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Note

A practical synthesis of 2-*O*-substituted β-D-galactopyranosyl (1 → 4) linked di- and tri-saccharides as specific acceptors for (1 → 3)-α-L-fucosyltransferase *,***

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In our laboratory, we are currently involved in the synthesis of specific acceptors for (1 → 3)-α-L-fucosyltransferase. This enzyme catalyzes the transfer of an L-fucopyranosyl group from GDP-L-fucose to O-3 of 2-acetamido-2-deoxy-D-glucose or D-glucose, and exhibits a strict specificity for acceptors having the nonreducing terminal sequence, β-D-Gal*p*-(1 → 4)-D-GlcNAc or -D-Glc[2]. In recent studies, this class of enzymes has been shown to be responsible for the accumulation of the highly fucosylated polylactosamine compounds that are found in various human cancers[3–7].

Based on specificity for different acceptor-substrates and differences in biochemical properties between enzymes from different sources, at least seven (1 → 3)-α-L-fucosyltransferases are known[8]. In order to achieve a specific, quantitative determination for individual (1 → 3)-α-L-fucosyltransferases, we embarked on a synthetic program to obtain well defined, low-molecular-weight oligosaccharides capable of acting as acceptors for a single enzyme, even in the presence of other related enzymes. We have recently shown that the synthetic compound, 2′-*O*-methyl-*N*-acetyllactosamine acts as a specific acceptor for (1 → 3)-α-L-fucosyltransferase from human serum[9,10]. The same compound was employed in a number of clinical investigations directed at the specific assay of this enzyme activity in the

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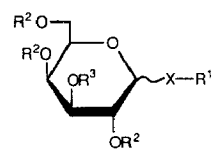
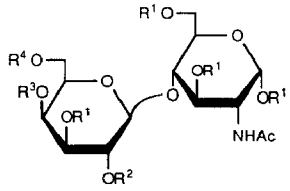
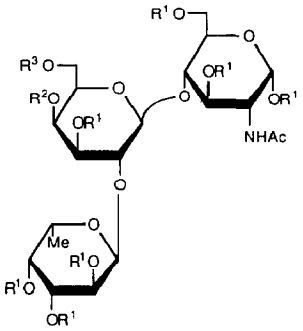


1 X = O; R^1 = R^2 = Ac; R^3 = Bn
2 X = S; R^1 = Ph; R^2 = Ac; R^3 = Bn



3 R^1 = Bn; R^2 = R^3 = R^4 = H
4 R^1 = Bn; R^2 = H; R^3, R^4 = PhCH
5 R^1 = Bn; R^2 = Me; R^3, R^4 = PhCH
6 R^1 = R^3 = R^4 = H; R^2 = Me
7 R^1 = Bn; R^2 = SO_3Na; R^3, R^4 = PhCH
8 R^1 = R^3 = R^4 = H; R^2 = SO_3Na



9 R^1 = Bn; R^2, R^3 = PhCH
10 R^1 = R^2 = R^3 = H

sera and saliva of patients with various cancers[11–14]. However, in the previously reported synthetic procedure[10], a substantial portion of the undesired (1 → 4)-α-D-linked disaccharide was produced and multiple steps were involved. For this reason, a more efficient method was developed for the coupling of a β-D-galactopyranosyl group to O′-4 of (1 → 4)-linked oligosaccharide. The present communication demonstrates that phenyl 2,4,6-tri-*O*-acetyl-3-*O*-benzyl-1-thio-α,β-galactopyranoside (**2**) is an effective glycosylating reagent for the desired compounds.

A common intermediate, namely, benzyl *O*-(3-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1 → 4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside (**4**) was used for the synthesis of 2-*O*′-substituted β-D-galactopyranosyl-(1 → 4)-linked oligosaccharides. Similarly, the reductive ring opening of the 4,6-*O*-benzylidene acetal of **4**, in an acidic medium in the presence of sodium cyanoborohydride, followed by conversion to the 2,4-bis(trifluoromethanesulfonate) and nucleophilic substitution with benzoate, could be utilized for the preparation of the corresponding β-D-mannopyranosyl-linked oligosaccharides[15].

Phenyl 2,4,6-tri-*O*-acetyl-3-*O*-benzyl-1-thio-α,β-D-galactopyranoside (**2**), obtained by acetolysis of methyl 2,4,6-tri-*O*-acetyl-3-*O*-benzyl-β-D-galactopyranoside[16], followed by treatment with (phenylthio)trimethylsilane and trimethylsilyl triflate, was the key glycosyl donor. Glycosylation of benzyl 2-acetamido-3,6,-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside[17] with **2** in dichloromethane in the presence

TABLE I

Tentative ^{13}C NMR chemical shift assignments (δ) [a] for **6**, **8**, and **10** in ^2H_2O

Residue or group	Compound	C-1	C-2	C-3	C-4	C-5	C-6	NAc or OMe
α-D-GlcNAc	**6**	93.32	56.53	73.23	81.26	72.01	62.90	24.70
β-D-GlcNAc		97.64	59.06	75.22	81.77	77.80	63.41	24.97
2′-*O*-Me-β-D-Gal*p*-(1 → 4), β anomer		105.47	83.72	75.07	71.41	78.01	63.76	62.80
2-*O*-Me-β-D-Gal*p*-(1 → 4), α anomer		105.40						
α-D-GlcNAc	**8**	93.31	56.52	73.03	81.56	71.92	62.58	24.70
β-D-GlcNAc		97.69	58.93	74.73	82.14	77.63	62.68	24.97
2′-*O*-SO_3Na-β-D-Gal*p*-(1 → 4), β anomer		103.70	81.63	74.68	71.47	78.09	63.65	
2-*O*-SO_3Na-β-D-Gal*p*-(1 → 4), α anome		103.64						
α-D-GlcNAc	**10**	93.39	56.70	75.21	78.91	73.37	62.89	24.72
β-D-GlcNAc		97.76	59.26	78.07	79.21	78.07	63.01	25.01
β-D-Gal*p*-(1 → 4)		103.13	79.28	76.41	71.03	78.15	63.92	
α-L-Fuc*p*-(1 → 2)		102.22	71.98	72.48	74.51	69.75	18.06	

[a] Relative to the signal of external tetramethylsilane.

of *N*-iodosuccinimide–trifluoromethanesulfonic acid[18], followed by *O*-deacetylation of the crude material afforded benzyl *O*-(3-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside (**3**) in 63% yield after silica gel column chromatography purification. The ^1H NMR spectrum of **3** was in accord with the structure assigned. Subsequent treatment of **3** with benzaldehyde dimethyl acetal and 4-toluenesulfonic acid monohydrate in *N*,*N*-dimethylformamide afforded a good yield of compound **4**. The ^1H NMR spectrum of **4** contained a one-proton resonance at δ 5.34, attributable to the benzylidene methine proton. The spectrum of **3** was devoid of such a resonance.

Methylation of **4** with trimethyloxonium tetrafluoroborate–2,6-di-(*tert*-butyl)-4-methylpyridine[19] in dichloromethane, gave the 2′-*O*-methyl derivative **5** in 69% yield. Hydrogenolysis of **5** in glacial acetic acid in the presence of 10% Pd–C furnished the known[10] 2′-*O*-methyl-*N*-acetyllactosamine **6**. Similarly, reaction of **4** with five molar equivalents of sulfur trioxide–pyridene complex[20] in *N*,*N*-dimethylformamide afforded a crude 2′-sulfate **7** which, after hydrogenolysis in the presence of Pd–C, produced the sodium salt of lactosamine 2′-sulfate (**8**) after passage through a cation-exchange resin (Na^+) column. The ^{13}C NMR spectrum of amorphous **8** was in agreement with the structure assigned (see Table I).

Reaction of **4** with methyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-fucopyranoside[21] in the presence of cupric bromide–tetrabutylammonium bromide gave, in 65% yield after column chromatography purification, the fully protected trisaccharide derivative **9**. ^1H NMR showed a resonance at δ 5.59 (J 3.5 Hz) confirming the α configuration of the L-fucopyranosyl group in compound **9**. Hydrogenolytic cleavage of the

benzyl and benzylidene groups of **9** in glacial acetic acid in the presence of 10% Pd–C then furnished, in 56% yield, 2′-*O*-α-L-fucosyllactosamine (**10**)[22]. The ^{13}C NMR spectrum of **10** was in accord with the structure assigned (see Table I). In the ^{13}C NMR spectra of the three compounds, **6**, **8**, and **10**, the resonances for C-1′ were observed at δ 103.13–105.47, a clear indicator of the β-D configuration for the galactose residue. Similarly, in the ^{13}C NMR spectrum of the aforementioned compounds, the resonance for C-4 of the 2-acetamido-2-deoxy-D-glucopyranose unit showed a downfield shift, which was evidence that O-4 was the site of glucosylation. However, in the ^{13}C NMR spectrum of **10**, the resonance underwent a downfield shift for C-2 of the D-galactopyranosyl residue, confirming the site of substitution, and the resonance for C-1″ was observed at δ 102.22, which accounts for the α configuration of the newly introduced L-fucosyl group. On the other hand, the D-galactopyranosyl residue showed two anomeric resonances, in compounds **6** and **8**, due to the presence of a 2-acetamido-2-deoxy-D-glucopyranose in both α and β configuration.

EXPERIMENTAL

General methods.—Melting points were determined with a Fisher–Johns apparatus and are uncorrected. Optical rotations were measured at ~25° with a Perkin–Elmer 241 polarimeter. TLC was conducted on aluminum sheets, precoated with 0.2-mm layers of Silica Gel 60F-254 (E. Merck, Darmstadt, Germany); the components were located either by exposure to UV light or by spraying with 5% H_2SO_4 in EtOH (or both) and charring. The silica gel used for column chromatography was Baker analyzed (60–200 mesh). NMR spectra were recorded at ~25°; ^1H NMR spectra with a Varian EM-390 and ^{13}C NMR spectra with a Bruker AM-400 instrument at 90 and 100.6 MHz, respectively; the chemical shifts (δ) are expressed from the Me_4Si signal. Solutions in organic solvents were generally dried with anhyd Na_2SO_4. Dichloromethane, dichloroethane, and *N*,*N*-dimethylformamide were dried over 4A molecular sieves. Elemental analysis were performed by Robertson Laboratory, 29 Samson Ave., Madison, NJ 07940, USA.

1,2,4,6-Tetra-O-acetyl-3-O-benzyl-D-galactopyranose (**1**).—A solution of methyl 2,4,6-tri-*O*-acetyl-3-*O*-benzyl-β-D-galactopyranoside[16] (6.0 g) in acetic anhydride (100 mL) containing ~1% by volume of concd H_2SO_4 was stirred for 6 h at room temperature. The mixture was then diluted with dichloromethane (500 mL) and successively washed with water, satd $NaHCO_3$ and water, dried and concentrated under reduced pressure. The residue was applied to a column of silica gel and eluted with 20% EtOAc in hexane to give **1** (5.7 g, 92%), $[\alpha]_D$ +10° (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$); δ 7.37–7.02 (m, 5 H, arom.), 6.37 (d, J ~ 4 Hz, 1 H, H-1), and 2.34–1.97 (cluster of s, 12 H, OAc).

Anal. Calcd for $C_{21}H_{26}O_{10}$: C, 57.53; H, 5.98. Found: C, 57.72; H, 6.01.

Phenyl 2,4,6-tri-O-acetyl-3-O-benzyl-1-thio-α,β-D-galactopyranoside (**2**).—To a stirred solution of **1** (6.2 g) in dichloromethane (75 mL) was added (phenylthio)trimethylsilane (9.0 mL) and trimethylsilyl triflate (5.0 mL). Stirring was continued for 15 h at room temperature, whereupon TLC in 1:1 (v/v) hexane–EtOAc showed the presence of two products in a 1:1 ratio. After neutralization with triethylamine, the reaction mixture was diluted with $CHCl_3$, washed with water, dried, and concentrated. The residue was applied to a column of silica gel and eluted with a solvent gradient consisting of 20–25% EtOAc in hexane. The earlier fractions collected contained the faster migrating α anomer, $[\alpha]_D$ + 89° (*c* 1.4, $CHCl_3$): ^{1}H NMR ($CDCl_3$): δ 7.43–7.07 (m, 10 H, arom), 5.80 (d, *J* ~ 4 Hz, 1 H, H-1), and 2.03–1.70 (cluster of s, 9 H, OAc).

Anal. Calcd for $C_{25}H_{21}O_8S$: C, 62.36; H, 4.40. Found: C, 62.21; H, 4.52.

The latter fractions contained the pure β anomer, $[\alpha]_D$ + 64° (*c* 1.4, $CHCl_3$): ^{1}H NMR ($CDCl_3$): δ 7.53–7.10 (m, 10 H, arom), 4.43 (d, *J* 10 Hz, 1 H, H-1), and 2.13–1.90 (cluster of s, 9 H, OAc).

Anal. Calcd for $C_{25}H_{21}O_8S$: C, 62.36; H, 4.40. Found: C, 62.39; H, 4.25.

The total yield of compound **2** was 80%.

Benzyl O-(3-O-benzyl-β-D-galactopyranosyl)-(1 → 4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-α-D-glucopyranoside (**3**).—A solution of **2** (3.5 g, 7.3 mmol), benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside[17] (3.4 g, 6.9 mmol), and *N*-iodosuccinimide (3.9 g, 17.3 mmol) in dichloromethane (55 ml) was stirred for 0.5 h with 4A molecular sieves (8.0 g) under an Ar atmosphere at ~ 0°. Then, a dilute solution of trifluoromethanesulfonic acid (0.2 mL in 70 mL dichloromethane) was added dropwise, and the stirring continued for 2 h at the same temperature. The mixture was filtered through Celite, the solids were thoroughly washed with $CHCl_3$, and the filtrate and washings were combined, successively washed with water, satd $NaHCO_3$ solution, 10% $Na_2S_2O_3$, dried, and concentrated under reduced pressure. The crude mixture in 0.05 M methanolic NaOMe (125 mL) was stirred overnight at room temperature. The base was neutralized with IR-120 (H^+) cation-exchange resin. The resin was filtered off and thoroughly washed with MeOH, and the filtrate and washings were combined and concentrated under reduced pressure. The residue was purified in a column of silica gel with 2% MeOH in $CHCl_3$ as the eluent to give **3** as an amorphous solid (3.2 g, 63% on the basis of acceptor), $[\alpha]_D$ + 93° (*c* 0.7, $CHCl_3$): ^{1}H NMR ($CDCl_3$): δ 7.37–7.20 (m, 20 H, arom), and 1.77 (s, 3 H, NAc).

Anal. Calcd for $C_{42}H_{49}NO_{11}$: C, 67.81; H, 6.64; N, 1.88. Found: C, 67.73; H, 6.72; N, 1.83.

Benzyl O-(3-O-benzyl-4,6-O-benzylidene-β-D-galactopyranosyl)-(1 → 4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-α-D-glucopyranoside (**4**).—To a stirred solution of **3** (0.8 g) in *N*,*N*-dimethylformamide (25 mL) were added 4-toluenesulfonic acid monohydrate (0.2 g) and α,α-dimethoxytoluene (2.0 mL). The stirring was continued for 16 h at room temperature. The acid was neutralized with a little triethylamine, and the solution concentrated under reduced pressure. The residue was

purified in a column of silica gel with 10% acetone in $CHCl_3$ as the eluent to give amorphous **4** (0.7 g, 78%), $[\alpha]_D + 95°$ (*c* 1.5, $CHCl_3$): ^1H NMR ($CDCl_3$): δ 7.43–7.10 (m, 25 H, arom), 5.34 (s, 1 H, $-CHC_6H_5$), and 1.77 (s, 3 H, NAc).

Anal. Calcd for $C_{49}H_{53}NO_{11}$: C, 70.73; H, 6.43; N, 1.68. Found: C, 70.48; H, 6.52; N, 1.63.

Benzyl O-(3-O-benzyl-4,6,-O-benzylidene-2-O-methyl-β-D-galactopyranosyl)-(1 → 4)-2-acetamido-3,6-di-O-benzyl-2-deoxy-α-D-glucopyranoside (**5**).—To a cold (0°, bath) and stirred solution of **4** (0.2 g, 0.25 mmol) in dichloromethane (10 mL) was added 2,6-di-(*tert*-butyl)-4-methylpyridine (0.132 g, 0.65 mmol) and trimethyloxonium tetrafluoroborate (0.074 g, 0.5 mmol), stirring was continued for 16 h at room temperature. The mixture was diluted with $CHCl_3$ and successively washed with satd aq $NaHCO_3$, water, dried, and concentrated under reduced pressure. The residue was applied to a column of silica gel and eluted with 10% acetone in $CHCl_3$ to give **6** (0.14 g, 69%); $[\alpha]_D + 90°$ (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.48–7.10 (m, 25 H, arom), 5.34 (s, 1 H, CHC_6H_5), 3.52 (s, 3 H, OMe), and 1.74 (s, 3 H, NAc).

Anal. Calcd for $C_{50}H_{55}NO_{11}$: C, 71.01; H, 6.55; N, 1.66. Found: C, 71.08; H, 6.42; N, 1.37.

O-(2-O-Methyl-β-D-galactopyranosyl)-(1 → 4)-2-acetamido-2-deoxy-D-glucopyranose (**6**).—A mixture of **5** (0.1 g) and 10% Pd–C (0.2 g) in glacial acetic acid (10 mL), was shaken under H_2 at ~ 345 kPa for 2 days at room temperature. The suspension was filtered off (a bed of Celite), the solids were thoroughly washed with glacial acetic acid, the filtrate and washings were combined, and the solvent was evaporated. The residue was purified in a column of silica gel with 5:4:1 (v/v) $CHCl_3$–MeOH–water as the eluent. The fractions corresponding to **6** were combined and concentrated to furnish **6** as an amorphous solid (0.03 g, 64%), $[\alpha]_D + 45°$ (initial) → +33° (24 h; *c* 0.5, H_2O); lit.[8] $[\alpha]_D + 47.9$ (initial) → 34.9° (16 h; *c* 1.1, H_2O); for ^{13}C NMR, see Table I.

O-(Sodium β-D-galactopyranosyl 2-sulfate)-(1 → 4)-2-acetamido-2-deoxy-D-glucopyranose (**8**).—To a stirred solution of **4** (0.25 g, 0.3 mmol) in dry *N*,*N*-dimethylformamide (15 mL) was added dropwise a solution of SO_3–pyridine complex[20] (0.28 g, 1.75 mmol) in *N*,*N*-dimethylformamide (15 mL). Stirring was continued for an additional 3 h at room temperature when excess reagent was removed by the addition of MeOH. The solvent was evaporated, and the residue was dissolved in $CHCl_3$ and washed with cold water. Evaporation of the solvent gave a syrup which was passed through a small silica gel column with 10% MeOH in $CHCl_3$ as the eluent. The fractions corresponding to the product were concentrated and dissolved in MeOH and passed through Amberlite IR-120 P (Na^+) cation-exchange resin in MeOH. Solvent removal afforded crude **7**, which was utilized without any further characterization in the next step.

A solution of **7** in 90% EtOH (20 mL) was hydrogenolyzed in the presence of 10% Pd–C (0.4 g) as described for **5** (to give **6**). The crude mixture was purified in a column of silica gel with 5:4:1 (v/v) $CHCl_3$–MeOH–water as the eluent. The

fractions corresponding to **8** were combined and concentrated. The residue was purified in a column of Dowex I (AcO^-) anion-exchange resin in 5–100 mM pyridine acetate buffer, pH 5.0. The fractions corresponding to **8** were combined and lyophilized, and the residue was dissolved in water and passed through an Amberlite IR-120 P (Na^+) cation-exchange resin. Lyophilization of the fractions corresponding to **8** gave an amorphous solid (0.09 g, 62%); $[\alpha]_D + 1.6°$ (*c* 0.6, H_2O); for ^{13}C NMR data, see Table I.

Anal. Calcd for $C_{14}H_{24}NNaO_{14}S \cdot H_2O$; C, 33.40; H, 4.81; N, 2.78. Found: C, 33.10; H, 4.59; N, 2.62.

Benzyl O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-(1 → 2)-O-(3-O-benzyl-4,6-O-benzylidene-β-D-galactopyranosyl)-(1 → 4)-2-acetamido-3,6,-di-O-benzyl-2-deoxy-α-D-glucopyranoside (**9**).—A solution of methyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-fucopyranoside[21] (0.48 g, 1.04 mmol) and **4** (0.66, 0.8 mmol) in 5 : 1 dichloroethane–*N*,*N*-dimethylformamide (30 mL) was stirred for 0.5 h with 4A molecular sieves (2.0 g) under protection from light and moisture, and then tetrabutylammonium bromide (0.52 g, 1.6 mmol) and $CuBr_2$ (0.37 g, 1.6 mmol) were added and stirred for 16 h at room temperature. Further amounts of thiomethyl donor (0.24 g, 0.5 mmol) and $CuBr_2$–tetrabutylammonium bromide (0.8 mmol each) were added and the stirring was continued for another 16 h. The mixture was filtered through Celite, the solids were thoroughly washed with $CHCl_3$, and the filtrate and washings were combined and washed with aq $NaHCO_3$ and water, dried, and concentrated under reduced pressure. The residue was applied to a column of silica gel and eluted with 5% acetone in $CHCl_3$ to give amorphous **9** (0.6 g, 65.5%), $[\alpha]_D + 45°$ (*c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.53–7.06 (m, 40 H, arom), 5.59 (d, $J \sim 3.5$ Hz, 1 H, H-1″), 5.30 (s, 1 H, CHC_6H_5), 1.82 (s, 3 H, NAc), 1.09 (d, $J \sim 7$ Hz, 3 H, CMe).

Anal. Calcd for $C_{76}H_{81}NO_{15}$: C, 73.10; H, 6.55; N, 1.12. Found: C, 73.08; H, 6.42; N, 1.27.

O-α-L-Fucopyranosyl-(1 → 2)-O-β-D-galactopyranosyl-(1 → 4)-2-acetamido-2-deoxy-D-glucopyranose (**10**).—A mixture of **9** (0.5 g) and 10% Pd–C (0.6 g) in glacial acetic acid (30 mL) was shaken under H_2 for 3 days at room temperature. The suspension was filtered through a bed of Celite, the solids were thoroughly washed with glacial acetic acid, and the filtrate and washings were combined and concentrated under reduced pressure. The crude product was applied to a column of silica gel and eluted with 5 : 4 : 1 (v/v) $CHCl_3$–MeOH–water. The ^{13}C NMR of the fractions corresponding to **10** showed additional peaks in the anomeric region (presumably due to hydrolysis of the α-L-fucosyl groups during hydrogenolysis). Therefore, it was further purified on a column of Bio-Gel P-2 with pyridine acetate buffer (100 mM, pH 5.5) as the eluent. The fractions corresponding to **10** were combined and lyophilized to give an amorphous solid (0.13 g, 56%); $[\alpha]_D - 52°$ (initial) → $-48°$ (after 72 h; *c* 0.5, H_2O); lit.[19] $[\alpha]_D - 46.5°$; For ^{13}C NMR data, see Table I.

Anal. Calcd for $C_{20}H_{35}NO_{15}$: C, 45.36; H, 6.66; N, 2.64. Found: C, 45.59; H, 6.55; N, 2.92.

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