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OLIGOSACCHARIDES FROM "STANDARDIZED INTERMEDIATES". THE 2-AMINO-2-DEOXY-D-GALACTOSE ANALOG OF THE BLOOD-GROUP O(H) DETERMINANT, TYPE 2, AND ITS PRECURSORS

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ABSTRACT

The selectively benzylated glycoside allyl 2-acetamido-4,6-di-*O*-benzyl-2-deoxy-β-D-galactopyranoside (**4**) was prepared from the corresponding derivative of 2-acetamido-2-deoxy-D-glucose *via* the *p*-bromobenzenesulfonate and the benzoate. 2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-α-D-galactopyranosyl chloride (**10**) was obtained from allyl 6-*O*-benzyl-2-*O*-(2-butenyl)-α-D-galactopyranoside *via* known intermediates. To complete the sequence, the 1-propenyl 3,4,6-tri-*O*-benzyl galactoside was successively converted into the 2-benzoate, the free sugar, and the chloride **10**. A fully protected form (**11**) of the trisaccharide α-L-Fuc*p*-(1→2)-β-D-Gal*p*-(1→4)-D-GalNAc was then synthesized by coupling **10** to **4**, partially deblocking the disaccharide product, and L-fucosylating the resulting intermediate. Cleavage of the *O*-benzyl groups from **11**, with concomitant saturation of the allyl group, gave the propyl β-glycoside of the unsubstituted trisaccharide.

INTRODUCTION

In work on the assembly of oligosaccharides from "building block" derivatives of the common sugars, we have emphasized the use of differentially substituted hexoses carrying benzyl ether groups as persistent protecting-groups. We now report the synthesis of *O*-benzyl derivatives suitable for use as precursors of reducing-end (**4**), or interior, β-linked (**3**), 2-acetamido-2-deoxy-D-galactopyranose residues having chain extension at O-4. The first of these has been incorporated into a trisaccharide analog (**15**) of the human blood-group O(H) determinant (type 2 chain). We also record an alternative synthesis of the known 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-galactopyranosyl chloride (**10**), used as the precursor of the β-linked D-galactopyranosyl residue in **15**.

RESULTS AND DISCUSSION

Although numerous *O*-benzyl derivatives (*e.g.* **1**)[1] of 2-acetamido-2-deoxy-D-glucose have been prepared in recent years for use as glycosyl acceptors and glycosyl donors in oligosaccharide synthesis, the corresponding chemistry of 2-acetamido-2-deoxy-D-galactose (D-GalNAc) is less well developed. This may result, in part, from an emphasis on products containing α-linked GalNAc residues, for which the precursors are usually substituted 2-azido-2-deoxy-D-galactopyranosyl halides[2]. The latter are prepared from D-galactose, rather than from the parent amino sugar. Another factor may be the high cost of 2-amino-2-deoxy-D-galactose, which makes the synthesis of D-GalNAc derivatives from substituted 2-amino-2-deoxy-D-glucoses seem attractive.

Stereochemical inversion by the displacement of a methanesulfonate group from C-4 of a 2-amino-2-deoxy-D-glucose derivative has been practised by a number of workers, with varying degrees of success (references are cited by Gent *et al.*[3]). More recently, Nashed[4] obtained good results by treating the 4-*p*-bromobenzenesulfonate ("brosylate") of allyl 2-acetamido-3,6-di-*O*-benzoyl-2-deoxy-β-D-glucopyranoside, a precursor of **1**, with sodium benzoate in hexamethylphosphoric triamide at high temperature. The application of this procedure to the 3,6-di-*O*-benzyl derivative **1** appeared straightforward, and we therefore undertook the preparation and displacement of the 4-brosylate **2**.

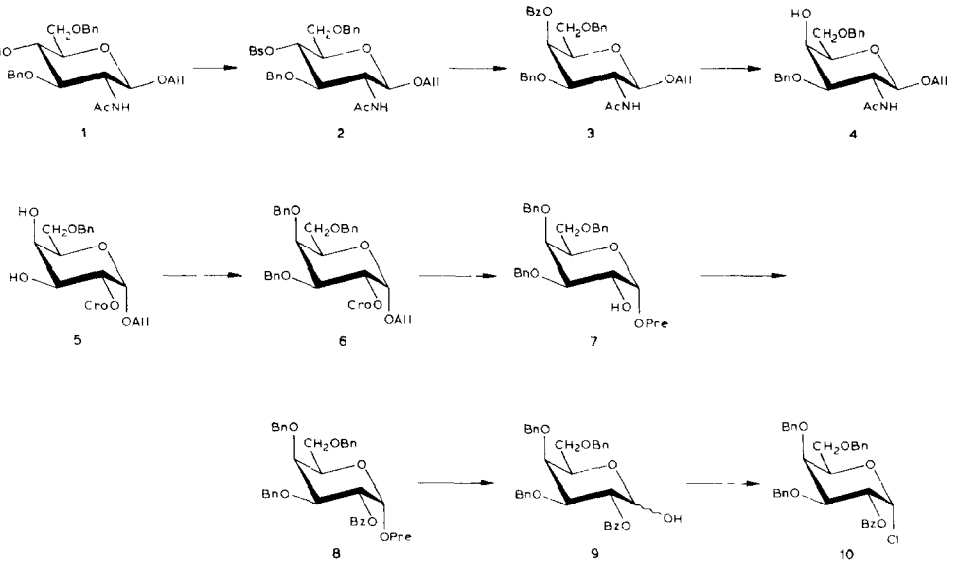
The reaction of **1** with *p*-bromobenzenesulfonyl chloride in pyridine under the usual conditions gave a complex mixture, but a clean preparation of **2** was accomplished by employing dichloromethane as the solvent, with small proportions of pyridine and 4-(dimethylamino)pyridine as acid acceptors and catalysts. We then found that the displacement step (**2** → **3**) could be conducted in *N*,*N*-dimethylformamide, instead of in hexamethylphosphoric triamide, when cesium benzoate was substituted for the (less-soluble) sodium salt as the source of benzoate ion[5]. The *galacto* product **3**, formed in good yield, was amorphous, but readily purified by chromatography on silica gel. As **3** could certainly be converted, *via* the 1-propenyl glycoside, into an oxazoline[1,4], it may be regarded as a synthon ("4-GalNAc-β")[6] for interior D-GalNAc residues. Zemplén *O*-debenzoylation of **3** gave allyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-galactopyranoside (**4**), which has a free hydroxyl group at C-4, and is therefore able to function as a glycosyl acceptor* Compound **4** became the reducing-end residue of the trisaccharide glycoside **15**.

As the building block for the central, D-galactopyranosyl residue of **15**, we chose the 2-*O*-benzoyltri-*O*-benzyl-D-galactopyranosyl chloride **10**. This chloride was first prepared, and used in glycosylation reactions, by Schuerch and his collaborators[8]. The benzoyl substituent serves both as a β-directing group in the coupling of **10** to an acceptor, and as a temporary protecting-group that can be removed to unmask

*Benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranoside, which serves the same purpose as compound **4**, has been prepared from 2-acetamido-2-deoxy-D-galactose by Matta and co-workers[7].

O-2′ in the coupling product. In Schuerch's laboratory, the compound was prepared by a route involving the orthoester 3,4,6-tri-*O*-benzyl-1,2-*O*-(1-methoxyethylidene)-α-D-galactopyranose as the key intermediate.

Alternatively, it appeared that **10** could be obtained from 1-propenyl 3,4,6-tri-*O*-benzyl-α-D-galactopyranoside (**7**), which Gent and Gigg[9] had synthesized some years ago from allyl 6-*O*-benzyl-2-*O*-(2-butenyl)-α-D-galactopyranoside (**5**), as shown in Scheme I. In that work, they used crude **5**, and found it unnecessary to purify **6** or **7** before proceeding to the next step of their synthesis. However, Gigg[10] later separated, and characterized, the *cis* and *trans* isomers (with respect to the 1-propenyl group) of **7** obtained from a 2-*O*-(3-methyl-2-butenyl) ("prenyl") precursor.



All = $H_2C{=}CHCH_2$, Bn = $PhCH_2$, Bs = $SO_2C_6H_4Br$-*p* ,

Bz = PhCO , Cro = $MeCH{=}CHCH_2$, Pre = $MeCH{=}CH$

Scheme 1

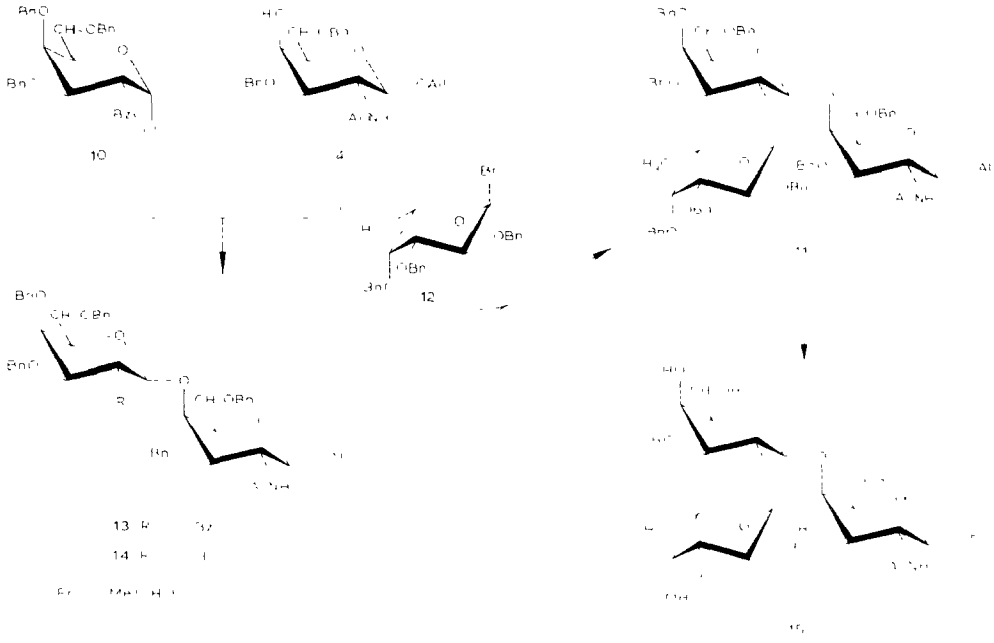
Having on hand a good supply of compound **5**, which had been used in an earlier project[11], it was expedient to use this material for the preparation of **10**. As expected, the conversion proceeded readily. First, the product of the benzylation of **5** was purified; it was characterized (^{1}H-n.m.r.) as allyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-butenyl)-α-D-galactopyranoside (**6**). Then, successive treatment with potassium *tert*-butoxide, benzoyl chloride, and aqueous methanolic hydrochloric acid furnished **7**, the 2-*O*-benzoyl compound **8**, and 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-D-galactose (**9**). Intermediate **9** was purified, and the chloride **10** was generated from it by the action of oxalyl chloride in *N*,*N*-dimethylformamide[12]. The overall yield of **10** from **5** was 52%.

The reaction of the chloride **10** (1.2 molar proportions) with the amino-D-

galactoside **4** was effected in dichloromethane solution by the addition of silver trifluoromethanesulfonate and 1,1,3,3-tetramethylurea[13]. Even though coupling was to the supposedly unreactive 4-hydroxyl group of the acceptor, the product was obtained in 81% yield. Together with the similarly high yields we have obtained in related cases[14,15], this result bespeaks the efficiency of the Hanessian–Banoub procedure. The formulation of the coupling product as the disaccharide glycoside **13** was supported by its ^{1}H-n.m.r. spectrum, in which signals for H-1′ and H-2′ were clearly discernible, along with lines characteristic of the 2-acetamido-2-deoxy-D-galactoside moiety. The value of $J_{1',2}$ was 8.1 Hz, clearly establishing the β configuration of the added D-galactosyl group.

The *O*-debenzoylation of **13** furnished the selectively deprotected intermediate **14**, which was L-fucosylated by treatment with tri-*O*-benzyl-α-L-fucopyranosyl bromide (**12**) in the presence of tetraethylammonium bromide ("common-ion method"[16]). The ^{1}H-n.m.r. spectrum of the product showed signals characteristic of an α-fucopyranosyl group (δ 5.74, d, J 3.0 Hz, H-1″; 1.02, d, J 6.3 Hz, $CHCH_3$), permitting its formulation as **11**

In considering the deprotection of **11**, we elected to leave the aglycone allyl group in place. Because the protecting groups remaining were *O*-benzyl groups, only hydrogenolysis was needed in order to obtain the deblocked product, propyl *O*-α-L-fucopyranosyl-(1→2)-*O*-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-galactopyranoside (**15**). The assigned stereochemistry of the glycosidic linkages in **15** was confirmed by the presence, in the ^{1}H-n.m.r spectrum, of doublets for one α-anomeric and two β-anomeric protons.



The glycone portion of **15** differs from the nonreducing terminal structure of the human blood-group O(H), type 2 oligosaccharide[17], in that the *N*-acetylhexosamine residue has the *galacto*, not the *gluco*, configuration. The natural trisaccharide was synthesized chemically by Jacquinet and Sinaÿ[18] in 1976, and later by Paulsen and Kolář[19]. It has also been prepared in Barker's laboratory[20] by enzymic means.

EXPERIMENTAL

General methods. — The instrumental and chromatographic procedures employed were those given previously[1]. ^{1}H-N.m.r. spectra were recorded at 270 MHz, with decoupling, as required, for the identification of signals that could not be assigned unambiguously by inspection. ^{13}C-N.m.r. spectra were recorded with a Nicolet NT-200 instrument operating at 50.31 MHz, with 1,4-dioxane as the internal standard. Chromatography on silica gel was accomplished with ethyl acetate–hexane, acetone–chloroform, or methanol–chloroform. Elemental analyses were made at the Galbraith Laboratories, Inc., Knoxville, TN.

Allyl 2-acetamido-3,6-di-O-*benzyl-4*-O-p-*bromophenylsulfonyl-2-deoxy-β*-D-*glucopyranoside* (**2**). — Compound **1** was prepared as described by Nashed *et al.*[1]; ^{1}H-n.m.r. ($CDCl_3$): δ 7.40–7.11 (m, Ph-H), 5.94–5.73 (-C*H*=), 5.69 (d, $J_{NH,2}$ 7.7 Hz, D_2O-exchangeable, N*H*), 5.26–5.12 (m, -CH=CH_2), 4.85 (d, $J_{1,2}$ 8.1 Hz, H-1), 4.73 (AB, *J* 11.8 Hz, PhCH_2), 4.57 (AB, *J* 11.8 Hz, PhCH_2), 4.32–3.28 (m, OCH_2CH=, sugar C*H* and CH_2), 2.91 (bs, D_2O-exchangeable, O*H*), and 1.89 (s, COCH_3). To a solution of **1** (200 mg, 0.45 mmol) in dry dichloromethane (2 mL) and pyridine (0.2 mL, 2.5 mmol) were added 4-(dimethylamino)pyridine (20 mg, 0.16 mmol) and *p*-bromobenzenesulfonyl chloride (350 mg, 1.37 mmol), and the mixture was stirred for ~2 days at room temperature, diluted with chloroform, and processed by conventional, aqueous washing. Evaporation of the solution gave a crude residue, which was purified on a column of silica gel. Crystallization, and recrystallization, from methanol furnished 203 mg (68%) of compound **2** as long needles, m.p. 110–111°, $[\alpha]_D^{25}$ −9.8°, $[\alpha]_{436}^{25}$ −15.5° (*c* 1.12, chloroform); ^{1}H-n.m.r. ($CDCl_3$): similar to that of **1**, except for new signals at δ 7.52 (q, *J* 10 Hz, BrC$_6H_4$) and 4.78 (downfield shift, t, *J* 8.7 Hz, H-4), and loss of the O*H* signal.

Anal. Calc. for $C_{31}H_{34}BrNO_8S$ (660.59): C, 56.37; H, 5.19; Br, 12.10; N, 2.12. Found: C, 56.41; H, 5.26; Br, 12.40; N, 2.10.

Allyl 2-acetamido-3,6-di-O-*benzyl-2-deoxy-β*-D-*galactopyranoside* (**4**). — A solution of compound **2** (100 mg, 0.15 mmol) in *N*,*N*-dimethylformamide (1 mL) was stirred with cesium benzoate* (77 mg, 0.30 mmol) overnight at 130–135°. The mixture was cooled, diluted with chloroform, washed with water, and dried. Evaporation gave a thick syrup that, on purification on a column of silica gel, furnished

*Prepared by the addition of cesium hydroxide (5 g) in methanol (10 mL) to benzoic acid (4.3 g; 5% excess) in chloroform (10 mL). After brief stirring, part of the salt was isolated by filtration. The rest was obtained in friable form by evaporating the filtrate, triturating the residue with toluene, decanting, and evaporating the traces of toluene from the solid.

amorphous *allyl 2-acetamido-4-O-benzoyl-3,6-di-O-benzyl-2-deoxy-β-D-galactopyranoside* (**3**); ^{1}H-n.m.r. ($CDCl_3$): similar to that of **2**, except for the replacement of the low-field quartet (BrC_6H_4) by a signal for C_6H_5CO at slightly higher field, modification of the signal for H-4 (δ 5.96) to the form characteristic of galactopyranose derivatives (broadened d, $J_{3,4}$ ~4 Hz), and shift of the signal for H-1 to δ 5.20. Zemplén *O*-debenzoylation of compound **3** yielded 44 mg (66% from **2**) of compound **4**, amorphous; $[\alpha]_D^{25}$ +5.9 (*c* 0.73, chloroform); ^{1}H-n.m.r. ($CDCl_3$): similar to that of **3**, except for loss of the benzoyl signal, disappearance (upfield shift) of the H-4 signal, and appearance of a D_2O-exchangeable signal at δ 2.85 (s, *OH*).

Anal. Calc. for $C_{25}H_{31}NO_6$ (441.52): C, 68.01; H, 7.08; N, 3.17. Found: C, 68.05; H, 7.20; N, 3.17.

Allyl 3,4,6-tri-O-benzyl-2-O-(2-butenyl)-α-D-galactopyranoside (**6**). — A solution of allyl 6-*O*-benzyl-2-*O*-(2-butenyl)-α-D-galactopyranoside[11] (**5**; 5 g, 13.7 mmol) in dry *N*,*N*-dimethylformamide (50 mL) was cooled to ~5°, and sodium hydride (2.5 g) was added portionwise. Benzyl bromide (4 mL, 33.6 mmol) was then added dropwise, while the suspension was stirred at ~5°. The reaction was brought to completion, as judged by t.l.c., by allowing the stirred mixture to warm to 25° and keeping it for 2 h at this temperature. After the addition of methanol to decompose the excess of sodium hydride, the mixture was diluted with chloroform, and the product was isolated as a syrup by conventional processing. Purification on a column of silica gel furnished 6.8 g (91%) of compound **6**: $[\alpha]_D^{25}$ +39.8° (*c* 3.0, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.45–7.18 (m, Ph-H), 6.05–5.85 (m, -C*H*= of allyl), 5.75–5.55 (m, 2 H, C*H*=C*H*), 5.38–5.15 (m, CH=CH_2), 4.98 (d, $J_{1,2}$ 3.3 Hz, H-1), 4.79, 4.77, and 4.44 (3 AB, *J* 12.0, 11.3, and 11.3 Hz, PhCH_2), 4.24–3.40 (m, OCH_2 of allyl and butenyl, sugar C*H* and CH_2), 1.68 (major), and 1.61 (minor) (2 d, *J* 6.0 Hz, =CHCH_3). The occurrence of two methyl signals indicates *cis–trans* isomerism in the crotyl group.

Anal. Calc. for $C_{34}H_{40}O_6$ (544.69): C, 74.97; H, 7.40. Found: C, 74.69; H, 7.30.

2-O-Benzoyl-3,4,6-tri-O-benzyl-D-galactopyranose (**9**). — A solution of pure **6** (4 g, 7.34 mmol) in dry *N*,*N*-dimethylformamide (100 mL) containing potassium *tert*-butoxide (3.6 g, 32.1 mmol) was stirred for 4 h at 80–85° under dry nitrogen, and then poured into water. Conventional chloroform extraction, followed by evaporation, gave **7** as a syrup. Benzoylation with benzoyl chloride in pyridine then converted the crude **7** into *1-propenyl 2-O-benzoyl-3,4,6-tri-O-benzyl-α-D-galactopyranoside* (**8**). The benzoate was isolated by conventional chloroform extraction, and subjected to acid hydrolysis[6] to remove the propenyl group. Purification of the resulting free sugar (**9**) on a column of silica gel furnished 2.7 g (66% overall) of pure material, a syrup; $[\alpha]_D^{25}$ +70.0° (*c* 0.74, chloroform). The ^{1}H-n.m.r. spectrum ($CDCl_3$) resembled that of **6**, but it lacked signals for the allyl and crotyl groups, and showed new, or down-shifted, signals at δ 8.10–7.08 (C_6H_5CO), 5.55 (dd, $J_{1,2}$ 4.0, $J_{2,3}$ 10 Hz, H-2α), 5.46 (dd, $J_{1,2}$ 8.3, $J_{2,3}$ 10.2 Hz, H-2β), and 1.78 (s, *OH*).

Anal. Calc. for $C_{34}H_{34}O_7$ (554.64): C, 73.63; H, 6.18. Found: C, 73.39; H, 6.44.

2-O-Benzoyl-3,4,6-tri-O-benzyl-α-D-galactopyranosyl chloride (**10**). — A solu-

tion of compound **9** (2 g, 3.61 mmol) in dry *N,N*-dimethylformamide (20 mL) was cooled to ~5°, and oxalyl chloride (0.5 mL, 5.73 mmol) was added dropwise, with stirring. The mixture was allowed to warm to room temperature, stirring was continued for 2 h, and it was then diluted with chloroform, washed with 5% sodium hydrogencarbonate, and evaporated under diminished pressure, to give crude D-galactosyl chloride **10**. This was rapidly chromatographed on a short column of silica gel, to yield 1.8 g (87%) of a thick syrup; $[\alpha]_D^{25}$ +126° (*c* 1.0, chloroform). The ^{1}H-n.m.r. spectrum ($CDCl_3$), similar to that of **9**, had the features expected[8], namely, δ 6.48 (d, $J_{1,2}$ 4.1 Hz, H-1α) and a well resolved signal at δ 5.70 (dd, $J_{1,2}$ 4.1, $J_{2,3}$ 10.3 Hz, H-2).

Anal. Calc. for $C_{34}H_{33}ClO_6$ (573.09): C, 71.26; H, 5.80; Cl, 6.19. Found: C, 71.03; H, 5.82; Cl, 7.02.

Allyl O-(*2,3,4-tri*-O-*benzyl*-α-L-*fucopyranosyl*)-(*1*→*2*)-O-(*3,4,6-tri*-O-*benzyl*-β-D-*galactopyranosyl*)-(*1*→*4*)-*2-acetamido-3,6-di*-O-*benzyl-2-deoxy*-β-D-*galactopyranoside* (**11**). — The *O*-debenzoylation of compound **13** (150 mg, 0.15 mmol) with methanolic sodium methoxide gave *allyl* O-(*3,4,6-tri*-O-*benzyl*-β-D-*galactopyranosyl*)-(*1*→*4*)-*2-acetamido-3,6-di*-O-*benzyl-2-deoxy*-β-D-*galactopyranoside* (**14**); ^{1}H-n.m.r. ($CDCl_3$) similar to that of **13**, except for the absence of signals for C_6H_5CO, the disappearance (upfield shift) of H-2′, and the appearance of a D_2O-exchangeable signal at δ 1.27 (s, O*H*). Also, the signal for H-1′ was shifted to higher field, and the N*H* signal was clear at δ 5.66 (d, 1 H, $J_{NH,2}$ 6.8 Hz, D_2O-exchangeable).

The details of the coupling procedure have already been given[14]. A two-armed reactor[14] was charged with the product just described, plus tetraethylammonium bromide (52 mg, 0.25 mmol) and powdered molecular sieves 4A (0.5 g) (flat-bottomed arm), and tri-*O*-benzyl-α-L-fucosyl bromide[21] (**12**) freshly prepared from the 1-acetate[14] (120 mg, 0.25 mmol) (conical arm). The reactants were dried on the liquid-nitrogen-cooled Dewar flask, and then the acceptor (**14**) was dissolved in dry dichloromethane (3 mL) and the fucosyl bromide in dichloromethane (2 mL) and dry *N,N*-dimethylformamide (1 mL). The solutions were mixed, and the mixture was stirred under dry nitrogen for 2 days at room temperature, processed in the conventional way, and the resulting, crude syrup purified on a column of silica gel. The yield of syrup was 147 mg (74% overall); $[\alpha]_D^{25}$ −34.3° (*c* 2.4, chloroform); ^{1}H-n.m.r. ($CDCl_3$): similar to that of **14**, except for additional signals at δ 7.47–6.82 (Ph-H), 5.74 (d, $J_{1'',2''}$ 3.0 Hz, H-1″), 4.70–3.30 (PhCH_2, C*H* of sugar), and 1.02 (d, *J* 6.3 Hz, CHCH_3), and loss of the O*H* signal.

Anal. Calc. for $C_{79}H_{87}NO_{15}$ (1290.56): C, 73.52; H, 6.80; N, 1.09. Found: C, 73.21; H, 6.80; N, 0.97.

Allyl O-(*2*-O-*benzoyl-3,4,6-tri*-O-*benzyl*-β-D-*galactopyranosyl*)-(*1*→*4*)-*2-acetamido-3,6-di*-O-*benzyl-2-deoxy*-β-D-*galactopyranoside* (**13**). — In the flat-bottomed arm of a two-armed reactor (see previous step) were placed the allyl aminogalactoside **4** (200 mg, 0.45 mmol) and silver trifluoromethanesulfonate (231 mg, 0.90 mmol), and, in the conical arm, the D-galactosyl chloride **10** (311 mg, 0.54 mmol). The reactants were vacuum-dried, and then dichloromethane (1.5 mL) and 1,1,3,3-tetramethylurea

(0.16 mL, 1.3 mmol) were added to the flat-bottomed side. The D-galactosyl chloride was dissolved in dichloromethane (2 mL), and transferred, and the mixture was stirred overnight at room temperature. Processing gave a syrupy residue, which was fractionated on a column of silica gel to afford 360 mg (81 %) of compound **13** as a thick syrup; $[\alpha]_D^{25}$ +33.6° (*c* 1.15, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 8.02–7.04 (m, Ph-H), 5.88–5.68 (m, 1 H, -C*H*=), 5.59 (dd, overlapped by D_2O-exchangeable N*H*, $J_{1',2'}$ 8.1, $J_{2',3'}$ 9.9 Hz, H-2'), 5.22–5.05 (m, CH=CH_2), 4.94 (d, $J_{1,2}$ 8.7 Hz, H-1), 4.78 (d, $J_{1',2'}$ 8.1 Hz, H-1'), 4.70–3.40 (m, PhCH_2, OCH_2CH=, sugar C*H* and CH_2), and 1.68 (s, CH_3CO).

Anal. Calc. for $C_{59}H_{63}NO_{12}$ (978.15): C, 72.45; H, 6.49; N, 1.43. Found: C, 71.98; H, 6.69; N, 2.07.

Propyl O-α-L-*fucopyranosyl*-(1→2)-O-β-D-*galactopyranosyl*-(1→4)-*2-acetamido-2-deoxy*-β-D-*galactopyranoside* (**15**). — Compound **11** (100 mg) was catalytically hydrogenolyzed in methanol (15 mL), in the presence of 10 % palladium-on-charcoal (50 mg), overnight at room temperature and atmospheric pressure. The catalyst was filtered off, and the filtrate evaporated, to yield 38 mg (78 %) of amorphous compound **15**; $[\alpha]_D^{25}$ −66.4° (*c* 1.12, methanol); ^{1}H-n.m.r. (D_2O; sodium 2,2,3,3-tetradeuterio-4,4-dimethyl-4-silapentanoate as the internal standard, at 50°): δ 5.45 (d, $J_{1'',2''}$ 4.2 Hz, H-1''), 4.74 (d, $J_{1,2}$ 7.8 Hz, anomeric H), 4.45 (d, $J_{1,2}$ 8.2 Hz, anomeric H), 4.50–3.60 (m, OCH_2CH_2, sugar C*H* and CH_2), 2.03 (s, COCH_3), 1.55 (m, OCH$_2$-CH_2CH$_3$), 1.23 (d, *J* 7 Hz, CHCH_3), and 0.87 (t, *J* 7.7 Hz, CH$_2$CH_3); ^{13}C-n.m.r. (D_2O, 1,4-dioxane as the internal standard, δ = 67.86) δ 103.57 and 102.96 (C-1 and C-1'), and 99.88 (C-1'').

Anal. Calc. for $C_{23}H_{41}NO_{15} \cdot 3\ H_2O$ (625.62): C, 44.16; H, 7.57; N, 2.24. Found: C, 43.83; H, 7.08; N, 2.27.

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