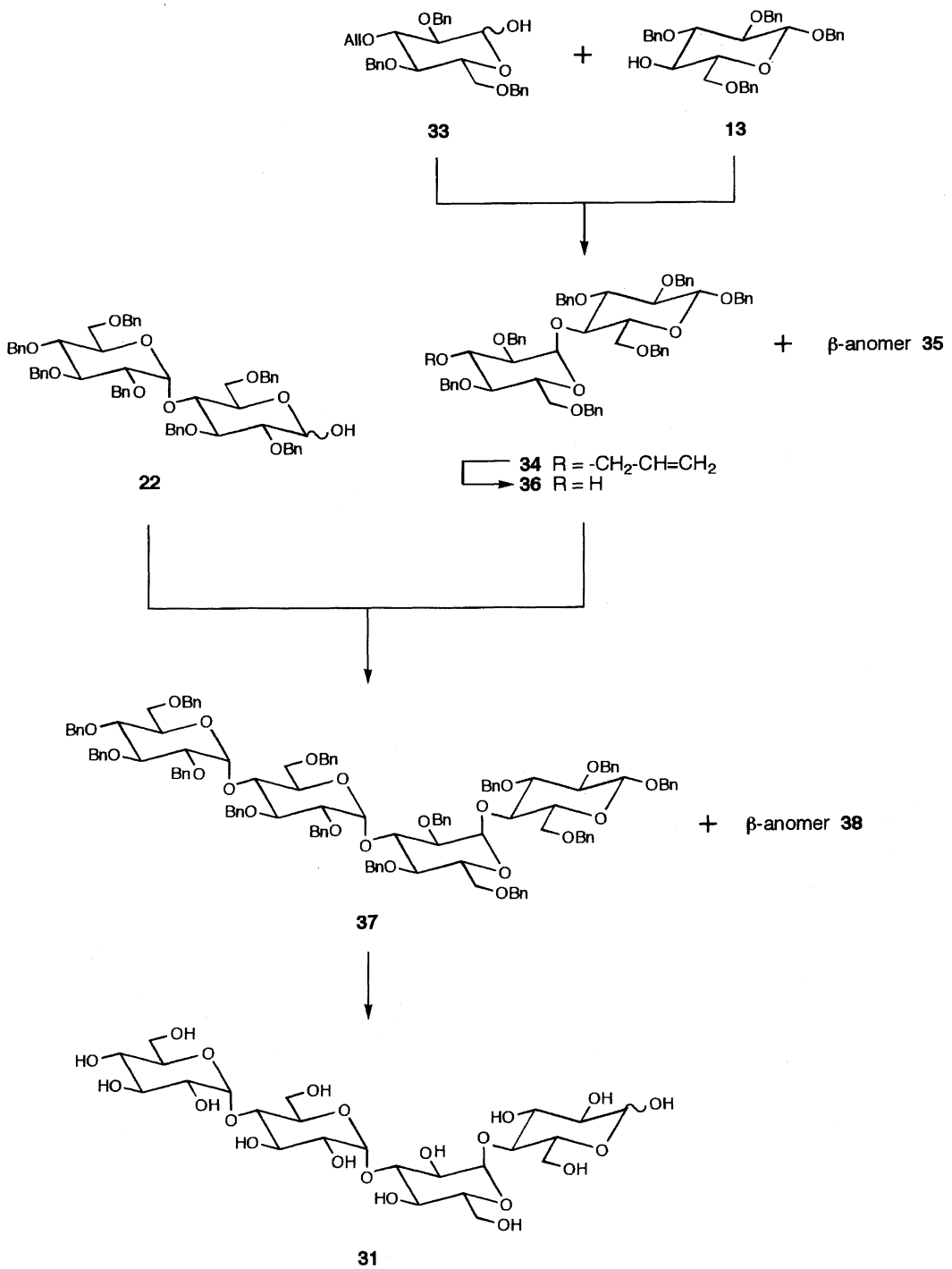
duced by the action of human salivary α-amylase on elsinan, a fungal α-D-glucan elaborated extracellularly by *Elsinoe leucospila*. The latter is the tetrasaccharide S4 produced by *Acremonium* sp. S4G13. Since the trisaccharide *O*-α-D-glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→4)-D-glucopyranose synthesized by us[14] is one of the candidates for an anticariogenic sugar substitute,[17] the tetrasaccharides **31** and **32** are expected to have such activity. Condensation (Run 26) of the 3-*O*-allyl donor **33**[18] and the 4-OH acceptor **13**[19] gave the condensates **34** and **35** in 52% yield (**34**/**35** = 63/37). Removal of allyl group of **34** gave the acceptor **36**, which was reacted (Run 27) with the biosyl donor **22** to afford the tetrasaccharide derivatives **37** and **38** in 57% yield (**37**/**38** = 67/33). Catalytic total debenzylation furnished the target tetrasaccharide **31**. To synthesize the other tetrasaccharide **32**, an efficient derivatization of maltose **39** into the 4′-OH derivative **43** was carried out. The sequential reactions of the direct acetobromination[20] of **39**, treatment with benzyl alcohol and mercury(II) cyanide in nitromethane, and deacetylation all in one-pot fashion gave benzyl β-maltoside **40**. Subsequent benzylidenation and benzylation gave **42**, treatment of which with triethylsilane and trifluoroacetic acid[21] cleanly gave the desired acceptor **43** in overall yield of 18% from **39**. A similar easy preparation of the useful acceptor **13**,[19] employed in this study, was performed with overall yield of 52% from D-glucose. Glycosylation (Run 28) of **33** with **43** gave **44** and **45** in 45% yield (**44**/**45** = 58/42). Condensation (Run 29) of **1** and the trisaccharide acceptor **46** obtained after deallylation of **44** afforded **47** and **48** in 52% yield with a high α-selectivity (**47**/**48** = 90/10). Hydrogenolytic total debenzylation of **47** furnished the target tetraose **32**.

Thus, the convenient dehydrative glycosylation using the 1-OH sugar derivatives was performed by the aid of a condensing reagent system composed of DAST, Sn(OTf)$_2$, Bu_4NClO_4, and Et_3N.

Experimental[22]

Compound **1** was the product of Pfanstiehl Lab., Inc. DAST was purchased from Aldrich Chemical Co., Inc. and Sn(OTf)$_2$ as well as Bu_4NClO_4 were from Tokyo Kasei Kogyo Co., Inc. Compounds **4**,[13,23] **5**,[24] **18**,[25] **21**,[13] **22**,[14] **23**,[14] **24**,[14] **33**[18] and **44**[14] were prepared by way of published methods. The products obtained in the present study: **6**,[11] **7**,[11] **8**,[26] **9**[26] **10**,[27] **11**,[13] **12**,[13] **25**,[14] **26**,[14] **27**,[14] **28**,[14] **29**,[14] and **30**,[14] were identified with the corresponding substances published earlier by us. The solvent systems for column chromatography on silica gel (Kanto Chemical, No. 37047; gradient elusion) and thin-layer chromatography (TLC) (Merck, DC-Plastikfolien Kieselgel 60 F 254, Art. 5735) was chloroform–methanol (CM), hexane–ethyl acetate (HE), and toluene–2-butanone (TK). Evaporation was carried out under reduced pressure. The optical rotations were measured on a JASCO DIP-180 Digital Polarimeter at room temperature. The mass spectra were recorded on a JEOL JMS-AX505HA mass spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded with a Varian VXR300 spectrometer, accompanied with the measurements of H,H-COSY, C,H-COSY, and DEPT spectra. The ^{1}H NMR spectrum of **1**, measured in $CDCl_3$ showed that the content of the α-anomer was 75% [δ = 3.40 (0.25H, H2β, dd, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.0 Hz); δ = 5.23 (0.75H, H1α, t, $J_{1,2}$ = 3.0 Hz, $J_{1,OH}$ = 3.0 Hz)].

2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-glucopyranosyl Fluorides (2 and 3). To a solution of **1** (54 mg) in CH_2Cl_2 (0.5 ml) was

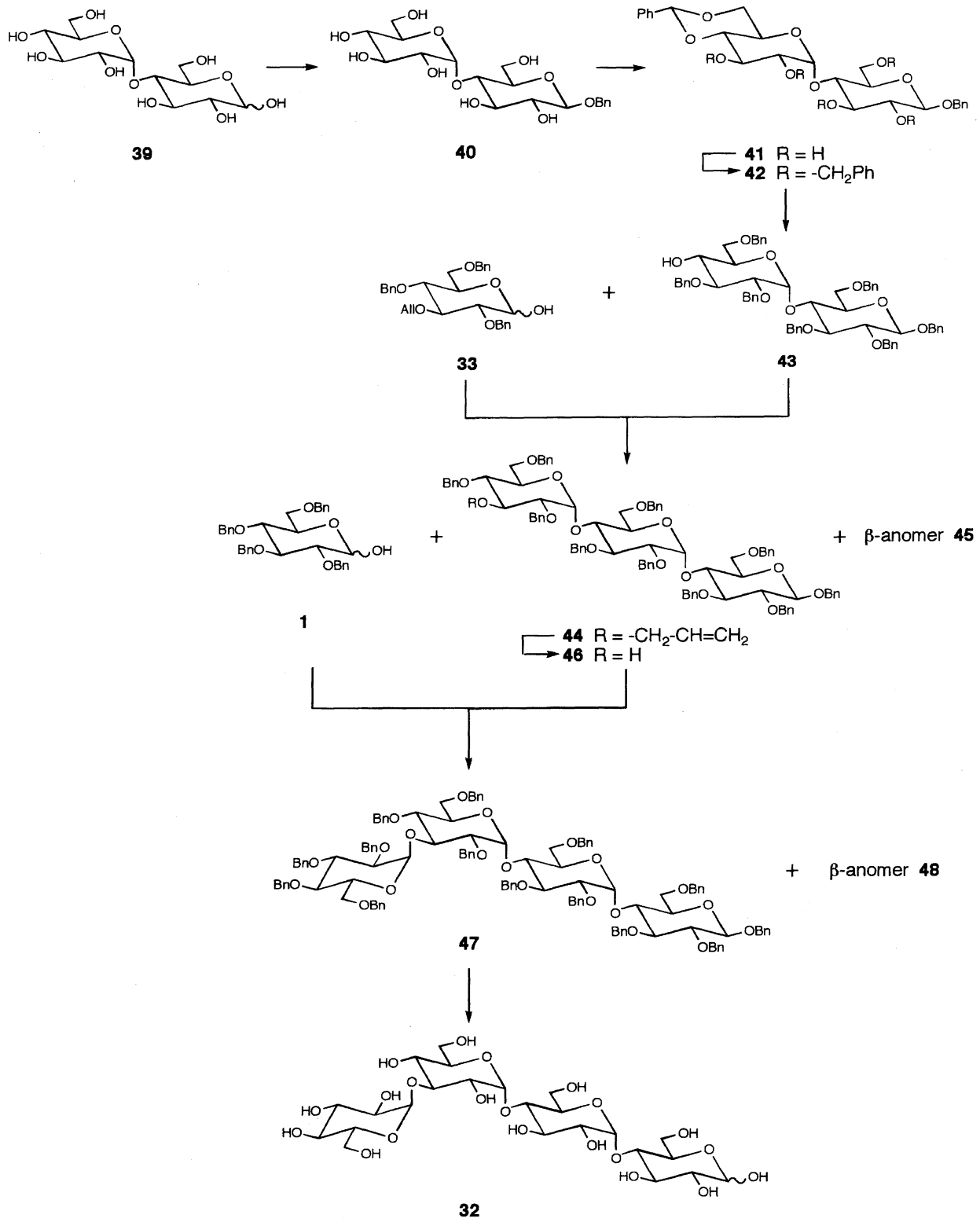


Scheme 2. Synthesis of *O*-α-D-Glc*p*-(1→4)-*O*-α-D-Glc*p*-(1→3)-*O*-α-D-Glc*p*-(1→4)-D-Glc*p* (**31**).

added DAST (13 μl, 1.0 equiv) at −60 °C (bath temperature) under stirring. The mixture was warmed to 0 °C at a rate of ca. 0.3 °C min^{-1} and diluted with toluene. The mixture was transferred onto a silica-gel column, which was developed with a TK system to give **2** (13.5 mg, 25%) and **3** (38.2 mg, 70%). Their ^{1}H NMR and ^{13}C NMR spectral data were coincident with those in the literature.[6)]

Glycosylation. DAST (26.4 μl, 0.2 mmol) was injected into a rubber-stoppered round-flask containing a donor (0.1 mmol), an acceptor (0.2 mmol), $Sn(OTf)_2$ (83.4 mg, 0.2 mmol), Bu_4NClO_4 (68.4 mg, 0.2 mmol), Et_3N (27.9 μl, 0.2 mmol), and solvent (0.5 ml) at −60 °C (bath temperature) under magnetic stirring. The bath temperature was allowed to rise at a rate of ca. 0.3 °C min^{-1} up to 0 °C, at which temperature the mixture was stirred for 24 h. After toluene (2 ml), methanol (24 μl), and powderized sodium hydrogencarbonate (168 mg) were added under stirring for 15 min, the whole mixture was poured onto a column of silica gel, eluted with TK system to give the products. Rechromatography of the products were performed using HE system. The results are summarized in Tables 1 and 2.

Octa-*O*-benzyl-β,β-trehalose[27)] **(10).** Mp 115—116 °C, $[\alpha]_D$ +8 (*c* 0.9, $CHCl_3$) (lit,[28)] mp 121 °C, $[\alpha]_D$ +14.5 ($CHCl_3$)); ^{1}H NMR ($CDCl_3$) δ = 4.90 (d, $J_{1,2}$ = 8.0 Hz, H1); ^{13}C NMR ($CDCl_3$) δ = 68.9



Scheme 3. Synthesis of *O*-α-D-Glc*p*-(1→3)-*O*-α-D-Glc*p*-(1→4)-*O*-α-D-Glc*p*-(1→4)-D-Glc*p* (**32**).

(C6), 75.0 (C5), 77.7 (C4), 82.2 (C2), 84.6 (C3), 99.3 (C1).

Found: C, 76.64; H, 6.60%. Calcd for $C_{68}H_{70}O_{11}$: C, 76.81; H, 6.64%.

Benzyl *O*-(2,3,6-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (43). Maltose **39** (monohydrate, Wako Pure Chemicals, Ltd. 10 g) was added to a stirred mixture of acetyl bromide (36 ml)[20] and acetic acid (145 ml) at 0 °C. After being stirred at 20 °C for 1 h, the mixture was evaporated to give a crude aceto bromide, which was reacted with benzyl alcohol (6.0 ml) and mercury(II) cyanide (7.4 g) in nitromethane (50 ml) at room temperature. After the usual demercurization and concentration, the resulting mixture was treated with dil meth-

anolic sodium methoxide (0.3%, 150 ml). Neutralization with acetic acid, concentration, and chromatography with CM system gave **benzyl β-maltoside 40** (6.86 g, 57%), $[\alpha]_D$ +60 (*c* 1.5, H_2O) (lit,[29] $[\alpha]_D$ 47.64 (*c* 1.0, H_2O)). A mixture of **40** (6.80 g), α,α-dimethoxytoluene (6.8 ml), *p*-toluenesulfonic acid (monohydrate, 0.68 g), and *N*,*N*-dimethylformamide (DMF) (68 ml) was kept standing overnight. After sodium hydrogencarbonate (1.2 g) was added, the mixture was evaporated and chromatographed with CM system to give the acetal **41** (4.22 g, 52%), mp 114—116 °C, $[\alpha]_D$ +12 (*c* 2.0, C_5H_5N) (lit,[30] mp 112—116 °C, $[\alpha]_D$ +15.8±1 (*c* 1.2, C_5H_5N)). To a mixture of **41** (4.20 g), benzyl bromide (7.25 ml), and DMF (30 ml) was added sodium hydride (ca. 60% dispersion in mineral oil, 2.44 g) at 0 °C. After the mixture was stirred at 20 °C for 2 h, cold methanol (7.25 ml) was cautiously added to it. The content was then partitioned between toluene and water. The organic layer was concentrated and chromatographed (TK system) to afford **42** (6.98 g, 89%), $[\alpha]_D$ 0 (*c* 0.6, $CHCl_3$) (lit,[31] $[\alpha]_D$ −8 (*c* 0.79, $CHCl_3$)).

To a solution of **42** (6.74 g) and triethylsilane (7.0 ml) in CH_2Cl_2 (35 ml) was added trifluoroacetic acid (2.7 ml) at 0 °C.[21] After being stirred at room temperature for 30 min, the solution was concentrated and chromatographed (TK system) to give **43** (4.53 g, 67%), $[\alpha]_D$ +18 (*c* 2.5, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ = 3.48 (dd, *J* = 4.0, 10.0 Hz, $H2^B$), # 3.63 (t, *J* = 8.0 Hz, $H2^A$), 3.67 (t, *J* = 9.0 Hz, $H4^B$), 3.79 (t, *J* = 9.0 Hz, $H3^B$), 3.83 (t, *J* = 8.5 Hz, $H3^A$), 4.13 (t, *J* = 9.0 Hz, $H4^A$), 4.59 (d, *J* = 8.0 Hz, $H1^A$), 5.71 (d, *J* = 4.0 Hz, $H1^B$); ^{13}C NMR ($CDCl_3$) δ = 69.2 ($C6^B$), 69.7 ($C6^A$), 70.6 ($C5^B$), 71.4 ($C4^B$), 72.6 ($C4^A$), 74.6 ($C5^A$), 78.9 ($C2^B$), 81.2 ($C3^B$), 82.2 ($C2^A$), 84.8 ($C3^A$), 96.5 ($C1^B$), 102.3 ($C1^A$). Found: C, 75.27; H, 6.74%. Calcd for $C_{61}H_{64}O_{11}$: C, 75.29; H, 6.63%.

Acetylation of **43** with acetic anhydride and pyridine and chromatography with TK system gave its acetate. ^{1}H NMR ($CDCl_3$) δ = 1.83 (s, Ac), 3.52 (dd, *J* = 3.5, 10.0 Hz, $H2^B$), 3.60 (dd, *J* = 8.0, 9.0 Hz, $H2^A$), 3.80 (t, *J* = 10.0 Hz, $H3^A$), 3.87 (t, *J* = 10.0 Hz, $H3^B$), 4.06 (t, *J* = 9.0 Hz, $H4^A$), 4.56 (d, *J* = 8.0 Hz, $H1^A$), 5.06 (t, *J* = 10.0 Hz, $H4^B$), 5.65 (d, *J* = 3.5 Hz, $H1^B$); ^{13}C NMR ($CDCl_3$) δ = 20.8 (Ac), 68.8 ($C6^B$), 69.5 ($C5^B$), 69.6 ($C6^A$), 70.7 ($C4^B$), 73.6 ($C4^A$), 74.7 ($C5^A$), 79.1 ($C2^B$, $C3^B$), 82.2 ($C2^A$), 84.6 ($C3^A$), 96.7 ($C1^B$), 102.3 ($C1^A$), 169.5 (Ac).

Convenient Preparation of Benzyl 2,3,6-Tri-*O*-benzyl-β-D-glucopyranoside (13). Treatment of D-glucose (15 g) with a mixture of acetyl bromide (53 ml) and acetic acid (42 ml) afforded crude acetobromoglucose,[20] which was condensed with benzyl alcohol (17 ml) in the presence of mercury(II) cyanide (21 g) in nitromethane (75 ml). Demercurization, treatment with dil methanolic sodium methoxide (0.4%, 360 ml), chromatography with CM system gave crystalline **benzyl β-D-glucopyranoside** (19.2 g, 86%). This (5.8 g) was dissolved in DMF (30 ml) containing α,α-dimethoxytoluene (13 ml) and *p*-toluenesulfonic acid (monohydrate, 0.42 g). After sodium hydrogen carbonate (0.37 g) was added, concentration and chromatography with CM system afforded crystalline **benzyl 4,6-*O*-benzylidene-β-D-glucopyranoside** (5.8 g, 75%). This acetal (12.0 g) was stirred in benzyl chloride (79 ml) containing crushed potassium hydroxide (23 g) at 120 °C for 2 h. The cooled mixture was diluted with toluene (500 ml) and water (300 ml). The organic layer was washed with water, concentrated and chromatographed with Tk system to give crystalline **benzyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside** (15.2 g, 85%). The benzyl ether (2.55 g) was treated with triethylsilane (4.2 ml) and trifluoroacetic acid (2.1 ml) in CH_2Cl_2 (25 ml). Chromatography with TK system gave **13** (2.42 g, 95%), mp 62—63 °C, $[\alpha]_D$ −40 (*c* 1.0, $CHCl_3$) (lit,[19] mp 66—67 °C, $[\alpha]_D$ −42 (*c*1.07, $CHCl_3$), $[\alpha]_{589.5}$ −41 (*c*2.0, $CHCl_3$)).

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (14 and 15). **14** (faster-moving by TK system), $[\alpha]_D$ +22 (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.49 (dd, *J* = 4.0, 9.5 Hz, $H2^B$), 3.59 (t, *J* = 9.0 Hz, $H2^A$), 3.64 (t, *J* = 9.0 Hz, $H4^B$), 3.79 (t, *J* = 9.0 Hz, $H3^B$), 3.90 (t, *J* = 9.0 Hz, $H3^B$), 4.08 (t, *J* = 9.0 Hz, $H4^A$), 4.55 (d, *J* = 8.0 Hz, $H1^A$), 5.67 (d, *J* = 4.0 Hz, $H1^B$); ^{13}C NMR ($CDCl_3$) δ = 68.3 ($C6^B$), 69.2 ($C6^A$), 71.1 ($C5^B$), 72.8 ($C4^A$), 74.6 ($C5^A$), 77.7 ($C4^B$), 79.4 ($C2^B$), 82.0 ($C3^B$), 82.3 ($C2^A$), 84.8 ($C3^A$), 96.7 ($C1^B$), 102.4 ($C1^A$), and **15**, mp 94—96 °C, $[\alpha]_D$ +9 (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.31 (ddd, *J* = 2.0, 4.0, 10.0 Hz, $H5^A$), 3.38 (ddd, *J* = 2.0, 4.0, 10.0 Hz, $H5^B$), 3.39 (t, *J* = 8.0 Hz, $H2^B$), 3.50 (t, *J* = 8.0 Hz, $H2^A$), 3.55 (t, *J* = 9.0 Hz, $H3^A$), 3.59 (t, *J* = 9.0 Hz, $H3^B$), 3.64 (t, *J* = 9.0 Hz, $H4^A$), 3.71 (ddd, *J* = 2.0, 4.0, 11.0 Hz, $H6^A$), 3.85 (ddd, *J* = 2.0, 4.0, 10.0 Hz, $H6^B$), 4.04 (t, *J* = 9.0 Hz, $H4^B$), 4.49 (d, *J* = 9.0 Hz, $H1^A$), 4.53 (d, *J* = 8.0 Hz, $H1^B$); ^{13}C NMR ($CDCl_3$) δ = 68.2 ($C6^B$), 68.9 ($C6^A$), 75.0 ($C5^A$), 75.1 ($C5^B$), 76.6 ($C4^B$), 78.0 ($C4^A$), 81.7 ($C2^A$), 82.8 ($C2^B$), 82.9 ($C3^B$), 84.9 ($C3^A$), 102.4 ($C1^B$), 102.5 ($C1^A$).

Found: **14** C, 76.86; H, 6.62% and **15** C, 76.78; H, 6.64%. Calcd for $C_{68}H_{70}O_{11}$: C, 76.81; H, 6.64%.

Methyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranosides (16 and 17). **16** (faster-moving by TK system), mp 101—102 °C, $[\alpha]_D$ +40 (*c* 1.2, $CHCl_3$) (lit,[32] $[\alpha]_D$ +43.3 (*c* 1.6, $CHCl_3$)); ^{1}H NMR ($CDCl_3$) δ = 3.32 (dd, *J* = 8.0, 9.0 Hz, $H2^A$), 3.51 (ddd, *J* = 2.0, 3.0, 9.0 Hz, $H5^A$), 3.53 (s, Me), 3.59 (dd, *J* = 3.5, 9.0 Hz, $H2^B$), 3.64 (t, *J* = 9.0 Hz, $H3^A$), 3.66 (t, *J* = 9.0 Hz, $H4^B$), 3.67 (t, *J* = 9.0 Hz, $H4^A$), 3.88 (ddd, *J* = 2.0, 3.0, 10.0 Hz, $H5^B$), 4.00 (t, *J* = 9.0 Hz, $H3^B$), 4.31 (d, *J* = 8.0 Hz, $H1^A$), 5.05 (d, *J* = 3.5 Hz, $H1^B$); ^{13}C NMR ($CDCl_3$) δ = 56.9 (Me), 65.7 ($C6^A$), 68.5 ($C6^B$), 70.1 ($C5^B$), 74.7 ($C5^A$), 77.6 ($C4^A$), 77.9 ($C4^B$), 80.0 ($C2^B$), 81.7 ($C3^B$), 82.4 ($C2^A$), 84.6 ($C3^A$), 97.1 ($C1^B$), 104.5 ($C1^A$), and **17**, mp 127—129 °C, $[\alpha]_D$ +19 (*c* 0.4, $CHCl_3$) (lit,[32] $[\alpha]_D$ +14 (*c* 1.7, $CHCl_3$)); ^{1}H NMR ($CDCl_3$) δ = 3.41 (dd, *J* = 7.5, 8.0 Hz, $H2^B$), 3.42 (t, *J* = 9.0 Hz, $H4^B$), 3.44 (s, Me), 3.56 (m, $H5^A$), 3.61 (t, *J* = 8.5 Hz, $H4^A$), 3.65 (t, *J* = 9.0 Hz, $H3^A$), 4.26 (d, *J* = 8.0 Hz, $H1^B$), 4.47 (d, *J* = 7.5 Hz, $H1^A$); ^{13}C NMR ($CDCl_3$) δ = 57.1 (Me), 68.7 ($C6^A$), 68.9 ($C6^B$), 74.8 ($C5^A$, $C5^B$), 77.8 ($C4^A$), 78.3 ($C4^B$), 82.1 ($C2^A$), 82.3 ($C2^B$), 84.6 ($C3^A$), 84.7 ($C3^B$), 104.0 ($C1^A$), 104.6 ($C1^B$).

Found: **16** C, 75.61; H, 6.89% and **17** C, 75.42; H, 6.77%. Calcd for $C_{62}H_{66}O_{11}$: C, 75.43; H, 6.74%.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranosides (19 and 20). **19** (faster-moving by TK system), mp 122—124 °C, $[\alpha]_D$ +24 (*c* 0.4, $CHCl_3$) (lit,[33] mp 129—130 °C, $[\alpha]_D$ +26 (*c* 0.8, $CHCl_3$)); ^{1}H NMR ($CDCl_3$) δ = 3.39 (dd, *J* = 8.0, 9.0 Hz, $H2^A$), 3.53 (ddd, *J* = 2.0, 3.0, 8.0 Hz, $H5^B$), 3.58 (dd, *J* = 3.5, 9.0 Hz, $H2^B$), 3.62 (ddd, *J* = 2.0, 5.0, 11.0 Hz, $H6^A$), 3.66 (t, *J* = 9.0 Hz, $H4^B$), 3.69 (t, *J* = 10.0 Hz, $H4^A$), 3.91 (ddd, *J* = 2.0, 4.0, 10.0 Hz, $H5^A$), 4.01 (t, *J* = 9.0 Hz, $H3^B$), 4.52 (d, *J* = 8.0 Hz, $H1^A$), 5.02 (d, *J* = 3.5 Hz, $H1^B$); ^{13}C NMR ($CDCl_3$) δ = 65.8 ($C6^A$), 68.5 ($C6^B$), 70.1 ($C5^A$), 74.7 ($C5^B$), 77.6 ($C4^A$), 77.9 ($C4^B$), 80.0 ($C2^B$), 81.8 ($C3^B$), 82.4 ($C2^A$), 84.7 ($C3^A$), 97.0 ($C1^B$), 102.3 ($C1^A$), and **20**, mp 161—162 °C, $[\alpha]_D$ +3 (*c* 1.1, $CHCl_3$) (lit,[33] mp 166—168 °C, $[\alpha]_D$ +3 (*c* 0.8, $CHCl_3$)); ^{1}H NMR ($CDCl_3$) δ = 3.45 (t, *J* = 9.0 Hz, $H4^A$), 3.59 (t, *J* = 9.0 Hz, $H3^A$), 3.66 (t, *J* = 9.0 Hz, $H3^A$), 4.47 (d, *J* = 7.5 Hz, $H1^A$), 4.54 (d, *J* = 8.0 Hz, $H1^B$); ^{13}C NMR ($CDCl_3$)

In the positional code of oligosaccharides described in this paper, the superscript A always expresses the saccharide located at the reducing end.

δ = 68.6 ($C6^B$), 69.0 ($C6^A$), 74.9 ($C5^A$), 75.2 ($C5^B$), 77.8 ($C4^B$), 78.3 ($C4^A$), 82.2 ($C2^A$), 82.3 ($C2^B$), 84.7 ($C3^B$), 84.8 ($C3^A$), 102.6 ($C1^A$), 104.0 ($C1^B$).

Found: **19** C, 76.62; H, 6.68% and **20** C, 76.62; H, 6.69%. Calcd for $C_{68}H_{70}O_{11}$: C, 76.81; H, 6.64%.

Benzyl *O*-(3-*O*-Allyl-2,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (34 and 35). **34** (faster-moving by TK system), $[\alpha]_D$ +32 (*c* 1.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.45 (dd, *J* = 4.0, 10.0 Hz, $H2^B$), 3.58 (t, *J* = 8.0 Hz, $H2^A$), 3.59 (t, *J* = 10.0 Hz, $H4^B$), 3.76 (t, *J* = 9.0 Hz, $H3^B$), 3.78 (t, *J* = 9.0 Hz, $H3^A$), 4.07 (t, *J* = 9.0 Hz, $H4^A$), 4.55 (d, *J* = 8.0 Hz, $H1^A$), 5.66 (d, *J* = 4.0 Hz, $H1^B$), 5.95 (m, allyl); ^{13}C NMR ($CDCl_3$) δ = 68.3 ($C6^B$), 69.2 ($C6^A$), 71.0 ($C5^B$), 72.8 ($C4^A$), 74.6 ($C5^A$), 77.7 ($C4^B$), 79.2 ($C2^B$), 81.7 ($C3^B$), 82.3 ($C2^A$), 84.8 ($C3^A$), 96.8 ($C1^B$), 102.3 ($C1^A$), 116.4, 135.3 (allyl), and **35**, mp 93—95 °C, $[\alpha]_D$ +13 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.33 (t, *J* = 8.0 Hz, $H2^B$), 3.41 (t, *J* = 9.0 Hz, $H3^B$), 3.50 (d, *J* = 8.0 Hz, $H2^A$), 3.54 (t, *J* = 9.0 Hz, $H4^B$), 3.59 (t, *J* = 9.0 Hz, $H3^A$), 4.03 (t, *J* = 9.0 Hz, $H4^A$), 4.49 (d, *J* = 8.0 Hz, $H1^B$), 4.50 (d, *J* = 7.5 Hz, $H1^A$), 5.96 (m, allyl); ^{13}C NMR ($CDCl_3$) δ = 68.2 ($C6^A$), 68.9 ($C6^B$), 75.0 ($C5^B$), 75.1 ($C5^A$), 76.7 ($C4^A$), 77.9 ($C4^B$), 81.7 ($C2^A$), 82.6 ($C2^B$), 82.9 ($C3^A$), 84.7 ($C3^B$), 102.4 ($C1^B$), 102.5 ($C1^A$), 116.5, 135.2 (allyl).

Found: **34** C, 75.70; H, 6.74% and **35** C, 75.97; H, 6.84%. Calcd for $C_{64}H_{68}O_{11}$: C, 75.87; H, 6.76%.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α- and β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (37 and 38). **37** (faster-moving by TK system), $[\alpha]_D$ +41 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.34 (t, *J* = 9.0 Hz, $H3^B$), 3.44 (dd, *J* = 4.0, 10.0 Hz, $H2^D$), 3.47 (dd, *J* = 4.0, 9.0 Hz, $H2^B$), 3.49 (t, *J* = 9.0 Hz, $H4^B$), 3.55 (dd, *J* = 4.0, 8.0 Hz, $H2^C$), 3.65 (t, *J* = 9.0 Hz, $H3^A$, t, *J* = 10.0 Hz, $H4^C$), 3.73 (t, *J* = 9.0 Hz, $H3^C$), 3.79 (t, *J* = 9.0 Hz, $H4^D$), 3.82 (t, *J* = 10.0 Hz, $H3^D$), 4.12 (t, *J* = 9.0 Hz, $H4^A$), 4.48 (d, *J* = 7.0 Hz, $H1^A$), 5.57 (d, *J* = 3.5 Hz, $H1^B$), 5.58 (d, *J* = 3.5 Hz, $H1^C$), 5.68 (d, *J* = 3.5 Hz, $H1^C$); ^{13}C NMR ($CDCl_3$) δ = 68.2 ($C6^C$), 68.3 ($C6^B$), 69.0 ($C6^D$), 69.4 ($C6^A$), 70.5 ($C5^C$), 70.9 ($C5^{B,D}$), 71.7 ($C4^A$), 73.5 ($C5^A$), 74.6 ($C3^B$), 77.7 ($C4^{B,C}$), 78.4 ($C2^B$, $C4^D$), 79.6 ($C2^D$), 80.1 ($C2^C$), 81.9 ($C3^C$), 82.0 ($C2^A$, $C3^D$), 84.6 ($C3^A$), 95.4 ($C1^B$), 96.8 ($C1^C$), 97.2 ($C1^D$), 102.2 ($C1^A$).

Found: C, 75.99; H, 6.68%. Calcd for $C_{122}H_{126}O_{21}$: C, 75.99; H, 6.59%.

Further elution gave **38**, $[\alpha]_D$ +28 (*c* 0.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 4.51 (d, *J* = 7.5 Hz, $H1^A$), 4.53 (d, *J* = 7.5 Hz, $H1^C$), 5.66 (d, *J* = 3.5 Hz, $H1^B$), 5.70 (d, *J* = 3.5 Hz, $H1^D$); ^{13}C NMR ($CDCl_3$) δ = 95.1 ($C1^B$), 95.8 ($C1^D$), 102.2 ($C1^{A,C}$); MS(FAB) *m/z* 1950.7 $(M+Na)^+$.

Benzyl *O*-(3-*O*-Allyl-2,4,6-tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (44 and 45). **44** (faster-moving by TK system), $[\alpha]_D$ +56 (*c* 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.51 (dd, *J* = 3.5, 10.0 Hz, $H2^C$), 3.58 (dd, *J* = 3.5, 9.0 Hz, $H2^B$), 3.63 (t, *J* = 9.0 Hz, $H4^A$), 3.68 (t, *J* = 10.0 Hz, $H4^C$), 3.84 (t, *J* = 8.5 Hz, $H3^A$), 3.85 (t, *J* = 10.0 Hz, $H3^C$), 4.08 (t, *J* = 9.0 Hz, $H3^B$), 4.14 (t, *J* = 9.0 Hz, $H4^B$), 4.61 (d, *J* = 7.5 Hz, $H1^A$), 5.63 (d, *J* = 3.5 Hz, $H1^B$), 5.71 (d, *J* = 3.5 Hz, $H1^C$), 5.99 (allyl); ^{13}C NMR ($CDCl_3$) δ = 68.2 ($C6^C$), 69.0 ($C6^A$, $C6^B$), 70.8 ($C5^B$), 70.9 ($C5^C$), 72.9 ($C5^A$), 73.4 ($C4^B$), 74.7 ($C4^A$), 77.6 ($C4^C$), 79.4 ($C2^B$, $C2^C$), 81.5 ($C3^B$), 81.7 ($C3^C$), 82.0 ($C2^A$), 84.6 ($C3^A$), 96.3 ($C1^B$), 96.9 ($C1^C$), 102.3 ($C1^A$), 116.3, 135.3 (allyl), and **45**, $[\alpha]_D$ +31 (*c* 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.26 (t, *J* = 9.0 Hz, $H4^C$), 3.28 (t, *J* = 8.0 Hz, $H2^C$), 3.31 (t, *J* = 9.0 Hz, $H3^C$), 3.43 (dd, *J* = 3.5, 9.0 Hz, $H2^B$), 3.52 (t, *J* = 9.0 Hz, $H4^A$), 3.55 (t, *J* = 8.0 Hz, $H2^A$), 3.77 (t, *J* = 8.0 Hz, $H3^A$), 3.85 (t, *J* = 9.0 Hz, $H3^B$), 4.00 (t, *J* = 9.0 Hz, $H4^B$), 4.37 (d, *J* = 8.0 Hz, $H1^C$), 4.52 (d, *J* = 7.5 Hz, $H1^A$), 5.65 (d, *J* = 3.5 Hz, $H1^B$), 5.90 (allyl); ^{13}C NMR ($CDCl_3$) δ = 67.9 ($C6^C$), 69.0 ($C6^A$), 69.3 ($C6^B$), 71.2 ($C5^B$), 73.1 ($C5^A$), 74.8 ($C4^A$), 75.1 ($C4^C$), 76.5 ($C4^B$), 78.0 ($C5^C$), 78.4 ($C2^B$), 80.4 ($C3^B$), 82.4 ($C2^A$, $C2^C$), 84.6 ($C3^C$), 84.8 ($C3^A$), 96.9 ($C1^B$), 102.3 ($C1^A$), 102.5 ($C1^C$), 116.5, 135.2 (allyl).

Found: **44** C, 75.38; H, 6.76% and **45** C, 75.48; H, 6.75%. Calcd for $C_{91}H_{96}O_{16}$: C, 75.60; H, 6.69%.

Benzyl *O*-(2,3,4,6-Tri-*O*-benzyl-α- and -β-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-(2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (47 and 48). **47** (slower-moving by TK system), $[\alpha]_D$ +64 (*c* 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 3.52 (dd, *J* = 4.0, 9.0 Hz, $H2^D$), 3.53 (dd, *J* = 4.0, 9.0 Hz, $H2^C$), 3.61 (t, *J* = 8.0 Hz, $H2^A$), 3.62 (t, *J* = 10.0 Hz, $H4^D$), 3.63 (t, *J* = 8.0 Hz, $H4^A$), 3.64 (t, *J* = 10.0 Hz, $H4^C$), 3.78 (t, *J* = 8.0 Hz, $H3^A$), 3.81 (t, *J* = 9.0 Hz, $H3^C$), 3.97 (dd, *J* = 4.0, 8.0 Hz, $H2^B$), 4.00 (t, *J* = 8.0 Hz, $H3^B$), 4.01 (t, *J* = 10.0 Hz, $H3^D$), 4.07 (t, *J* = 9.0 Hz, $H4^B$), 4.56 (d, *J* = 7.5 Hz, $H1^A$), 5.60 (d, *J* = 4.0 Hz, $H1^D$), 5.62 (d, *J* = 4.0 Hz, $H1^C$), 5.68 (d, *J* = 4.0 Hz, $H1^B$); ^{13}C NMR ($CDCl_3$) δ = 68.1 ($C6^C$), 68.1 ($C6^D$), 68.7 ($C6^B$), 69.0 ($C6^A$), 70.3 ($C5^{C,D}$), 70.8 ($C5^B$), 72.1 ($C5^A$), 72.7 ($C4^B$), 73.8 ($C4^A$), 78.0 ($C4^{C,D}$), 78.3 ($C2^B$), 78.5 ($C3^C$), 79.3 ($C2^C$), 79.7 ($C2^D$), 81.7 ($C3^B$), 82.1 ($C2^A$), 82.2 ($C3^D$), 84.8 ($C3^A$), 95.5 ($C1^B$), 96.0 ($C1^D$), 97.4 ($C1^C$), 102.4 ($C1^A$).

Found: C, 75.68; H, 6.65%. Calcd for $C_{122}H_{126}O_{21}$: C, 75.99; H, 6.59%.

Further elution gave **48**, $[\alpha]_D$ +42 (*c* 0.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 4.60 (d, *J* = 7.5 Hz, $H1^A$), 4.61 (d, *J* = 7.5 Hz, $H1^C$), 5.66 (d, *J* = 3.5 Hz, $H1^D$), 5.67 (d, *J* = 3.5 Hz, $H1^B$); ^{13}C NMR ($CDCl_3$) δ = 95.8 ($C1^B$), 96.0 ($C1^D$), 102.3 ($C1^C$), 102.4 ($C1^A$); MS (FAB) *m/z* 1950.3 $(M+Na)^+$.

Benzyl *O*-(2,4,6-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (36). A mixture of **34** (303.5 mg, 300 mmol), chloro tris(triphenylphosphine)rhodium-(I)[29] (28 mg), ethanol (14 ml), benzene (6 ml), and water (2 ml) were stirred at 90 °C overnight. After concentration, the mixture was warmed in acetone (26 ml) containing dil hydrochloric acid (3.6%, 1.0 ml) at 45 °C for 1 h. Evaporation and chromatography (TK system) gave **36** (244 mg, 84%), $[\alpha]_D$ +45 (*c* 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 2.31 (d, *J* = 2.0 Hz, OH), 3.35 (dd, *J* = 3.5, 9.5 Hz, $H2^B$), 3.56 (t, *J* = 9.0 Hz, $H4^B$), 3.62 (t, *J* = 8.5 Hz, $H2^A$), 3.78 (t, *J* = 8.5 Hz, $H3^A$), 4.01 (t, *J* = 9.0 Hz, $H3^B$), 4.10 (t, *J* = 9.0 Hz, $H4^A$), 4.55 (d, *J* = 8.0 Hz, $H1^A$), 5.72 (d, *J* = 3.5 Hz, $H1^B$); ^{13}C NMR ($CDCl_3$) δ = 68.2 ($C6^B$), 69.1 ($C6^A$), 70.5 ($C5^B$), 72.5 ($C4^A$), 73.3 ($C3^B$), 74.6 ($C5^A$), 77.5 ($C4^B$), 78.9 ($C2^B$), 82.2 ($C2^A$), 84.7 ($C3^A$), 96.0 ($C1^B$), 102.3 ($C1^A$).

Found: C, 75.14; H, 6.68%. Calcd for $C_{61}H_{64}O_{11}$: C, 75.29; H, 6.63%.

Benzyl *O*-(2,4,6-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (46). Similarly, **44** (186.0 mg, 129 mmol) afforded **46** (147.3 mg 82%), $[\alpha]_D$ +57 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 2.30 (d, *J* = 2.0 Hz, OH), 3.34 (dd, *J* = 3.5, 9.5 Hz, $H2^B$), 3.53 (dd, *J* = 3.5, 9.0 Hz, $H2^C$), 3.58 (t, *J* = 9.0 Hz, $H4^{A,C}$), 3.61 (t, *J* = 8.5 Hz, $H2^A$), 3.69 (t, *J* = 9.0 Hz, $H3^A$), 4.00 (t, *J* = 9.0 Hz, $H3^B$), 4.03 (t, *J* = 10.0 Hz, $H3^C$), 4.06 (t, *J* = 10.0, Hz, $H5^A$), 4.09 (t, *J* = 9.0 Hz, $H4^C$), 4.51 (d, *J* = 8.0 Hz, $H1^A$), 5.61 (d, *J* = 3.5 Hz, $H1^C$), 5.72 (d, *J* = 3.5 Hz, $H1^B$); ^{13}C NMR ($CDCl_3$)

δ = 68.2 ($C6^C$), 68.8 ($C6^B$), 68.9 ($C6^A$), 70.5 ($C5^B$), 70.8 ($C5^B$), 72.4 ($C5^A$), 73.0 ($C4^B$), 73.3 ($C3^C$), 74.7 ($C4^A$), 77.4 ($C4^C$), 79.0 ($C2^B$), 79.5 ($C2^C$), 81.6 ($C3^B$), 82.1 ($C2^A$), 84.7 ($C3^A$), 96.0 ($C1^B$), 96.2 ($C1^C$), 102.3 ($C1^A$).

Found: C, 75.02; H, 6.73%. Calcd for $C_{88}H_{92}O_{16}$: C, 75.19; H, 6.60%.

***O*-α-D-Glucopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→4)-D-glucopyranose (31).** Hydrogenation of **37** (47.6 mg, 25 mmol) over palladium on carbone (Kawaken Fine Chemicals Co., Ltd., 10%, 48 mg) in acetic acid (6 ml) containing water (0.15 ml) under 3.4×10^5 N cm^{-2} of hydrogen at room temperature ovenight. After removal of the catalyst, the solution was evaporated. The residue obtained was chromatographed using CM system to give glassy **31** (10.2 mg, 62%), mp 173—175 °C, $[\alpha]_D$ +166 (*c* 0.7, H_2O) (lit,[15] $[\alpha]_D$ +184 (*c* 1.2, H_2O)); ^{1}H NMR (D_2O) δ = 3.24 (dd, *J* = 8.0, 9.0 Hz, H2β^B), 3.39 (t, *J* = 9.5 Hz, $H4^D$), 3.54 (dd, *J* = 4.0, 9.5 Hz, H2α^A), 3.55 (dd, *J* = 4.0, 10.0 Hz, $H2^D$), 3.56 (dd, *J* = 4.0, 9.5 Hz, $H2^B$), 3.58 (dd, *J* = 4.0, 9.5 Hz, $H2^C$), 3.63 (t, *J* = 9.5 Hz, H4α^A), 3.64 (t, *J* = 9.0 Hz, H4β^A), 3.65 (t, *J* = 9.5 Hz, $H4^C$), 3.66 (t, *J* = 9.5 Hz, $H4^B$), 3.70 (ddd, *J* = 2.0, 5.0, 10.0 Hz, $H5^D$), 3.75 (t, *J* = 9.0 Hz, H3β^A), 3.81 (t, *J* = 9.5 Hz, $H3^D$), 3.82 (t, *J* = 9.5 Hz, $H3^B$), 3.95 (t, *J* = 9.5 Hz, H3α^A), 3.99 (t, *J* = 9.5 Hz, $H3^C$), 4.12 (qt, *J* = 3.5, 10.0 Hz, $H5^C$), 4.63 (d, *J* = 8.0 Hz, H1β^A), 5.20 (40%α, d, *J* = 4.0 Hz, H1α^A), 5.33 (d, *J* = 4.0 Hz, $H1^C$), 5.38 (d, *J* = 4.0 Hz, $H1^{B,D}$); ^{13}C NMR (D_2O) δ = 62.9 ($C6^B$), 63.1 ($C6^{C,D}$), 63.3 ($C6^A$), 72.0 ($C4^D$), 72.4 ($C4^B$), 72.6 (C5α^A), 73.0 ($C2^B$), 73.1 ($C5^C$), 73.9 (C2α^A), 74.1 ($C2^C$), 74.4 ($C2^D$), 75.1 ($C5^B$), 75.3 ($C5^D$), 75.5 ($C3^D$), 75.8 (C3α^A), 75.9 ($C3^C$), 76.6 (C2β^A), 77.2 (C5β^A), 78.8 (C3β^A), 79.4 ($C4^C$), 79.6 (C4β^A), 79.8 (C4α^A), 82.0 (C3β^B), 82.1 (C3α^B), 94.5 (C1α^A), 98.4 (C1β^A), 101.5 ($C1^C$), 102.2 ($C1^D$), 102.5 (C1β^B), 102.6 (C1α^B).

Found: C, 41.27; H, 6.37%. Calcd for $C_{24}H_{42}O_{21}\cdot2H_2O$: C, 41.03; H, 6.60%.

***O*-α-D-Glucopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→4)-D-glucopyranose (32).** Similar hydrogenation of **45** (35.6 mg, 19 mmol) afforded glassy **32** (8.6 mg, 70%), $[\alpha]_D$ +168 (*c* 0.6, H_2O); ^{1}H NMR (D_2O) δ = 3.25 (dd, *J* = 8.0, 9.0 Hz, H2β^B), 3.41 (t, *J* = 9.5 Hz, $H4^D$), 3.55 (dd, *J* = 3.5, 9.5 Hz, H2α^A, $H2^D$), 3.60 (dd, *J* = 4.0, 10.0 Hz, $H2^B$), 3.63 (t, *J* = 9.0 Hz, $H4^{A,B,C}$), 3.67 (dd, *J* = 4.0, 9.5 Hz, $H2^C$), 3.73 (t, *J* = 9.5 Hz, $H3^D$), 3.76 (t, *J* = 9.0 Hz, H3β^A), 3.81 (t, *J* = 9.5 Hz, $H3^C$), 3.93 (t, *J* = 10.5 Hz, $H3^B$), 3.95 (t, *J* = 9.5 Hz, H3α^A), 4.01 (ddd, *J* = 2.0, 4.0, 10.0 Hz, $H5^D$), 4.63 (d, *J* = 8.0 Hz, H1β^A), 5.21 (42%α, d, *J* = 4.0 Hz, H1α^A), 5.34 (d, *J* = 3.5 Hz, $H1^D$), 5.37 (d, *J* = 4.0 Hz, $H1^C$), 5.38 (d, *J* = 4.0 Hz, $H1^B$); ^{13}C NMR (D_2O) δ = 62.9 ($C6^C$), 63.1 ($C6^D$), 63.2 ($C6^B$), 63.3 ($C6^A$), 72.1 ($C4^D$), 72.4 ($C4^C$), 72.6 (C5α^A), 73.1 ($C2^C$), 73.9 (C2α^A, $C5^B$), 74.1 (C2β^B), 74.2 (C2α^B), 74.3 ($C2^D$), 74.5 ($C5^D$), 75.2 ($C5^C$), 75.5 ($C3^D$), 75.8 (C3α^A), 75.9 ($C3^B$), 76.6 (C2β^A), 77.2 (C5β^A), 78.8 (C3β^A), 79.5 (C4α^A), 79.7 (C4β^A, $C4^B$), 82.2 ($C3^C$), 94.5 (C1α^A), 98.4 (C1β^A), 101.7 ($C1^D$), 102.1 ($C1^B$), 102.7 ($C1^C$).

Found: C, 41.20; H, 6.49%. Calcd for $C_{24}H_{42}O_{21}\cdot2H_2O$: C, 41.03; H, 6.60%.

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