A Convenient Method for the Preparation of Disaccharides by Transglycosylation of Methyl Glycosides

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Abstract. Transglycosylation of methyl glycosides with various glycosyl acceptors using a $Sn(OTf)_2$–Me_3SiCl promoter system in the presence of molecular sieves 5A afforded the corresponding glycosides. Several useful disaccharides are effectively prepared in good yields with moderate to good stereoselectivities.

INTRODUCTION

The development of efficient synthetic methods for the preparation of complex saccharide chains containing glycoconjugates is one of the most important problems in modern carbohydrate chemistry[1] because of their vital roles in biological processes.[2] Many glycosylation methods have been studied and the desired glycosides have been obtained in high yield with good stereoselectivity by employing appropriate glycosyl donors.[3] Some of these glycosyl donors are synthesized from the simple and readily available methyl glycosides via the corresponding 1-hydroxy sugars prepared by their hydrolysis.[4] However, this hydrolysis is frequently realized in only moderate yield due to rather severe reaction conditions, and is also accompanied by side reactions such as partial loss of protecting groups present in the glycosides.[5] It therefore seemed that a more convenient and efficient glycosylation method would be a direct transglycosylation using methyl glycosides as glycosyl donors with glycosyl acceptors. Although such transglycosylation has already been reported, the example is limited to the synthesis of the simple ethyl glycoside,[6] and further study of this approach appeared desirable. A convenient and practical method for the transglycosylation of methyl glycosides with various glycosyl acceptors, affording the corresponding glycosides, has now been developed and is described herein.

RESULTS AND DISCUSSION

The transglycosylation reaction of methyl glycoside does not generally proceed smoothly in the presence of a Lewis acid because the formed methanol or methoxide is more nucleophilic than the glycosyl acceptor and it readily recombines with the intermediate oxocarbenium ion to regenerate the original methyl glycoside. It is well known, on the other hand, that *N*- and *C*-glycosides are rather easily prepared from methyl glycosides by irreversible pathways. It was expected that the transglycosylation should then proceed smoothly when methanol or methoxide was selectively captured by an appropriate reagent. The most convenient and potential reagents were considered to be molecular sieves. The transglycosylation reactions of methyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside with cyclohexanol and its silyl derivatives were tried using a Me_2SiCl_2–2AgOTf promoter system in the presence of several molecular sieves (Table 1). Interestingly, the reaction proceeded smoothly to afford the desired glycoside in good yield with moderate stereoselectivity (74%, α/β=72/28) when silylated cyclohexanol and molecular sieves 5A were used. All kinds of silyl ethers, even the *tert*-butyldimethylsilyl ether, were more reactive than free cyclohexanol, and all molecular sieves other than MS5A were quite ineffective.

Next, the effect of solvent was examined. The reaction proceeded smoothly in dichloromethane, toluene, or pivalonitrile (^{t}BuCN) (Table 2). The hindered polar solvent pivalonitrile,[7] was more effective than the less hindered acetonitrile (MeCN) because of the absence of competitive interaction with MS5A.

Next, several kinds of Lewis acids were screened, and it was found that both (a) Me_3SiOTf and (b) $Sn(OTf)_2$–Me_3SiCl[8] promoter systems in pivalonitrile

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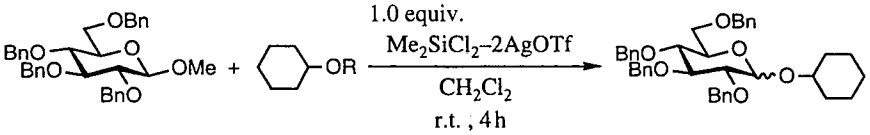


Table 1. Effects of molecular sieves and nucleophiles

R	Molecular sieves (mg/mmol)	Yield, %	α / β
Me_3Si	none	13	72 / 28
Me_3Si	3A (1500)	No reaction	–
Me_3Si	4A (1500)	No reaction	–
Me_3Si	**5A (1500)**	**74**	**72 / 28**
Me_3Si	5A (500)	25	72 / 28
Me_3Si	5A (1000)	70	72 / 28
Me_3Si	5A (3000)	51	72 / 28
Me_3Si	13X (1500)	No reaction	–
H	5A (1500)	20	72 / 28
Et_3Si	5A (1500)	70	72 / 28
$^tBuMe_2Si$	5A (1500)	59	72 / 28
$PhMe_2Si$	5A (1500)	51	72 / 28
Bu_3Sn	5A (1500)	No reaction	–

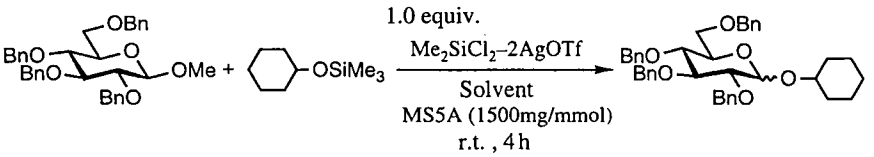


Table 2. Effects of solvents

Solvent	Yield, %	α / β
CH_2Cl_2	74	72 / 28
$ClCH_2CH_2Cl$	44	68 / 32
Toluene	74	78 / 32
$EtNO_2$	27	67 / 33
MeCN	39	69 / 31
^tBuCN	**77**	**71 / 29**

were effective for this reaction (Table 3). The effect of reaction temperature showed that both yield and stereoselectivity were lowered at 0 °C. On the other hand, the reaction proceeded rapidly at higher temperature (40 °C) while the yield was also lowered due to side reactions such as the formation of 1,6-anhydro sugar via 6-*O*-debenzylated methyl glycoside.

Transglycosylation reactions using methyl glycosides and trimethylsilylated cyclohexanol or cyclohexylmethanol were tried at room temperature using promoter system (b) (Table 4). In every case, the reactions proceeded smoothly to give the corresponding glucopyranosides, galactopyranoside, ribofuranoside, and fucopyranoside in good yields. Except in the synthesis of glucopyranoside, the amount of the promoter system could in most cases be reduced to half an equivalent of the donor. The present transglycosylation is thus applicable to the synthesis of various alkyl glycosides including furanosides and deoxy glycosides.

The synthesis of disaccharides is shown in Table 5. Transglycosylation was successfully applied even when sugar derivatives having a secondary hydroxyl group were employed as glycosyl acceptors. Several important saccharide linkages such as a Galα1–3Gal linkage found in blood group B determinant and a Fucα1–3GlcNAc linkage found in sialyl Lewis X were formed in good yields.

Molecular discrimination based on the difference of reactivities between two anomers of methyl glycoside was clearly demonstrated. In general, the β-anomer of

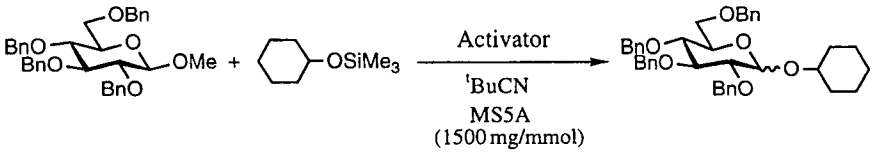


Table 3. Effects of activators and temperature

Activator (mol %)	Temp	Time, h	Yield, %	α/β
Me_2SiCl_2(100)–AgOTf(200)	r.t.	4	77	72 / 28
Me_3SiOTf(100)	r.t.	5	87	68 / 32
Me_3SiCl(100)	r.t.	5	No reaction	–
$Sn(OTf)_2$(100)	r.t.	5	Trace	–
Me_3SiCl(100)–$Sn(OTf)_2$(100)	**r.t.**	**5**	**88**	**71 / 29**
Me_3SiCl(50)–$Sn(OTf)_2$(50)	r.t.	5	14	37 / 63
Me_3SiCl(50)–$Sn(OTf)_2$(100)	r.t.	5	54	49 / 51
Me_3SiOAc(100)–$Sn(OTf)_2$(100)	r.t.	5	Trace	–
$Me_3SiOC(O)CF_3$(100)–$Sn(OTf)_2$(100)	r.t.	5	No reaction	–
Me_3SiCl(100)–$Sn(OTf)_2$(100)	0 °C[a]	24	31	35 / 65
Me_3SiCl(100)–$Sn(OTf)_2$(100)	40 °C	0.75	69	69 / 31

[a]The reaction was carried out in ^tBuCN / CH_2Cl_2 = 4 / 1.

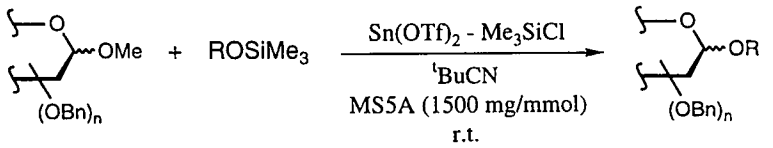
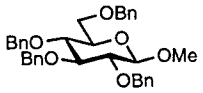
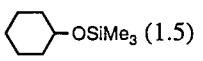
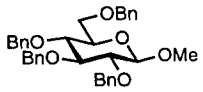
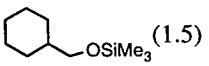
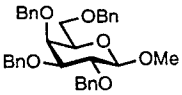
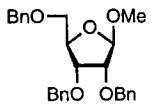
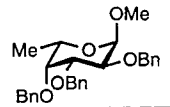
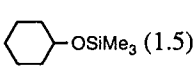


Table 4. Synthesis of several alkyl glycosides

Methyl glycoside	$ROSiMe_3$ (equiv.)	Activator equiv.	Time, h	Yield, %	α/β
		1.0	5	88	71 / 29[a]
		1.0	5	91	68 / 32
		1.0	5	88	62 / 38
		0.5	4	87	28 / 72
		0.5	1	94	60 / 40

[a]The ratio of two anomers was improved to α / β = 93 / 7 by one-pot anomerization procedure using $TiCl_4$, reported by Koto et al.[9] (at room temperature, 85% yield from methyl glycoside).

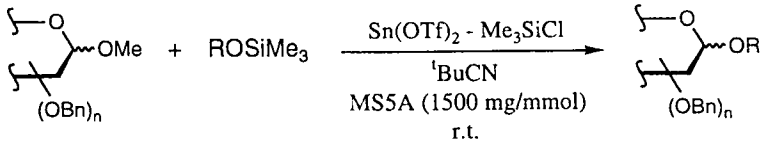
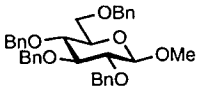
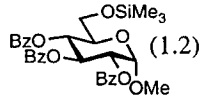
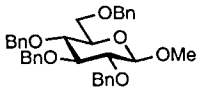
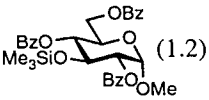
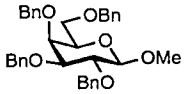
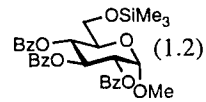
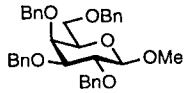
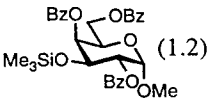
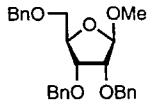
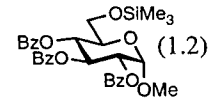
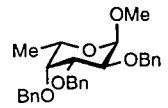
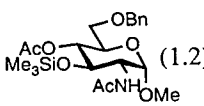
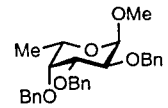
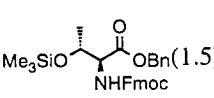
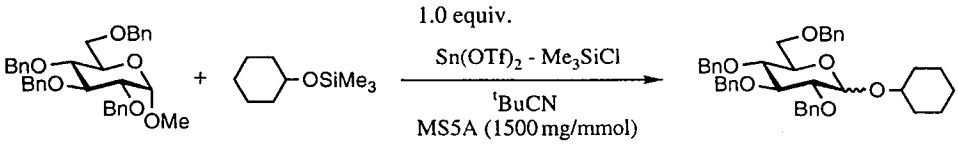


Table 5. Synthesis of several disaccharides

Methyl glycoside	$ROSiMe_3$ (equiv.)	Activator, equiv.	Time, h	Yield, %	α/β
	 (1.2)	1.0	6	86	78 / 22[a]
	 (1.2)	1.0	5	77	74 / 26
	 (1.2)	0.5	6	94	77 / 23
	 (1.2)	0.5	4	96	80 / 20
	 (1.2)	0.5	3	96	44 / 56
	 (1.2)	1.0[b]	1	94	82 / 18
	 (1.5)	1.0	3	92	73 / 27

[a]The ratio of two anomers was improved to α / β = 83 / 17 by one-pot anomerization procedure using $TiCl_4$, reported by Koto et al.[9] (at −15 °C, 80% yield from methyl glycoside).
[b]2.0 equiv. of Me_3SiCl was used.



Scheme 1. Transglycosylation of methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside

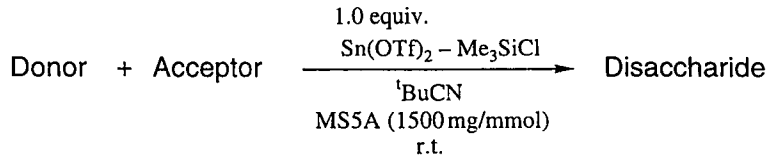
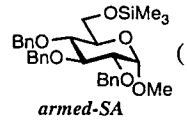
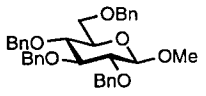
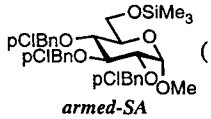
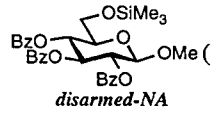
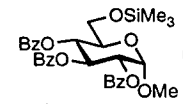
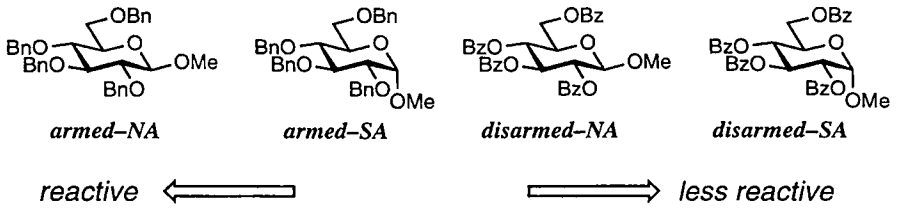


Table 6. Synthesis of disaccharides based on SA–NA classification

Donor	Acceptor (equiv.)	Time, h	Yield, %	α / β
	 (1.2) *armed-SA*	4	64	71 / 29
 *armed-NA*	 (1.5) *armed-SA*	4	86	73 / 27
	 (1.2) *disarmed-NA*	5	78	72 / 28
	 (1.2) *disarmed-SA*	6	86	78 / 22



Scheme 2. SA–NA classification

methyl glucoside is more reactive than the α-anomer under acidic conditions, as shown in their hydrolysis,[10–12] since the α-anomer is stabilized by the anomeric effect.[13] Expectedly, the reactivity of the α-anomer was poorer than that of the β-anomer, and the yield of the glycoside was significantly lowered when α-methyl glucoside (methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside) was reacted with cyclohexanol (Scheme 1).

Based on this result, the cross-coupling reaction of β-methyl glucoside (methyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside) with α-methyl glucoside (methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside) was tried, and the desired disaccharide, shown in Table 6, was obtained in good yield, as expected. Further, it was observed that both yield and stereoselectivity were improved when a *p*-chlorobenzyl protected glycosyl acceptor was used in place of the more common benzylated one.

It is important to note that the above anomer-selective cross-coupling reactions are dependent on the characteristic behavior of methyl glycosides. Such a cross-coupling reaction between anomers having the same type of anomeric substituent and protective groups has not yet been observed in glycosylations using other glycosyl donors, such as trichloroacetimidates, glycosyl fluorides, and 1-*O*-acyl sugars. These conventional glycosyl donors show higher reactivities, but the difference in reactivities between the two anomers is not enough to

realize a cross-coupling reaction. The relative reactivities of the two methyl glycoside anomers suggests an SA–NA classification (Scheme 2). The designation SA refers to the anomeric-effect-*stabilized-anomer* such as the less reactive α-methyl glucoside, while NA refers to the anomeric-effect-*non-stabilized-anomer* such as the more reactive β-methyl glucoside. According to this classification, the two anomers of methyl glycosides behave as independent and clearly-distinguishable glycosyl donor and glycosyl acceptor.

The armed-disarmed concept proposed by Fraser-Reid[14] is commonly accepted for efficient synthesis of saccharide chains using pentenyl glycosides[14,15] or thioglycosides.[16] Within the framework of the armed-disarmed concept, disaccharide synthesis by cross-coupling of two monosaccharides having the same type of anomeric substituent takes place when an armed glycosyl donor is treated with a disarmed glycosyl acceptor. We now suggest a refinement of this concept by combining it with the SA–NA classification. This leads to the expected order of reactivity of glycosyl donor armed-NA > armed-SA > disarmed-NA > disarmed-SA. Actually, the most reactive armed-NA coupled with all of the other less reactive anomers in good yields (Table 6); that is, three types of cross-coupling reactions were successfully carried out. The disaccharide produced by coupling of armed-NA with armed-SA may be used directly in the synthesis of trisaccharide, while the disaccharide obtained from armed-NA and disarmed-NA could be "armed" and converted to a glycosyl donor by replacing acyl protecting groups to benzyl groups.[14] Further investigations leading to an effective method of activation of less reactive armed-SA would exploit the full scope of this extended classification.

EXPERIMENTAL

IR spectra were recorded on a Horiba FT-300 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were respectively recorded at 270 MHz and 67.80 MHz with a JEOL JNM-EX270L spectrometer with tetramethylsilane as an internal standard. Optical rotations were measured with a JASCO DIP-370 digital polarimeter. Purification of products was performed by column chromatography on silica gel (Merck, Art. 7734 Kieselgel 60) or preparative TLC on silica gel (Wakogel B-5F).

All reactions were carried out under an argon atmosphere. Dichloromethane, 1,2-dichloroethane, acetonitrile and pivalonitrile were successively distilled from P_2O_5 and CaH_2, and stored over proper molecular sieves. Toluene was distilled from Na metal and stored over molecular sieves. Nitroethane was dried over $CaCl_2$ and distilled under reduced pressure. Tin(II) trifluoromethanesulfonate was dried at 100 °C under reduced pressure (0.1 mmHg) for 1 h prior to use. Molecular sieves were dried at 200 °C under reduced pressure (0.1 mmHg) for 1 h prior to use.

General Procedure for Glycosylation Using Me_2SiCl_2 and AgOTf

A solution of dichlorodimethylsilane in toluene was added to a solution of silver trifluoromethanesulfonate and molecular sieves in dichloromethane (1.5 mL), and the mixture was shielded from the light and stirred for 1 h. To this mixture was added a solution of a methyl glycoside (0.1 mmol) and a silyl ether (0.15 mmol) in dichloromethane (2.0 mL). The reaction mixture was stirred for the appropriate number of hours at room temperature and was quenched by adding saturated aqueous sodium hydrogen carbonate. The mixture was filtered, the organic phase was separated, and the aqueous phase was extracted with dichloromethane. The combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure.The residue was purified by preparative TLC to afford the corresponding glycoside.

General Procedure for Transglycosylation Using Sn $(OTf)_2$–Me_3SiCl Catalyst System

To a solution of tin (II) trifluoromethanesulfonate and molecular sieves in pivalonitrile (1.5 mL) was added a solution of chlorotrimethylsilane in toluene at room temperture. To this mixture was added a solution of a methyl glycoside (0.1 mmol) and a silyl ether (0.15 mmol) in pivalonitrile (2.0 mL). The reaction mixture was stirred for the appropriate number of hours at room temperature, and was quenched by adding saturated aqueous sodium hydrogen carbonate. The corresponding glycoside was isolated by the usual workup and purification by preparative TLC.

One-Pot Anomerization Procedure Using $TiCl_4$[9]

The reaction mixture (0.1 mmol scale) resulting from the transglycosylation reaction was evaporated at room temperature. To the residue was successively added dichloromethane (2 mL) and titanium tetrachloride (0.1 mmol) at room temperature or at –15 °C. After stirring the reaction mixture for 10 min at the same temperature, it was quenched by adding aqueous sodium hydrogen carbonate. The anomerization product was isolated by the usual workup and purification by preparative TLC.

Physical Properties of Glucopyranosides

*Cyclohexyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside*

$[\alpha]_D^{26}$ +42.1° (*c* 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$) δ = 1.15–1.92 (10H, m), 3.52 (1H, m, OCH), 3.55 (1H, dd, *J* = 9.6 and 3.6 Hz, H-2), 3.63 (1H, t, *J* = 9.4 Hz, H-4), 3.63 (1H, dd, *J* = 10.6 and 2.0 Hz, Ha-6), 3.74 (1H, dd, *J* = 10.6 and 3.6 Hz, Hb-6), 3.88 (1H, ddd, *J* = 9.6, 3.6 and 2.0 Hz, H-5), 4.00 (1H, t, *J* = 9.6 Hz, H-3), 4.46 and 4.62 (2H, AB, *J* = 11.9 Hz, CH_2Ph), 4.46 and 4.83 (2H, AB, *J* = 10.6 Hz, CH_2Ph), 4.65 and 4.75 (2H, AB, *J* = 12.2 Hz, CH_2Ph), 4.81 and 5.00 (2H, AB, *J* = 10.9 Hz, CH_2Ph), 4.95 (1H, d, *J* = 3.6 Hz, H-1), 7.11–7.42 (20H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 94.7 (C-1).

Lit.[17] $[\alpha]_D^{20}$ +45° (*c* 1.3, $CHCl_3$)

*Cyclohexyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside*

mp = 104–105 °C; $[\alpha]_D^{23}$ +7.5° (*c* 1.0, $CHCl_3$)

^{1}H NMR (CDCl3) δ = 1.15–1.98 (10H, m), 3.44 (1H, dd,

J = 8.9 and 7.9 Hz, H-2), 3.46 (1H, m, H-5), 3.54 (1H, t, J = 8.9 Hz, H-4), 3.64 (1H, t, J = 8.9 Hz, H-3), 3.65 (1H, dd, J = 10.7 and 5.0 Hz, Ha-6), 3.72 (1H, m, OCH), 3.74 (1H, dd, J = 10.7 and 1.7 Hz, Hb-6), 4.53–5.30 (9H, m), 7.13-7.40 (20H, m, Ph).

Lit.[17] mp = 105–106 °C; $[\alpha]_D^{20}$ +8° (*c* 1.6, $CHCl_3$).

Cyclohexylmethyl 2,3,4,6-tetra-O-benzyl-α-D-glucopyranoside

$[\alpha]_D^{26}$ +34.4° (*c* 1.0, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 0.85-0.95 (2H, m), 1.12–1.32 (3H, m), 1.60–1.85 (6H, m), 3.20 (1H, dd, J = 9.6 and 5.9 Hz, OCH_2), 3.41 (1H, dd, J = 9.6 and 7.3 Hz, OCH_2), 3.56 (1H, dd, J = 9.7 and 3.6 Hz, H-2), 3.59–3.80 (4H, m, H-4, H-5, Ha-6 and Hb-6), 3.98 (1H, t, J = 9.1 Hz, H-3), 4.47 and 4.61 (2H, AB, J = 12.2 Hz, CH_2Ph), 4.47 and 4.83 (2H, AB, J = 10.6 Hz, CH_2Ph), 4.64 and 4.77 (2H, AB, J = 12.1 Hz, CH_2Ph), 4.73 (1H, d, J = 3.6 Hz, H-1), 4.81 and 5.00 (2H, AB, J = 10.9 Hz, CH_2Ph), 7.11–7.37 (20H, m, Ph).

Lit.[17] $[\alpha]_D^{20}$ +33° (*c* 1.0, $CHCl_3$).

Cyclohexylmethyl 2,3,4,6-tetra-O-benzyl-β-D-glucopyranoside

mp = 103–104 °C; $[\alpha]_D^{24}$ +4.3° (*c* 1.0, $CHCl_3$).

^1H NMR ($CDCl3$) δ = 0.90–1.32 (2H, m), 1.12–1.32 (3H, m), 1.60–1.88 (6H, m), 3.32 (1H, dd, J = 9.4 and 7.2 Hz, OCH_2), 3.44 (1H, m, H-5), 3.45 (1H, dd, J = 8.9 and 7.6 Hz, H-2), 3.57 (1H, t, J = 8.9 Hz, H-4), 3.64 (1H, t, J = 8.9 Hz, H-3), 3.65–3.77 (2H, m, Ha-6 and Hb-6), 3.80 (1H, dd, J = 9.4 and 5.8 Hz, OCH_2), 4.37 (1H, d, J = 7.6 Hz, H-1), 4.52 and 4.81 (2H, AB, J = 10.6 Hz, CH_2Ph), 4.55 and 4.62 (2H, AB, J = 12.2 Hz, CH_2Ph), 4.71 and 4.96 (2H, AB, J = 10.9 Hz, CH_2Ph), 4.78 and 4.93 (2H, AB, J = 10.7 Hz, CH_2Ph), 7.11–7.37 (20H, m, Ph).

Lit.[17] mp = 103–104°C; $[\alpha]_D^{20}$ +4° (*c* 1.6, $CHCl_3$).

Methyl 2,3,4-tri-O-(p-chlorobenzyl)-6-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-α-D-glucopyranoside

mp = 130–131 °C; $[\alpha]_D^{28}$ +55.4° (*c* 1.0, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 3.36 (3H, s, OCH_3), 3.36–3.39 (1H, m), 3.52–3.98 (11H, m), 4.40–5.02 (10H, m), 7.10–7.29 (32H, m).

^{13}C NMR ($CDCl_3$) δ = 97.7, 97.23, 81.85, 81.65, 80.18, 80.06, 77.63, 77.20, 76.35, 75.46, 75.01, 74.63, 73.98, 73.41, 72.38, 70.33, 70.30, 68.36, 65.72, 55.17.

IR (KBr) υ = 1022.09, 1051.01, 1074.16, 1097.30, 1137.80, 1162.87, 1326.79, 1359.57, 1455.99, 1492.63, 1600.63 cm^{-1}.

Anal. Calcd for $C_{62}H_{63}Cl_3O_{11}$: C, 68.29; H, 5.82. Found: C, 68.10; H, 5.74.

Methyl 2,3,4-tri-O-(p-chlorobenzyl)-6-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-α-D-glucopyranoside

mp = 149–150 °C; $[\alpha]_D^{27}$ +11.7° (*c* 1.0, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 3.34 (3H, s, OCH_3), 3.41–3.78 (10H, m), 3.92 (1H, t, J = 9.24 Hz), 4.17 (1H, d, J = 9.56 Hz), 4.33 (1H, d, J = 7.91 Hz), 4.42–4.98 (15H, m), 6.86–7.55 (32H, m).

^{13}C NMR ($CDCl_3$) δ = 103.65, 97.74, 84.78, 82.00, 81.74, 79.86, 77.92, 77.86, 77.20, 75.74, 75.04, 74.97, 74.84, 74.65, 73.89, 73.37, 72.36, 69.67, 68.99, 68.34, 55.22.

IR (KBr) υ = 1010.52, 1070.30, 1116.58, 1157.08, 1357.64, 1394.28, 1455.99, 1494.56 cm^{-1}.

Anal. Calcd for $C_{62}H_{63}Cl_3O_{11}$: C, 68.29; H, 5.82. Found: C, 68.20; H, 5.75.

Methyl 2,3,4-tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-α-D-glucopyranoside

mp = 101–102 °C; $[\alpha]_D^{25}$ +60.2° (*c* 1.5, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 3.35 (3H, s, OCH_3), 3.44 (1H, dd, J = 9.6 and 3.6 Hz), 3.51–3.84 (9H, m), 3.92–4.02 (2H, m), 4.34–4.46 (1H, m), 4.54–4.96 (13H, m), 4.96 (1H, d, J = 3.4 Hz), 7.09–7.34 (35H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 97.33 (C-1').

Lit.[18] ^1H NMR ($CDCl_3$) δ = 3.35 (3H, s, OCH_3), 4.98 (1H, d, J = 3.36 Hz, H-1').

Methyl 2,3,4-tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-α-D-glucopyranoside

mp = 133–134 °C; $[\alpha]_D^{27}$ +18.1° (*c* 1.0, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 3.32 (3H, s, OCH_3), 3.40–3.75 (9H, m), 3.82 (1H, m), 3.99 (1H, J = 9.2 Hz), 4.18 (1H, dd, J = 10.6 and 1.7 Hz), 4.35 (1H, d, J = 7.6 Hz, H-1'), 4.48–4.99 (15H, m), 7.14–7.36 (35H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 103.76 (C-1').

IR (KBr) υ = 1000.87, 1066.44, 1114.65, 1159.01, 1263.15, 1357.64, 1454.06, 1496.49 cm^{-1}.

Lit.[18] ^1H NMR ($CDCl_3$) δ = 3.32 (3H, s, OCH_3), 4.35 (1H, d, J = 7.94 Hz, H-1').

Methyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-β-D-glucopyranoside

$[\alpha]_D^{26}$ +35.4° (*c*0.79, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 3.44 (3H, s, OCH_3), 3.52–3.70 (5H, m), 3.85–4.00 (3H, m), 4.08–4.13 (1H, m), 4.39–4.45 (2H, m), 4.58–4.94 (8H, m), 5.39–5.47 (2H, m), 5.86 (1H, t, J = 9.73 Hz), 7.07–7.97 (35H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 101.80, 96.75, 81.89, 79.86, 78.24, 77.22, 75.62, 74.74, 73.35, 73.30, 73.21, 73.03, 71.86, 69.97, 68.23, 66.38, 52.25.

IR (neat) υ = 1097.30, 1259.29, 1284.36, 1452.14, 1733.69 cm^{-1}.

Anal. Calcd for $C_{62}H_{60}O_{14}$: C, 72.36; H, 5.88. Found: C, 72.27; H, 5.96.

Methyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-β-D-glucopyranoside

$[\alpha]_D^{27}$ +2.1° (*c* 1.0, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 3.38 (3H, s, OCH_3), 3.38–3.44 (1H, m), 3.56–3.66 (4H, m), 3.88 (1H, dd, J = 8.25 and 11.54 Hz), 4.06–4.12 (2H, m), 4.41–5.01 (11H, m), 5.36–5.49 (2H, m), 5.87 (1H, t, J = 9.73 Hz), 7.12–7.96 (35H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 103.92, 101.83, 84.53, 82.12, 75.67, 74.97, 74.77, 74.63, 74.29, 73.42, 72.94, 71.83, 70.05, 68.73, 68.50, 57.18.

IR (neat) υ = 1261.22, 1282.43, 1452.14, 1733.69 cm^{-1}.

Anal. Calcd for $C_{62}H_{60}O_{14}$: C, 72.36; H, 5.88. Found: C, 72.46; H, 5.76.

Methyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-α-D-glucopyranoside

$[\alpha]_D^{26}$ +73.4° (*c* 1.12, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 3.43 (3H, s, OCH_3), 3.43–3.66 (5H, m), 3.82–3.96 (3H, m), 4.29–4.65 (5H, m), 4.73–4.93 (5H, m), 5.20–5.28 (2H, m), 5.53 (1H, t, *J* = 9.9 Hz), 6.14 (1H, t, *J* = 9.57 Hz), 7.11–7.99 (35H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 97.20, 96.69, 81.73, 79.91, 77.23, 75.51, 74.75, 73.37, 73.10, 72.22, 70.57, 70.17, 69.62, 68.52, 68.20, 66.63, 55.56.

IR (neat) υ = 1101.15, 1259.29, 1280.50, 1729.83 cm^{-1}.

Anal. Calcd for $C_{62}H_{60}O_{14}$: C, 72.36; H, 5.88. Found: C, 72.44; H, 5.94.

Methyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-α-D-glucopyranoside

mp = 132–133 °C; $[\alpha]_D^{24}$ +38.8° (*c* 1.52, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 3.37 (3H, s, OCH_3), 3.37–3.49 (2H, m), 3.56–3.68 (4H, m), 3.81 (1H, dd, *J* = 10.89 and 7.59 Hz), 4.13 (1H, dd, *J* = 10.89 and 1.98 Hz), 4.35–4.55 (5H, m), 4.66–4.82 (3H, m), 4.91 (1H, d, *J* = 10.89 Hz), 5.06 (1H, d, *J* = 10.89 Hz), 5.20–5.28 (2H, m), 5.48 (1H, t, *J* = 10.18 Hz), 6.17 (1H, t, *J* = 9.73 Hz), 7.12–7.91 (35H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 103.97, 96.75, 84.51, 82.32, 77.61, 75.67, 74.93, 74.86, 74.79, 73.39, 72.09, 70.48, 69.86, 68.97, 68.82, 68.61, 55.47.

IR (KBr) υ = 1025.94, 1070.30, 1099.23, 1174.44, 1278.57, 1452.14, 1727.91 cm^{-1}.

Anal. Calcd for $C_{62}H_{60}O_{14}$: C, 72.36; H, 5.88. Found: C, 72.48; H, 5.77.

Methyl 2,4,6-tri-O-benzoyl-3-O-(2,3,4,6-tetra-O-benzyl-D-glucopyranosyl)-α-D-glucopyranoside (anomeric mixture)

^1H NMR ($CDCl_3$) δ = 3.43 (s, OCH_3), 3.45 (s, OCH_3), 3.10–3.92 (m), 4.10–4.87 (m), 4.93 (d, *J* = 2.97 Hz), 5.04 (d, *J* = 3.63 Hz), 5.17–5.22 (m), 5.28 (dd, *J* = 9.57 and 3.63 Hz), 5.46 (t, *J* = 9.74 Hz), 5.67 (t, *J* = 9.56 Hz), 6.93–8.10 (m, Ph).

IR (neat) υ = 1070.30, 1103.08, 1151.29, 1268.93, 1452.14, 1496.49, 1725.98 cm^{-1}.

Anal. Calcd for $C_{62}H_{60}O_{14}$: C, 72.36; H, 5.88. Found: C, 72.29; H, 5.92.

Physical Properties of Galactopyranosides

Cyclohexyl 2,3,4,6-tetra-O-benzyl-a-D-galactopyranoside

$[\alpha]_D^{28}$ +49.5° (*c* 0.67, $CHCl_3$).

^1H NMR (CDCl3) δ = 1.17–1.54 (6H, m), 1.72–1.89 (4H, m), 3.50–3.57 (3H, m), 3.94–4.08 (4H, m), 4.38–4.95 (8H, m, CH_2Ph), 5.01 (1H, d, *J* = 3.3 Hz, H-1), 7.20–7.40 (20H, m).

^{13}C NMR ($CDCl_3$) δ = 95.3 (C-1).

Lit.[19] ^{13}C NMR ($CDCl_3$) δ = 95.45 (C-1).

Methyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl)-α-D-glucopyranoside

$[\alpha]_D^{26}$ +62.8° (*c* 1.15, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 3.34 (3H, s, OCH_3), 3.42–3.48 (2H, m), 3.58 (1H, d, *J* = 10.88 Hz), 3.81–4.07 (5H, m), 4.26–4.41 (3H, m), 4.54–4.95 (7H, m), 5.16 (1H, d, *J* = 3.63 Hz), 5.22 (1H, d, *J* = 10.7 and 3.47 Hz), 5.53 (1H, t, *J* = 9.9 Hz), 6.13 (1H, t, *J* = 9.9 Hz), 7.16–8.00 (35H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 97.79, 96.69, 78.49, 76.37, 75.01, 74.72, 73.17, 73.12, 72.83, 72.13, 70.64, 69.53, 69.20, 68.63, 68.39, 66.56, 55.35.

IR (neat) υ = 1101.15, 1249.65, 1286.29, 1729.83 cm^{-1}.

Anal. Calcd for $C_{62}H_{60}O_{14}$: C, 72.36; H, 5.88. Found: C, 72.33; H, 5.96.

Methyl 2,3,4-tri-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl)-α-D-glucopyranoside

mp = 63–64 °C; $[\alpha]_D^{26}$ +24.5° (*c* 0.82, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 3.35 (3H, s, OCH_3), 3.46–3.53 (4H, m), 3.72–3.87 (3H, m), 4.08 (1H, d, *J* = 9.24 Hz), 4.27–4.45 (4H, m), 4.66–4.71 (3H, m), 4.59 and 4.91 (2H, AB, *J* = 11.55 Hz, CH_2Ph), 5.02 (1H, d, *J* = 10.56 Hz), 5.19 (1H, d, *J* = 3.63 Hz), 5.23–5.29 (2H, m), 5.41 (1H, t, *J* = 9.9 Hz), 6.16 (1H, t, *J* = 9.73 Hz), 7.18–7.98 (35H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 104.19, 96.60, 81.96, 79.61, 77.20, 75.13, 74.47, 73.46, 73.37, 73.30, 73.05, 72.17, 70.48, 69.94, 68.93, 68.57, 55.38.

IR (KBr) υ = 1099.23, 1251.58, 1282.43, 1729.83 cm^{-1}.

Anal. Calcd for $C_{62}H_{60}O_{14}$: C, 72.36; H, 5.88. Found: C, 72.42; H, 5.83.

Methyl 2,4,6-tri-O-benzoyl-3-O-(2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl)-α-D-galactopyranoside

$[\alpha]_D^{26}$ +100.59° (*c* 1.11, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 3.38 (3H, s, OCH_3), 3.38–3.48 (2H, m), 3.59–3.66 (2H, m), 3.95 (1H, dd, *J* = 9.57 and 2.97 Hz), 4.07 (1H, t, *J* = 6.27 Hz), 4.27–4.61 (11H, m), 4.79 (1H, d, *J* = 11.54 Hz), 5.24–5.30 (2H, m), 5.62 (1H, dd, *J* = 10.4 and 3.47 Hz), 5.97 (1H, s), 7.13–8.10 (35H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 97.41, 94.79, 78.71, 75.42, 74.95, 74.61, 73.19, 72.98, 72.58, 70.53, 69.67, 69.36, 68.72, 67.76, 67.10, 63.06, 55.40.

IR (neat) υ = 1051.01, 1103.08, 1268.93, 1452.14, 1724.05 cm^{-1}.

Anal. Calcd for $C_{62}H_{60}O_{14}$: C, 72.36; H, 5.88. Found: C, 72.36; H, 5.82.

Methyl 2,4,6-tri-O-benzoyl-3-O-(2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl)-α-D-galactopyranoside

$[\alpha]_D^{26}$ +80.75° (*c* 1.14, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 3.29 (1H, d, *J* = 9.56 Hz), 3.39 (3H, s, OCH_3), 3.54–3.62 (4H, m), 3.79 (1H, s), 4.30–4.52 (10H, m), 4.62–4.69 (2H, m), 4.83 (1H, d, *J* = 11.55 Hz), 5.23 (1H, d, *J* = 3.3 Hz), 5.65 (1H, dd, *J* = 10.4 and 3.47 Hz), 5.90 (1H, s), 6.83–8.11 (35H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 104.12, 97.52, 81.83, 79.44, 74.79, 74.43, 73.84, 73.75, 73.01, 72.22, 71.90, 71.79, 68.86, 67.69, 63.74, 55.60.

IR (neat) υ = 1068.37, 1106.94, 1268.93, 1452.14, 1724.05 cm^{-1}.

Anal. Calcd for $C_{62}H_{60}O_{14}$: C, 72.36; H, 5.88. Found: C, 72.25; H, 5.97.

Physical Properties of Ribofuranosides

Cyclohexyl 2,3,5-tri-O-benzyl-a-D-ribofuranoside

$[\alpha]_D^{25}$ +98.7° (*c* 1.2, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 1.12–2.02 (10H, m), 3.37 (1H, dd,

J = 10.5 and 4.2 Hz, Ha-5), 3.46 (1H, dd, J = 10.5 and 3.7 Hz, Hb-5), 3.61 (1H, m, OCH), 3.76 (1H, dd, J = 6.8 and 4.0 Hz, H-2), 3.84 (1H, dd, J = 6.8 and 4.0 Hz, H-3), 4.24 (1H, q, J = 4.0 Hz, H-4), 4.41 and 4.47 (2H, AB, J = 12.3 Hz, CH_2Ph), 4.52 and 4.72 (2H, AB, J = 12.6 Hz, CH_2Ph), 4.61 and 4.72 (2H, AB, J = 12.3 Hz, CH_2Ph), 5.17 (1H, d, J = 4.0 Hz, H-1), 7.20–7.40 (15H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 99.60 (C-1), 80.83 (C-4), 77.22 (C-2), 76.10 (OCH), 75.38 (C-3), 73.30, 72.24 and 72.06 (CH_2Ph), 69.87 (C-5).

Lit.[20] $[\alpha]_D^{27}$ +98.3° (*c* 1.0, $CHCl_3$).

*Cyclohexyl 2,3,5-tri-*O*-benzyl-β-D-ribofuranoside*

$[\alpha]_D^{27}$ –1.1° (*c* 1.0, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 1.10–1.19 (10H, m), 3.52 (1H, dd, J = 10.5 and 6.1 Hz, Ha-5), 3.56 (1H, m, OCH), 3.60 (1H, dd, J = 10.5 and 4.0 Hz, Hb-5), 3.83 (1H, dd, J = 4.8 and 1.3 Hz, H-2), 4.01 (1H, dd, J = 6.6 and 4.8 Hz, H-3), 4.32 (1H, m, H-4), 4.48 and 4.58 (2H, AB, J = 11.7 Hz, CH_2Ph), 4.54 and 4.58 (2H, AB, J = 12.1 Hz, CH_2Ph), 4.65 (2H, AB, J = 12.3 Hz, CH_2Ph), 5.17 (1H, d, J = 1.3 Hz, H-1), 7.21–7.38 (15H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 103.09 (C-1), 80.11 (C-2 and C-4), 78.73 (C-3), 75.11 (OCH), 73.09 and 72.27 (CH_2Ph), 71.74 (C-5).

Lit.[20] $[\alpha]_D^{25}$ –0.8° (*c* 1.0, $CHCl_3$).

*Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,5-tri-*O*-benzyl-α-D-ribofuranosyl)-α-D-glucopyranoside*

$[\alpha]_D^{23}$ +75.4° (*c* 1.1, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 3.36 (3H, s, OCH_3), 3.41–3.47 (2H, m), 3.74–3.98 (4H, m), 4.29–4.66 (8H, m), 5.00 (1H, d, J = 3.96 Hz, H-1'), 5.21–5.24 (2H, m), 5.51 (1H, t, J = 9.9 Hz), 6.13 (1H, t, J = 9.73 Hz), 7.20–7.99 (30H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 101.42, 96.57, 81.85, 77.63, 75.37, 73.35, 72.49, 72.22, 72.17, 70.71, 69.78, 69.72, 68.77, 66.61, 55.40.

IR (neat) υ = 1024.02, 1097.30, 1278.57, 1727.91 cm^{-1}.

Anal. Calcd for $C_{54}H_{52}O_{13}$: C, 71.35; H, 5.77. Found: C, 71.44; H, 5.87.

*Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,5-tri-*O*-benzyl-β-D-ribofuranosyl)-α-D-glucopyranoside*

$[\alpha]_D^{22}$ +57.4° (*c* 1.2, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 3.38 (3H, s, OCH_3), 3.48–3.64 (3H, m), 3.89–4.00 (3H, m), 4.13–4.16 (1H, m), 4.29–4.51 (5H, m), 4.63 and 4.70 (2H, AB, J = 12.2 Hz, CH_2Ph), 5.00 (1H, s, H-1'), 5.18–5.28 (2H, m), 5.58 (1H, t, J = 9.9 Hz), 6.12 (1H, t, J = 9.9 Hz), 7.24–8.00 (30H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 105.93, 96.87, 80.56, 79.26, 78.20, 73.08, 72.26, 72.04, 71.32, 70.53, 69.24, 68.61, 66.09, 55.40.

IR (neat) υ = 1024.02, 1103.08, 1278.57, 1727.91 cm^{-1}.

Anal. Calcd for $C_{54}H_{52}O_{13}$: C, 71.35; H, 5.77. Found: C, 71.44; H, 5.85.

Physical Properties of Fucopyranosides

*Cyclohexyl 2,3,4-tri-*O*-benzyl-a-L-fucopyranoside*

$[\alpha]_D^{27}$ –57.2° (*c* 1.12, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 1.10 (3H, d, J = 6.6 Hz, H-6), 1.11–1.93 (10H, m), 3.51 (1H, m, OCH), 3.66 (1H, d, J = 1.65 Hz), 3.92–4.04 (3H, m), 4.63–5.00 (7H, m), 7.05–7.42 (15H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 95.24 (C-1), 79.32, 77.68, 76.32, 75.10, 74.63, 73.07, 72.76, 65.91, 33.28, 31.48, 25.50, 24.40, 24.10, 16.53.

Lit.[21] $[\alpha]_D^{24}$ –56.8° (*c* 1.29, $CHCl_3$); ^{13}C NMR ($CDCl_3$) δ = 95.34 (C-1).

*Cyclohexyl 2,3,4-tri-*O*-benzyl-β-L-fucopyranoside*[18]

$[\alpha]_D^{26}$ –0.8° (*c* 1.30, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 1.15 (3H, d, J = 6.27 Hz, H-6), 1.08–1.93 (10H, m), 3.38–3.54 (3H, m), 3.65 (1H, m, OCH), 3.79 (1H, dd, J = 9.41 and 7.76 Hz), 4.42 (1H, d, J = 7.59 Hz), 4.68–4.82 (2H, m), 4.95–5.00 (2H, m), 7.25–7.39 (15H, m, Ph).

Lit.[21] $[\alpha]_D^{24}$ –0.4° (*c* 2.27, $CHCl_3$).

*Methyl 4-*O*-acetyl-6-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-2-acetamido-2-deoxy-α-D-glucopyranoside*

$[\alpha]_D^{24}$ –5.85° (*c* 1.2, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 1.06 (3H, d, J = 6.6 Hz, H-6), 1.35 (3H, s, $OCOCH_3$), 1.96 (3H, s, $OCOCH_3$), 3.43 (3H, s, OCH_3), 3.43–3.51 (2H, m), 3.63 (1H, d), 3.81–4.06 (6H, m), 4.49–4.82 (7H, m), 4.92–5.03 (3H, m), 5.14 (1H, d, J = 2.97 Hz), 6.88 (1H, d, J = 4.62 Hz, NH), 7.25–7.38 (20H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 101.33, 97.56, 79.46, 78.91, 78.35, 77.58, 75.04, 74.92, 73.53, 73.17, 71.54, 69.45, 69.18, 68.21, 55.47, 54.13, 22.14, 21.19, 16.28.

IR (neat) υ = 1051.01, 1097.30, 1226.51, 1675.84, 1747.19 cm^{-1}.

Anal. Calcd for $C_{45}H_{53}NO_{11}$: C, 68.95; H, 6.81; N, 1.79. Found: C, 69.06; H, 6.79; N, 1.82.

*Methyl 4-*O*-acetyl-6-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-benzyl-β-L-fucopyranosyl)-2-acetamido-2-deoxy-α-D-glucopyranoside*

mp = 141–142 °C; $[\alpha]_D^{26}$ +4.99° (*c* 0.82, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 1.29 (3H, d, J = 6.26 Hz, H-6), 1.77 (3H, s, $OCOCH_3$), 1.87 (3H, s, $OCOCH_3$), 3.37 (3H, s, OCH_3), 3.44–3.59 (5H, m), 3.69–3.82 (3H, m), 3.99 (1H, t, J = 10.06 Hz), 4.36 (1H, d, J = 7.59 Hz), 4.46–4.78 (7H, m), 4.97–5.08 (2H, m), 5.19 (1H, d, J = 3.30 Hz), 6.76 (1H, d, J = 4.29 Hz, NH), 7.24–7.32 (20H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 103.94, 97.59, 82.46, 79.00, 76.32, 75.44, 74.95, 74.75, 73.51, 72.99, 71.54, 70.44, 69.74, 69.31, 55.28, 53.64, 23.08, 20.67, 16.95.

IR (KBr) υ = 1045.23, 1068.37, 1110.80, 1241.93, 1654.62, 1743.33 cm^{-1}.

Anal. Calcd for $C_{45}H_{53}NO_{11}$: C, 68.95; H, 6.81; N, 1.79. Found: C, 69.11; H, 6.77; N, 1.75.

*N-(9-fluorenylmethoxy)-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-L-threonine benzyl ester*

$[\alpha]_D^{26}$ –47.93° (c 2.48, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 0.94 (3H, d, J = 6.27 Hz), 1.20 (3H, d, J = 5.94 Hz), 3.40–3.50 (2H, m), 3.68 (1H, dd, J = 10.1 and 2.48 Hz), 4.01 (1H, dd, J = 10.1 and 3.80 Hz), 4.24–5.18 (15H, m), 5.78 (1H, d, J = 9.57 Hz, NH), 7.22–7.76 (28H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 171.00, 157.27, 94.72 (C-1), 79.32, 77.93, 76.55, 75.08, 73.71, 73.53, 71.88, 67.67, 67.23, 59.46, 47.59, 16.95, 15.98.

IR (neat) υ = 1047.16, 1101.15, 1452.14, 1502.28,

1727.91, 1752.98 cm^{-1}.

Anal. Calcd for $C_{53}H_{53}NO_9$: C, 75.07; H, 6.30; N, 1.65. Found: C, 75.00; H, 6.32; N, 1.66.

N-(9-fluorenylmethoxy)-O-(2,3,4-tri-O-benzyl-β-L-fucopyranosyl)-L-threonine benzyl ester

mp = 149–150°C; $[\alpha]_D^{26}$ +1.81° (*c* 2.28, $CHCl_3$).

^1H NMR ($CDCl_3$) δ = 1.11 (3H, d, *J* = 6.6 Hz), 1.34 (3H, d, *J* = 6.27 Hz), 3.26 (1H, m), 3.40 (1H, m), 3.50 (1H, s), 3.73 (1H, t, *J* = 8.58 Hz), 4.20–4.47 (6H, m), 4.68–4.98 (8H, m), 5.70 (1H, d, *J* = 9.23 Hz, NH), 7.23–7.76 (28H, m, Ph).

^{13}C NMR ($CDCl_3$) δ = 170.35, 156.77, 103.47 (C-1), 82.82, 78.62, 76.39, 75.62, 74.90, 74.47, 72.99, 70.32, 67.23, 67.14, 58.91, 47.08, 19.07, 16.84.

IR (KBr) υ = 1068.37, 1108.87, 1265.07, 1452.14, 1540.85, 1695.12, 1735.62 cm^{-1}.

Anal. Calcd for $C_{53}H_{53}NO_9$: C, 75.07; H, 6.30; N, 1.65. Found: C, 74.96; H, 6.33; N, 1.71.

CONCLUSION

A new and efficient method for the preparation of various disaccharides by the transglycosylation of methyl glycosides with glycosyl acceptors has been successfully developed. A proposed SA–NA classification based on the characteristic activities of α- and β-methyl glycosides in the present transglycosylation should prove a useful concept in the further development of saccharide synthesis.

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