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Note

Chemo-enzymatic supported synthesis of the 3-sulfated Lewis[a] pentasaccharide on a multimeric polyethylene glycol

Annie Malleron and Christine Le Narvor*

Laboratoire de Chimie Organique Multifonctionnelle, Equipe Glycochimie Moléculaire et Macromoléculaire, CNRS, UMR 8182, Bât. 420, Univ Paris -Sud, Orsay F-91405, France

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Abstract—The 3-sulfated Lewis[a] pentasaccharide was synthesized on multimeric-based polyethylene glycol support. Coupling of *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate with (2,6-di-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-β-D-glucopyranoside) bound onto the polymer afforded lacto-*N*-tetraose, which was then regioselectively sulfated at the 3-OH position of the terminal galactose using the stannylene procedure. Fucosylation of the sulfated tetrasaccharide was performed using an immobilized fucosyltransferase FucTIII to give the title compound after cleavage.

Keywords: Chemo-enzymatic synthesis; Multimeric support; Glycosyltransferase; Selectins; Cell adhesion; Inflammation

Sulfated and sialylated Lewis[a] and Lewis[x] compounds are known to be good ligands for selectins, a family of adhesion molecules that mediates the interaction between circulating leucocytes and endothelial cells, a key step in their recruitment to the sites of inflammation.[1] A lot of attention has therefore been focused on the chemical synthesis of these oligosaccharides to study their mechanism of action and to develop inhibitors.[2] Enzymes are becoming powerful tools as catalysts in carbohydrate chemistry avoiding protection and deprotection steps due to the regio- and stereoselectivity of the reaction, they catalyze,[3] and they appear to be attractive reagents for solid phase synthesis.[4] However, enzymatic synthesis on solid support raises extra problems, such as the accessibility of the enzyme to the interior of a solid matrix[5] or the compatibility of the support with both aqueous and organic solvents. A solution would be to use soluble supports, which combine the advantages of both liquid phase (for the accessibility) and solid phase (for the purification) strategies. Polyethylene glycol (PEG) has been among the most studied soluble polymers for oligosaccharide synthesis.[6] In previous papers, we described the use of a modified PEG support. Our approach was to increase the loading capacity of the polymer by coupling a pentaerythritol derivative at both extremities of a PEG 6000 molecule, giving a soluble polymeric support with a loading capacity similar to that of a resin (1 mmol/g). Using this polymer, we have synthesized the Lewis[x] trisaccharide and lacto-*N*-tetraose by an enzymatic approach.[7,8]

Our interest in the 3-sulfated Lewis[a] pentasaccharide led us to envisage its synthesis on our support using our expertise in the conventional liquid phase chemo-enzymatic synthesis of this pentasaccharide.[9]

The supported tetrasaccharide **8**, obtained by glycosylation of the two disaccharides **6** and **7**, was enzymatically fucosylated after deprotection and **1** was obtained by cleavage from the multimeric support (Scheme 1).

In a previous work, we have shown that the coupling of a thiosugar derivative onto our multimeric support **3** was very efficient.[7] The lactose unit **2** was thus installed on the PEG support as 1-thiolactose (Scheme 2). Radical coupling onto compound **3** was realized under 254 nm UV irradiation using a 0.03 M solution of **3** in water and 1.3 equiv of sugar per allyl group. Purification

* Corresponding author. E-mail: chlenarv@icmo.u-psud.fr

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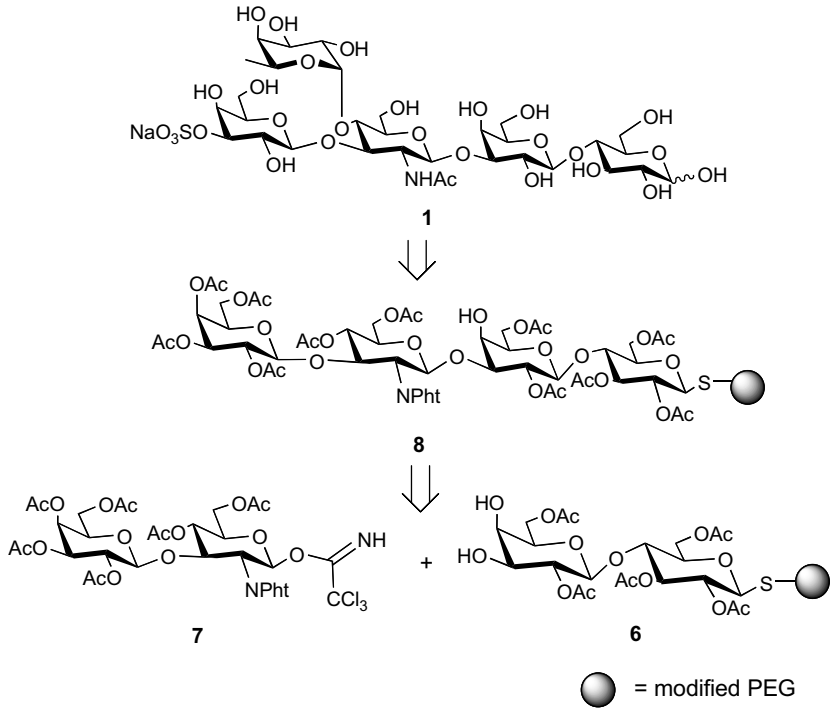
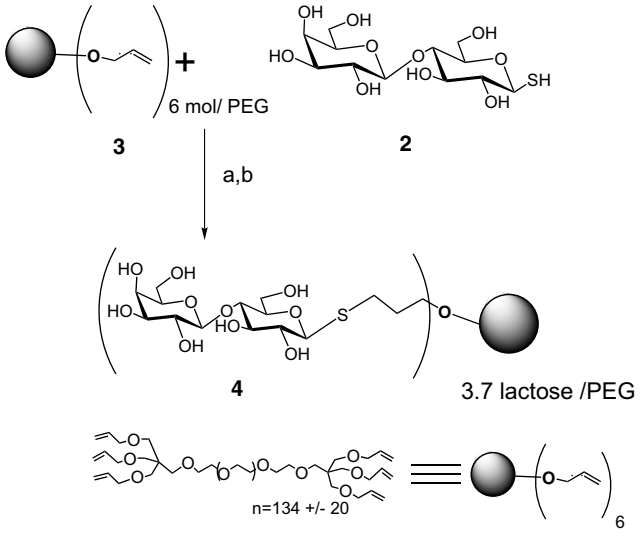


Scheme 1.

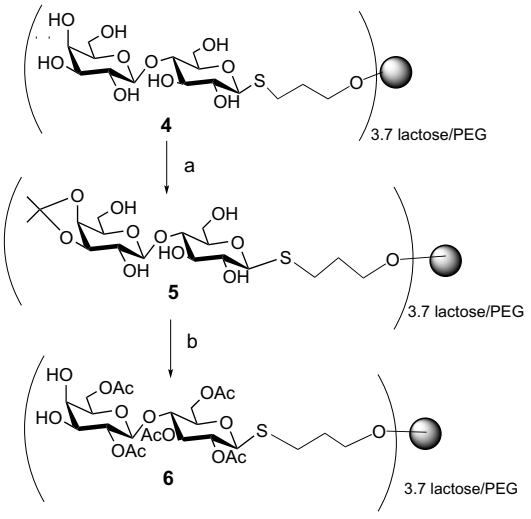


Scheme 2. Reagents and conditions: (a) *hv* (254 nm), H_2O, 10 h, rt; (b) dialysis.

was easily carried out by dialysis and the amount of the disaccharide covalently bound to support **4** was quantified by the phenol sulfuric acid method after cleavage of an aliquot using mercury(II) trifluoroacetate.[10] We found 3.7 mol of disaccharide/ mol of PEG (0.46 mmol/g of support).

The reaction of **4** with 2,2-dimethoxypropane in the presence of *p*-toluene sulfonic acid monohydrate as described by Catelani[11] gave the supported 3,4-*O*-isopropylidene lactose **5** (Scheme 3). Acetylation of the free alcohols followed by acid hydrolysis of the isopropylidene group and precipitation of the polymer using *tert*-butyl methyl ether gave **6** in 96% yield based on precipitated support. The disappearance of the 3,4-*O*-isopropylidene group was complete as confirmed by ^{1}H NMR.

Glycosylation of **6** with **7** was performed using 0.6 equiv boron trifluoride diethyl etherate as promotor at 0 °C in dry dichloromethane and led to the β(1→3)



Scheme 3. Reagents and conditions: (a) (i) 2,2-dimethoxypropane, cat. *p*-toluene-sulfonic acid monohydrate, 55 °C, 3 h; (ii) dialysis; (iii) MeOH–H_2O (9:1), reflux, 24 h; (b) (i) Ac_2O–pyridine, rt, 16 h; acetic acid 70%, reflux, 3 h; (ii) precipitation with *tert*-butylmethyl ether.

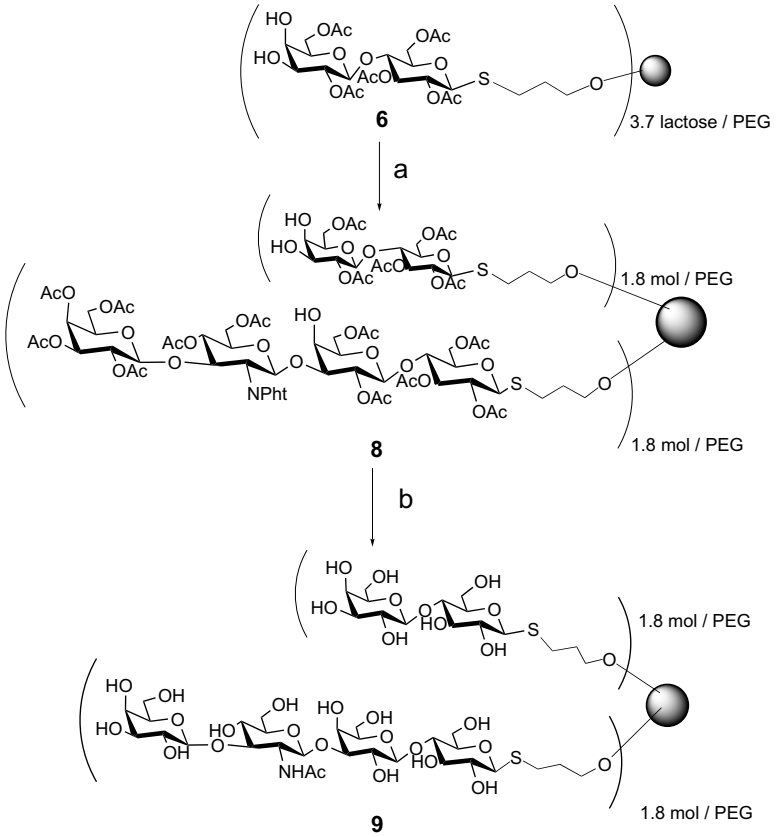
linked polymer-bound tetrasaccharide **8** that was purified by precipitation with *tert*-butyl methyl ether.

Then, the removal of the phthalimido group along with O-deacetylation of **8**, using ethylene diamine, and subsequent N-acetylation, using acetic anhydride in methanol, afforded the tetrasaccharide bound on support **9** (Scheme 4).

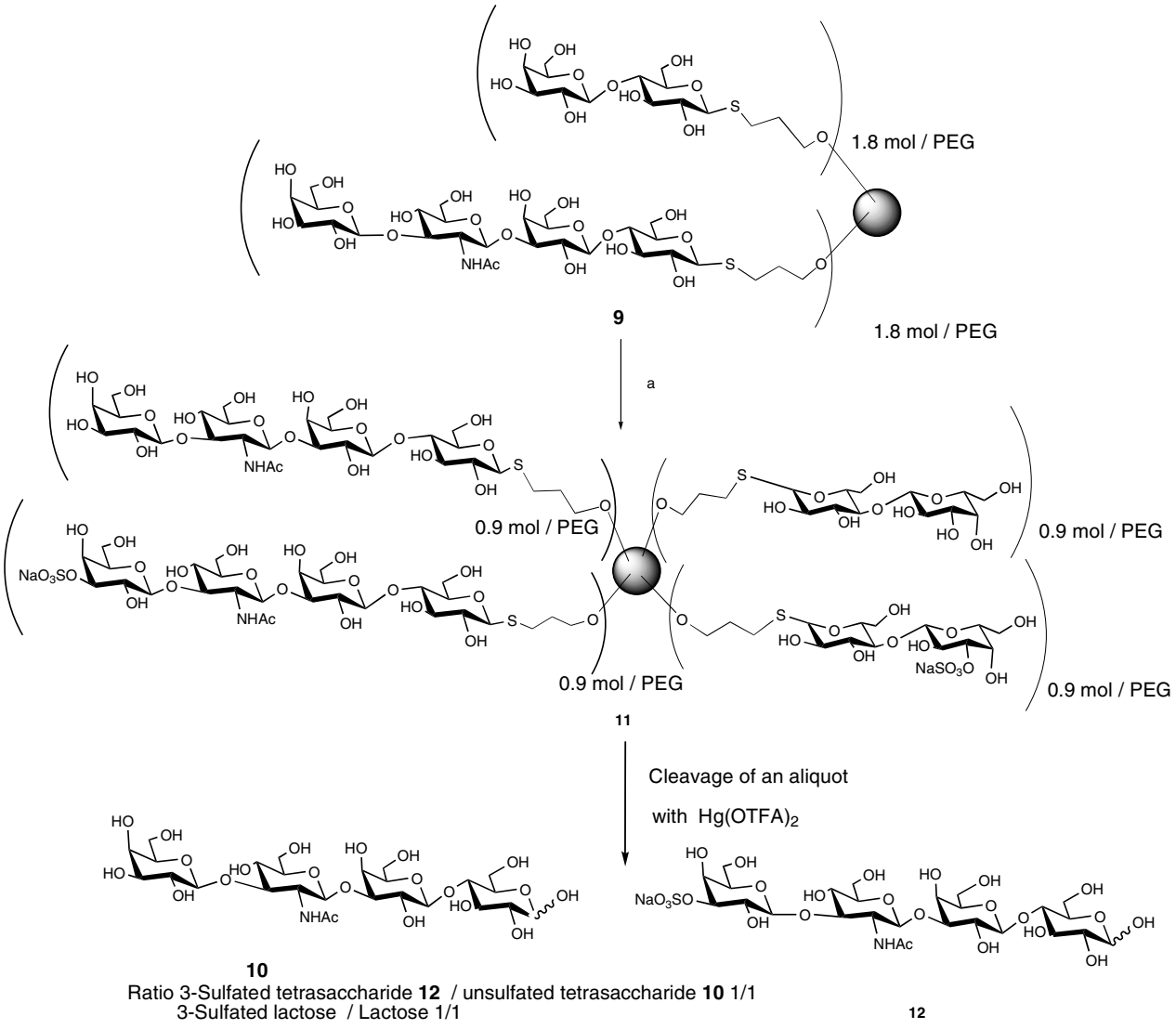
Cleavage of an aliquot of **9** with mercury(II) trifluoroacetate gave, after purification on a gel filtration column, tetrasaccharide **10** with 50% yield based on the initial loading of lactose in compound **4**. The spectral data of **10** were identical to those already published.[12] Compound **10** was also reduced and peracetylated. The NMR data were identical to those described for the 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-acetyl-β-D-glucopyranosyl-(1→3)-2,6-di-*O*-acetyl-β-D-galactopyranosyl-(1→4)-1,2,3,6-tetra-*O*-acetyl-glucitol tetrasaccharide.[13]

The sulfate group was then regioselectively introduced on the O-3 of the galactose moiety by stannylene-directed sulfation.[14] Compound **9**, having 12 free hydroxyl groups per tetrasaccharide residue, was heated at reflux in the presence of 1 equiv of dibutyltin(II) oxide in a 3:5 DMF/benzene mixture for 16 h. The benzene was then removed and 1.1 equiv of sulfur trioxide-trimethylamine complex was added. After 28 h at room temperature, the mixture was neutralized, dialyzed and lyophilized to give the sulfated tetrasaccharide bound onto polymer **11**. Cleavage of an aliquot of **11** with mercury(II) trifluoroacetate gave, after purification on a DEAE-Sephadex column and elution with triethylammonium hydrogen carbonate buffer, the known 3-sulfated tetrasaccharide **12** with 54% yield based on tetrasaccharide loading in **9** (Scheme 5).[15]

Fucosylation of **11** was achieved by incubation with recombinant FucT-III adsorbed on Ni^{2+}–agarose in 25 mM, pH 6.4, MES buffer and GDP-fucose.[16] Using the results found in our previous work,[9] GDP-fucose was introduced in less than stoichiometric amount to fucosylate only the O-4 of the GlcNAc residue without secondary fucosylation on the O-3 of the Glc residue. After 3 days, the enzyme was removed by filtration and the filtrate was dialyzed, lyophilized and treated with mercury(II) trifluoroacetate. After filtration and evaporation, the supernatant was passed through a DEAE-Sephadex column. First, nonsulfated compounds (lactose, tetrasaccharide, pentasaccharide) were eluted with water and then, elution with a triethylammonium hydrogen carbonate buffer gradient (0–1 M) allowed the separation of mono-sulfated compounds in



Scheme 4. Reagents and conditions: (a) (i) **6** (1 equiv), **7** (2.3 equiv/lactose), $BF_3{\cdot}Et_2O$, CH_2Cl_2, 0 °C, 4 h; (ii) precipitation with *tert*-butylmethyl ether; (b) (i) $NH_2CH_2CH_2NH_2$, EtOH, reflux, 16 h; (ii) Ac_2O, MeOH, rt, 3 h; (iii) dialysis.



Scheme 5. Reagents and conditions: (a) (i) Bu_2SnO (1.1 equiv), DMF–benzene, reflux, 16 h; (ii) $SO_3{\cdot}Me_3N$ (1.1 equiv); (iii) dialysis.

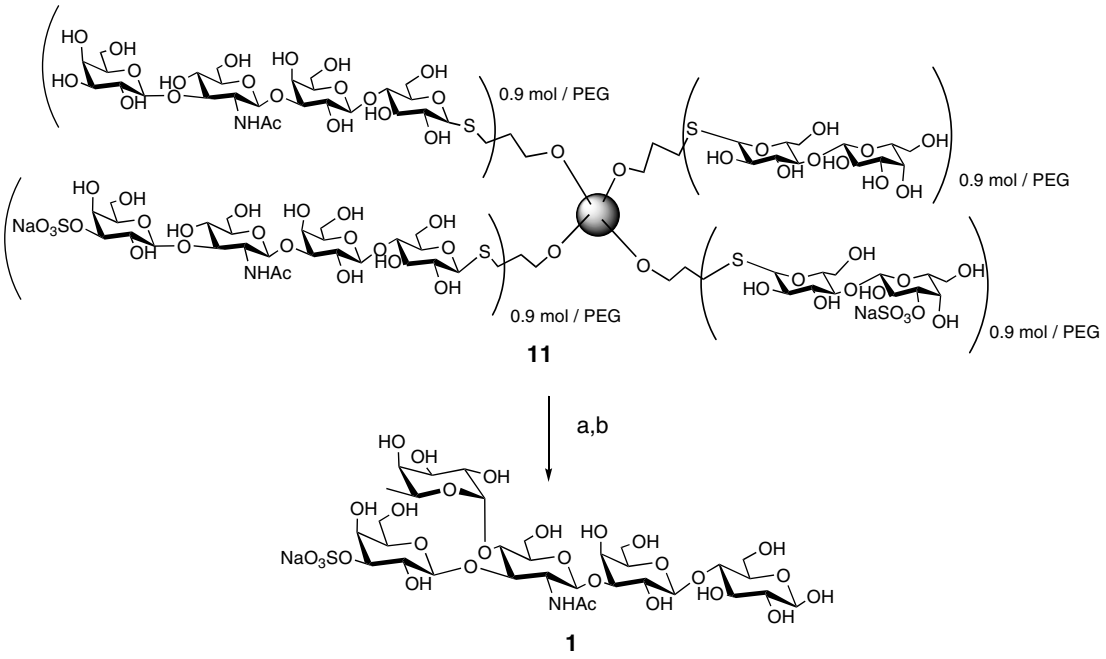
function of their molecular weight (pentasaccharide, tetrasaccharide, lactose). Compound **1** was obtained with a 10% overall yield based on the supported lactose. The individual yield of the enzymatic fucosylation step was estimated to 36%. In these conditions, only pentasaccharide **1** was obtained, and no trace of hexasaccharide resulting from the fucosylation onto the glucose residue was detected (Scheme 6).

The 3-sulfated Lewis[a] pentasaccharide has been totally synthesized on a soluble polymer using a chemo-enzymatic approach. The yield for each step was similar to the yield obtained in soluble phase. Our results demonstrated the possibility to extend solution-phase chemo-enzymatic synthesis methods to supported synthesis. The use of a soluble support greatly facilitated the purification of the different intermediates while a single, final chromatographical purification allowed easy isolation of pentasaccharide **1**.

1. Experimental

1.1. General methods

All moisture-sensitive reactions were performed under an argon atmosphere using oven-dried glassware. All solvents were dried over standard drying agents and freshly distilled prior to use. Flash column chromatography was performed on Silica Gel 60 A C.C (6–35 μm). Reactions were monitored by TLC on Silica Gel $60F_{254}$ plates with detection by UV at 254 nm and by charring with 10% H_2SO_4 in EtOH or 2% orcinol in 10% H_2SO_4 in EtOH. NMR spectra were recorded with Bruker AM-250, AMX-360, DRX-400 spectrometers. The chemical shifts spectra are given relative to Me_4Si in $CDCl_3$ and to acetone (δ 2.22 and 30.5 ppm) for spectra performed in D_2O. Mass Spectra were carried out with a Finnigan MATT 95 apparatus using ESI.



Scheme 6. Reagents and conditions: (a) (i) GDP-fucose, immobilized FucT-III, $MnCl_2$ (20 mM), 25 mM MES buffer pH 6.4, 37 °C, 3 days; (ii) filtration and dialysis; (b) (i) $Hg(OTFA)_2$, H_2O, 16 h, 55 °C; (ii) DEAE-Sephadex, elution Et_3NHCO_3 buffer pH 8 (0–1 M).

FucT-III was obtained within a French network (G3) devoted to the production and studies of recombinant glycosyltransferases.[17] GDP-fucose was synthesized according to published procedures.[18]

Carbohydrate content was determinated according to a modification of the Dubois method by the phenol sulfuric acid assay.[10]

1.2. Yield and recuperation of PEG-supported compounds

The yields of the PEG-supported compounds were determined by weighing, with the assumption that the MW of the PEG fragment was 7463 for **5** as determined by MALDI-TOF MS (commercial PEG 6000, found for the central peak 6952).

After reaction, the PEG-supported compounds were purified by dialysis using a regenerated cellulose membrane (Spectra/Por 6 MWCO 2000) or by precipitation. In the latter, PEG-supported compounds were precipitated after dissolution with dichloromethane followed by the addition of a 10-fold excess of *tert*-butylmethyl ether at 0 °C with vigorous stirring or by crystallization from absolute ethanol. This precipitate was filtered, dried under vacuo and used in the following step.

1.3. (β-D-Galactopyranosyl-(1→4)-*O*-1-thio-β-D-glucopyranoside supported) (4)

A solution of **3** (790 mg, 0.106 mmol) in water (4 mL) was allowed to react with β-D-1-thiolactose **2** (340 mg, 0.951 mmol, 1.5 equiv/allyl) under UV illumination using a germicide lamp for 16 h at rt. At the end of the reaction, the mixture was diluted with H_2O (20 mL), dialyzed and lyophilized to give **4** (993 mg).

^1H NMR (D_2O, 250 MHz,): 4.53 (d, $J_{1,2}$ 7.5 Hz, H-1^I), 4.42 (d, $J_{1,2}$ 7.0 Hz, H-1^{II}), 3.70–3.50 (m, CH_2CH_2O), 2.90–2.70 (m, CH_2–S), 2.00–1.80 (m, CH_2–CH_2).

An aliquot (10.7 mg) was hydrolyzed with mercuric(II) trifluoroacetate (5.3 mg) in H_2O (1 mL) during 4 h at rt. A phenol sulfuric detection gave 3.7 mmol of fixed disaccharide/ mmol of PEG.

1.4. [(2,6-Di-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside supported)] (6)

A soln of **4** (980 mg, 0.110 mmol) in 2,2-dimethoxypropane (20 mL) containing *p*-toluene-sulfonic acid monohydrate (10 mg) was heated at 55 °C for 3 h, then the mixture was neutralized with Et_3N, concentrated to dryness under reduced pressure. The residue was dissolved with H_2O (20 mL), dialyzed and concentrated. The resultant residue was refluxed with 9:1 MeOH–H_2O for 24 h and the solvents were evaporated. The mixture was acetylated with 1:2 Ac_2O–pyridine (30 mL) during 16 h. A soln of the previous compound in 70% aq AcOH (50 mL) was kept for 3 h under reflux. After evaporation and coevaporation with toluene, the residue was dissolved in CH_2Cl_2 and *tert*-butyl methyl ether was added at 0 °C with stirring. The precipitated solid was collected by filtration to give **6** (1.03 g, 0.107 mmol, 96%).

1.5. [(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→3)-2,6-di-*O*-acetyl-β-D- galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside supported] (8)

A mixture of **6** (1 g, 0.104 mmol) and **7** (0.75 g, 0.865 mmol, 2.3 equiv/lactose) in CH_2Cl_2 (20 mL) was stirred during 15 min at rt, then cooled at −10 °C and $BF_3{\cdot}Et_2O$ (35 μL) was added. The reaction mixture was stirred at 0 °C for 4 h. Et_3N was added and the mixture was concentrated. The residue was dissolved in CH_2Cl_2 and *tert*-butyl methyl ether was added at 0 °C with stirring. The precipitated solid was collected by filtration to give **8** (1.30 g).

1.6. [β-D-Galactopyranosyl-(1→3)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-β-D-galactopyranosyl-(1→4)-1-thio-β-D-glucopyranoside supported] (9)

A mixture of ethylene diamine (2.5 mL) and **8** (1.17 g, 1.07 mmol) in EtOH (25 mL) was refluxed for 20 h. After cooling and concentration, the residue was dialyzed, dried and treated with Ac_2O (8 mL) in MeOH (25 mL). The mixture was stirred for 3 h at rt, then concentrated to give **9** (887 mg, 94 μmol).

1.7. β-D-Galactopyranosyl-(1→3)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-β-D-galactopyranosyl-(1→4)-D-glucopyranose (10)

An aliquot of **8** (98 mg) was refluxed in EtOH containing ethylene diamine (0.5 mL) for 16 h. After cooling, the soln was concentrated and the residue was acetylated with Ac_2O (1.7 mL) in MeOH (5 mL). The product (65 mg) was cleaved using mercuric(II) trifluoroacetate (20 mg) in H_2O (4.5 mL), then the mixture was purified on a Biogel P2 gel filtration column (48 × 2.2 cm) to give 12.5 μmol of tetrasaccharide **10** (8.9 mg, condensation yield, 55%). This result agreed with the colorimetric determination, and spectral data were identical to those already published.[19]

^{1}H NMR (D_2O, 360 MHz): δ 5.18 (d, 0.33H, $J_{1,2}$ 4.0 Hz, H-1^{I} α), 4.68 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1^{III}), 4.62 (d, 0.66H, $J_{1,2}$ 7.5 Hz, H-1^{I}β), 4.40 (d, 2H, $J_{1,2}$ 8.0 Hz, H-1^{II}, H-1^{IV}), 4.11 (d, 1H, $J_{3,4}$ 3.5 Hz, H-4^{II}), 3.30–3.25 (m, 1H, H-2^{I}), 1.98 (s, 3H, CH_3CO).

1.8. [(3-Sulfo-β-D-galactopyranosyl)-(1→3)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-β-D-galactopyranosyl-(1→4)-1-thio-β-D-glucopyranoside sodium salt supported] (11)

A mixture of **9** (722 mg, 77 μmol) and dibutyltin(II)-oxide (75 mg, 0.30 mmol) in DMF–benzene (3:5, 80 mL) was refluxed for 16 h with continuous removal of water using a Dean–Stark apparatus. Then, the benzene was removed and the dibutylstannylene derivative was treated with $Me_3N{\cdot}$sulfur trioxide complex (42 mg., 0.30 mmol, 3.9 equiv) at rt for 28 h. The reaction mixture was then diluted with MeOH and neutralized with $NaHCO_3$. After evaporation, the residue was dissolved in H_2O and dialyzed to give **11** (673 mg) after lyophilization.

1.9. 3-Sulfo-β-D-galactopyranosyl-(1→3)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-β-D-galactopyranosyl-(1→4)-D-glucopyranose sodium salt (12)

An aliquot (100 mg) was hydrolyzed with mercuric(II) trifluoroacetate (40 mg) in H_2O (5 mL) during 4 h at rt, then the mixture was purified on DEAE-Sephadex A-25 column, eluted with a 0.1 M $Et_3N{\cdot}HCO_3$ buffer (pH 8). Fractions containing the starting compound were pooled to give **10** (6.8 mg, 10 μmol). Fractions containing the sulfated tetrasaccharide **12** (9 mg, 11 μmol, 54%) were pooled and twice lyophilized.

^{1}H NMR (D_2O, 400 MHz): 5.10 (d, 0.33H, $J_{1,2}$ 3.5 Hz, H-1^{I}α), 4.61 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1^{III}), 4.55 (d, 0.66H, $J_{1,2}$ 7.5 Hz, H-1^{I}β), 4.43 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1^{IV}), 4.30 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1^{II}), 4.20–4.17 (m, 2H, H-4^{IV}, H-3^{IV}), 4.03 (d, 1H, $J_{3,4}$ 3.5 Hz, H-4^{II}), 3.20–3.15 (m, 1H, H-2^{I}), 1.90 (s, 3H, CH_3CO).

1.10. 3-Sulfo-β-D-galactopyranosyl-(1→3)-[(α-L-fucopyranosyl)-(1→4)]-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-β-D-galactopyranosyl-(1→4)-D-glucopyranose sodium salt (1)

Compound **11** (371 mg), GDP-fucose (43 mg, 55 μmol), immobilized FucT-III (40 mU), $MnCl_2$ (217 mg) were incubated at 37 °C for 67 h in 25 mM MES buffer (55 mL, pH 6.4). After centrifugation, the supernatant was dialyzed and lyophilized to give **14** (377 mg).

Compound **14** (377 mg) was hydrolyzed with mercuric(II) trifluoroacetate (140 mg, 0.33 mmol) in H_2O (15 mL) in the presence of $BaCO_3$ during 16 h at 55 °C. After filtration, the supernatant was concentrated and the mixture was purified on DEAE-Sephadex A-25 column, eluted with a gradient of Et_3N HCO_3 buffer, pH 8 (0–1 M). The fractions containing compound **1** were lyophilized and the freeze-dried eluate was passed through a column of Bio-Rad AG 50W-X8 resin (Na^+ form) to give **1** (14.3 mg, 13.8 μmol, 36%). LRMS (negative mode): calcd for $C_{32}H_{54}NO_{28}NaS$ $[M-Na]^-$, 932.3; found, 932.5.

The spectral data were identical to those already published.[13]

Compound **1**: ^{1}H NMR (D_2O, 400 MHz): 5.22 (d, 0.33H, $J_{1,2}$ 3.5 Hz, H-1^{I}α), 5.03 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1^{V}), 4.87 (m, 1H, H-5^{V}), 4.71 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1^{III}), 4.67 (d, 0.66H, $J_{1,2}$ 7.5 Hz, H-1^{I}β), 4.61 (d,

1H, $J_{1,2}$ 7.5 Hz, H-1^{IV}), 4.44 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1^{II}), 4.32–4.27 (m, 2H, H-4^{IV}, H-3^{IV}), 4.16 (d, 1H, $J_{3,4}$ 3.5 Hz, H-4^{II}), 3.30–3.25 (m, 1H, H-2^{I}), 2.05 (s, 3H, CH_3CO), 1.19 (d, 3H, $J_{5,6}$ 6.5 Hz, CH_3).

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