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CARBOHYDRATE RESEARCH

Preliminary Communication

Synthesis of sialyl Le^x ganglioside analogues sulfated at C-6 of either the galactose or *N*-acetylglucosamine residues, and at both of the galactose and *N*-acetylglucosamine residues: probes for clarifying the real carbohydrate ligand of L-selectin [1]

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The selectins [2–8] are a family of carbohydrate-binding proteins that have been implicated in the initial interaction between leukocytes and the vascular endothelium.

The binding of selectin molecules to their carbohydrate ligands appears to be required for neutrophil extravasation, and such interaction plays a major role in lymphocyte recirculation and platelet adhesion. In order to clarify the real carbohydrate ligands for each selectin, we have synthesized [9–16] a variety of sialylated and sulfated Le^x and Le^a compounds and their analogues. There is now general agreement that all three selectins can recognize sialyl Lewis^x (sLe^x) and sialyl Lewis^a (sLe^a). Recently, the replacement of sialic acid with sulfate has received much attention. It has been shown [17–25] that L- and P-selectins can effectively bind to sulfated carbohydrates such as fucoidan, sulfatides, sulfated glucuronic acid (HNK-1) epitope, heparin, and sulfo-Le^x-like structures. L-Selectin has been discovered as a lymphocyte homing receptor and mediates the initial attachment of lymphocytes to high endothelial venules of lymph

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[1] Synthetic Studies on Sialoglycoconjugates. Part 86. For Part 85, see ref. [1].

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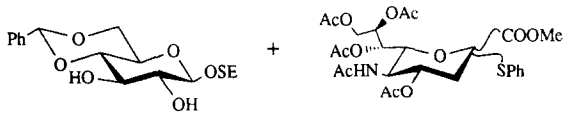
nodes. One of the endothelial-derived ligands for L-selectin is GlyCAM-1, a mucin-like glycoprotein with sulfated, sialylated, and fucosylated carbohydrates. Very recently, S.D. Rosen's group [26–29] has reported Gal and GlcNAc residues sulfated at C-6, and Galβ(1 → 4)6-*O*-sulfo-GlcNAc and 6-*O*-sulfo-Glcβ(1 → 4)GlcNAc by a mild hydrolysis of GlyCAM-1. These workers suggested that a sulfated sialyl Le^x structure may comprise a recognition determinant on GlyCAM-1. On the other hand, Jacob et al. [30] have enzymatically synthesized a 6′-sulfated sLe^x pentasaccharide and compared its inhibition property to the binding of L-selectin with sLe^x tetrasaccharide. A stronger activity was observed. In view of these facts and as a part of our continuing effort on the synthesis, biological functions, and structural elucidation of the carbohydrate ligands of cell-adhesion molecules, we describe here the synthesis of sialyl Le^x ganglioside analogues sulfated at C-6 of Gal or GlcNAc, as well as the analogue sulfated at C-6 of both the Gal and GlcNAc residues, for clarifying the real carbohydrate ligand of L-selectin.

For the synthesis of the desired sulfated sLe^x gangliosides **53–55**, the core oligosaccharides **21–23** were selected as the glycosyl acceptors. Compounds **21–23** have a free hydroxy group at C-3 of the GlcNAc residue for α-fucosylation, and also have levulinoyl groups at the desired positions to selectively provide a free hydroxy group at C-6 of the Gal or GlcNAc residues, or for both the Gal and GlcNAc residues as sites for further sulfation.

The glycosyl acceptors (**21–23**) were prepared as follows: glycosylation [31] of 2-(trimethylsilyl)ethyl 4,6-*O*-benzylidene-β-D-galactopyranoside (**1**) [32] with the phenyl 2-thioglycoside (**2**) [33] (1.5 equiv, relative to the acceptor) of Neu5Ac in acetonitrile for 3 h at −30 °C in the presence of *N*-iodosuccinimide (NIS; 2.3 equiv, relative to the donor)-TfOH, [34] gave the expected α-glycoside **3** {65%, $[\alpha]_D$ +4.2° ($CHCl_3$)}. The observed chemical shift and coupling constants [δ 2.75, $J_{3a,3e}$ 12.6, $J_{3e,4}$ 4.4 Hz; δ 4.88 (m) and 5.35, $J_{6,7}$ 1.2, $J_{7,8}$ 8.0 Hz] for H-3e, H-4, and H-7 in the Neu5Ac moiety are characteristic for α-glycosidic linkages [35].

Treatment of **3** with benzoic anhydride in the presence of 4-dimethylaminopyridine gave 2-benzoate **4** {86%, $[\alpha]_D$ +18.8° ($CHCl_3$)}, which was converted via reductive removal of the benzylidene group, selective 6-*O*-levulinoylation, and 4-*O*-benzoylation into 2-(trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranoside {**7**; $[\alpha]_D$ +40.5° ($CHCl_3$)}. Acetylation of **5** gave 4,6-di-*O*-acetate **8** {91%, $[\alpha]_D$ +23.0° ($CHCl_3$)}. Compounds **7** and **8** were converted into the corresponding trichloroacetimidates **10** and **12** in good yields by selective removal of the 2-(trimethylsilyl)ethyl group with trifluoroacetic acid and subsequent imidate formation [36,37].

Glycosylation of **13** [38] or **16** {64%, $[\alpha]_D$ −11.6° ($CHCl_3$)} (derived from **14** [38] by reductive removal of the benzylidene group, followed by selective levulinoylation with levulinic anhydride in pyridine in the presence of 4-dimethylaminopyridine for 2 h at −50 °C), with **10** in dichloromethane in the presence of TMS-triflate for 12 h at 7°C, afforded the corresponding pentasaccharides **18** {50%, $[\alpha]_D$ +13.5° ($CHCl_3$)} and **20** {45%, $[\alpha]_D$ +25.5° ($CHCl_3$)}, respectively. In essentially the same way, coupling of **12** and **16** gave **19** {77%, $[\alpha]_D$ +7.6° ($CHCl_3$)}.



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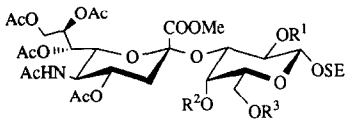
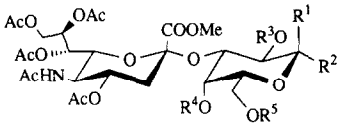
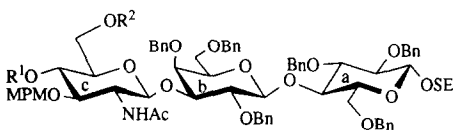


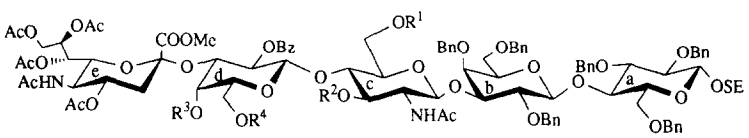
	R^1	R^2	R^3
3	H	benzylidene	
4	Bz	benzylidene	
5	Bz	H	H
6	Bz	H	Lev
7	Bz	Bz	Lev
8	Bz	Ac	Ac



	R^1	R^2	R^3	R^4	R^5
9	OH, H		Bz	Bz	Lev
10	$OC(=NH)CCl_3$, H		Bz	Bz	Lev
11	OH, H		Bz	Ac	Ac
12	$OC(=NH)CCl_3$, H		Bz	Ac	Ac



	R^1	R^2
13	H	OBn
14	benzylidene	
15	H	H
16	H	Lev
17	Ac	Lev



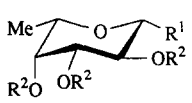
		R^1	R^2	R^3	R^4
10 + 13	**18**	Bn	MPM	Bz	Lev
12 + 16	**19**	Lev	MPM	Ac	Ac
10 + 16	**20**	Lev	MPM	Bz	Lev
	21	Bn	H	Bz	Lev
	22	Lev	H	Ac	Ac
	23	Lev	H	Bz	Lev

The β-configurations of **18**, **19**, and **20** were assigned from the ^1H NMR data that showed the signals at δ 5.46 (t, $J_{1,2} = J_{2,3} = 8.1$ Hz, **18**), 5.36 (t, $J_{1,2} = J_{2,3} = 8.4$ Hz, **19**), and 5.46 (dd, $J_{1,2}$ 9.9, $J_{2,3}$ 7.7 Hz, **20**) for H-2d of the pentasaccharides thus obtained. Removal of the 4-methoxybenzyl group in **18**–**20** in acetonitrile–water in the presence of ammonium cerium(IV) nitrate (CAN) for 1–3 h at room temperature afforded the expected glycosyl acceptors **21** {98%, $[\alpha]_D$ +22.1° ($CHCl_3$)}, **22** {90%,

$[\alpha]_D$ +20.1° ($CHCl_3$)}, and **23** (68%, $[\alpha]_D$ +22.6° ($CHCl_3$)}, respectively. Glycosylation of **21**, **22**, or **23** was effected with phenyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-fucopyranoside {**27**; mp 108–109 °C, $[\alpha]_D$ −14.0° ($CHCl_3$)}, newly synthesized from tetra-*O*-acetyl-L-fucose via replacement of the anomeric acetoxy group with a phenylthio group using thiophenol in the presence of boron trifluoride etherate, *O*-deacetylation, and *O*-benzylation. Reaction in the presence of dimethyl(methylthio)sulfonium triflate (DMTST) [39] and molecular sieves 4A (MS-4A) in benzene for 48–72 h at 7 °C gave the desired hexasaccharides **28** {58%, $[\alpha]_D$ −17.5° ($CHCl_3$)}, **29** {90%, $[\alpha]_D$ −12.3° ($CHCl_3$)}, and **30** {50%, $[\alpha]_D$ −14.3° ($CHCl_3$)}, respectively, showing in their ^{1}H NMR spectra signals at δ 5.15 (d, $J_{1,2}$ 3.6 Hz, H-1f of **28**), 5.03 (d, $J_{1,2}$ 3.3 Hz, H-1f of **29**), and 5.17 (d, $J_{1,2}$ 3.5 Hz, H-1f of **30**), characteristic of an α-fucopyranosyl unit.

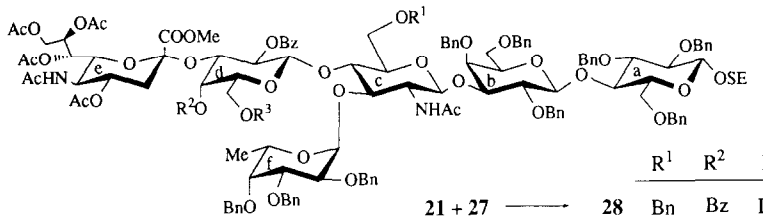
Removal of the benzyl groups from **28**, **29**, and **30** by catalytic hydrogenolysis over 10% Pd–C in 5:1 ethanol–acetic acid for 24–40 h at 40 °C, and subsequent acetylation gave the per-*O*-acylated hexasaccharides **31** {89%, $[\alpha]_D$ −10.2° ($CHCl_3$)}, **32** {94%, $[\alpha]_D$ −18.0° ($CHCl_3$)}, and **33** {82%, $[\alpha]_D$ −11.0° ($CHCl_3$)}, respectively. Selective removal of the 2-(trimethylsilyl)ethyl group from **31**, **32**, and **33** as described in the preparation of **9** gave the corresponding 1-hydroxy compounds **34**, **39**, and **43** in good yields. Treatment [36,37] of **34**, **39**, or **43** with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) for 2 h at 0 °C gave the trichloroacetimidates **35** {quant, $[\alpha]_D$ +6.6° ($CHCl_3$)}, **40** {93%, $[\alpha]_D$ +8.3° ($CHCl_3$)}, and **44** {98%, $[\alpha]_D$ +6.8° ($CHCl_3$)} as the α-anomers. Glycosylation [37,39] of (2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol (**36**) [40] with **35**, **40**, or **44** thus obtained, for 5 h at 0 °C in dichloromethane in the presence of boron trifluoride etherate and MS-4A, gave only the desired β-glycosides **37** {63%, $[\alpha]_D$ −7.4° ($CHCl_3$)}, **41** {48%, $[\alpha]_D$ −12.8° ($CHCl_3$)}, and **45** {58%, $[\alpha]_D$ −18.6° ($CHCl_3$)}, respectively. A significant signal in the ^{1}H NMR spectra of **37**, **41**, and **45**, a one-proton doublet at δ 4.43–4.49 ($J_{1,2}$ 7.0–7.7 Hz, H-1a), showed the newly formed glycosidic linkages to be β.

Selective reduction [37,41] of the azido group in **37**, **41**, or **45** with hydrogen sulfide in aq 83% pyridine for 72 h at 0 °C, and subsequent condensation with octadecanoic acid using 1-(3-dimethylaminopropyl)-3-ethyl-carbodiimide hydrochloride (WSC) in dichloromethane, furnished the corresponding ganglioside analogues **38** {54%, $[\alpha]_D$ −5.1° ($CHCl_3$)}, **42** {60%, $[\alpha]_D$ −6.0° ($CHCl_3$)}, and **46** {60%, $[\alpha]_D$ −9.8° ($CHCl_3$)}. Selective removal [14,42] of the levulinoyl group in **38**, **42**, or **46** was carried out in ethanol with hydrazine monoacetate at room temperature to give **47** {70%, $[\alpha]_D$ −6.4° ($CHCl_3$)}, **49** {50%, $[\alpha]_D$ −13.0° ($CHCl_3$)}, and **51** {49%, $[\alpha]_D$ −6.3° ($CHCl_3$)}, respectively. Treatment of compounds **47**, **49**, or **51** with the sulfur trioxide–pyridine complex in *N*,*N*-dimethylformamide for 2–4 h at room temperature afforded the corresponding sulfates **48** {98%, $[\alpha]_D$ −3.3° ($CHCl_3$)}, **50** {91%, $[\alpha]_D$ −17.8° ($CHCl_3$)}, and **52** {91%, $[\alpha]_D$ −7.9° ($CHCl_3$)} as their pyridine salts. *O*-Deacylation of **48**, **50**, and **52** with NaOMe in MeOH, with subsequent saponification by addition of water of the sialate methyl ester group, yielded the desired sulfated sLe^x gangliosides **53** {$[\alpha]_D$ −5.7° (5:4:0.7 $CHCl_3$–MeOH–H_2O)}, **54** {$[\alpha]_D$ −8.7° (5:7:2 $CHCl_3$–MeOH–H_2O)}, and **55** {$[\alpha]_D$ −10.3° (5:4:0.7 $CHCl_3$–MeOH–H_2O)} as their sodium salts in almost quantitative yields. FABMS (negative-ion mode): *m*/*z* $[M - Na]^-$ 1794 and $[M - 2Na]^{2-}$ 1771 for **53** and **54**, and *m*/*z* $[M - Na]^-$ 1896 for **55**.

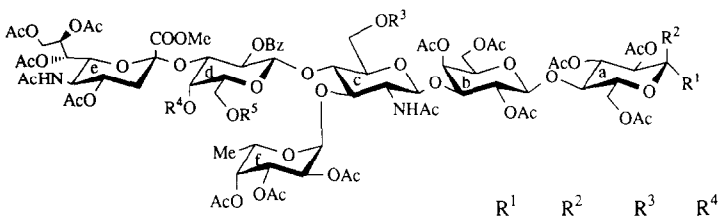


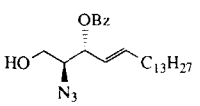
	R^1	R^2
24	OAc	Ac
25	SPh	Ac
26	SPh	H
27	SPh	Bn

SE = 2-(trimethylsilyl)ethyl
Bz = benzoyl
Bn = benzyl
Lev = levulinoyl
MPM = 4-methoxybenzyl



		R^1	R^2	R^3
21 + **27**	**28**	Bn	Bz	Lev
22 + **27**	**29**	Lev	Ac	Ac
23 + **27**	**30**	Lev	Bz	Lev





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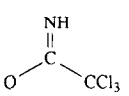
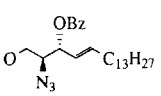
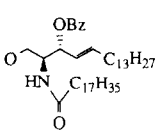
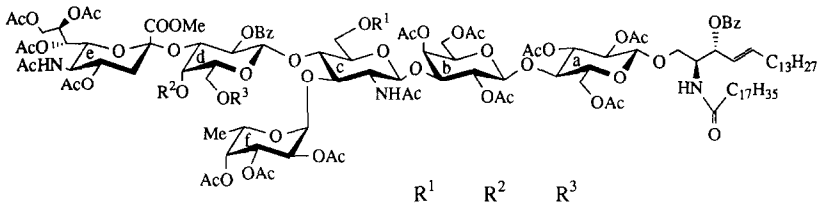
	R^1	R^2	R^3	R^4	R^5
31	OSE	H	Ac	Bz	Lev
32	OSE	H	Lev	Ac	Ac
33	OSE	H	Lev	Bz	Lev
34	OH, H		Ac	Bz	Lev
35	H	X	Ac	Bz	Lev
37	Y	H	Ac	Bz	Lev
38	Z	H	Ac	Bz	Lev
39	OH, H		Lev	Ac	Ac
40	H	X	Lev	Ac	Ac
41	Y	H	Lev	Ac	Ac
42	Z	H	Lev	Ac	Ac
43	OH, H		Lev	Bz	Lev
44	H	X	Lev	Bz	Lev
45	Y	H	Lev	Bz	Lev
46	Z	H	Lev	Bz	Lev

X= 

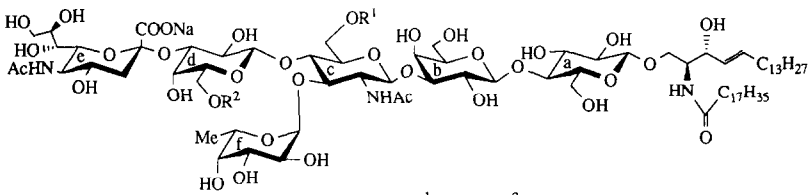
Y= 

Z = 

In conclusion, a stereocontrolled synthesis of the sulfated sialyl Le^x ganglioside analogues that are candidate structures for the L-selectin ligand has been first achieved using the selectively levulinoylated pentasaccharide acceptors **21**, **22**, and **23**. New compounds thus obtained have elemental analyses, IR, and ^1H NMR data in agreement with the structures assigned, and their biological activities are now under investigation.



	R^1	R^2	R^3
47	Ac	Bz	H
48	Ac	Bz	SO_3•pyr.
49	H	Ac	Ac
50	SO_3•pyr.	Ac	Ac
51	H	Bz	H
52	SO_3•pyr.	Bz	SO_3•pyr.



	R^1	R^2
53	H	SO_3Na
54	SO_3Na	H
55	SO_3Na	SO_3Na

Acknowledgements

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