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SYNTHESIS OF 2-METHYL-[2-ACETAMIDO-4-*O*-ACETYL-6-*O*-BENZYL-3-*O*-(2-BUTENYL)-1,2-DIDEOXY-α-D-GLUCOPYRANO]-[2,1-*d*]-2-OXAZOLINE, A VERSATILE INTERMEDIATE FOR THE SYNTHESIS OF COMPLEX OLIGOSACCHARIDES OF BACTERIAL CELL-WALL, HUMAN MILK, AND BLOOD-GROUP SUBSTANCES*

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ABSTRACT

2-Methyl-[2-acetamido-4-*O*-acetyl-6-*O*-benzyl-3-*O*-(2-butenyl)-1,2-dideoxy-α-D-glucopyrano]-[2,1-*d*]-2-oxazoline (**2**), a glycosylating agent in which the three hydroxyl groups are blocked with protecting groups of differing "persistence", is of utility in the synthesis of oligosaccharides containing highly branched 2-acetamido-2-deoxy-D-glucosyl residues, and it was synthesized in a ten-step sequence from 2-acetamido-2-deoxy-D-glucose *via* allyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**3**). Alkylation of **3** with 2-butenyl (crotyl) bromide, hydrolysis of the benzylidene acetal group, benzylation of the 6-hydroxyl group, and acetylation of the 4-hydroxyl group afforded allyl 2-acetamido-4-*O*-acetyl-6-*O*-benzyl-3-*O*-(2-butenyl)-2-deoxy-β-D-glucopyranoside (**10**). Treatment of **10** with chlorotris(triphenylphosphine)rhodium(I) gave mainly the corresponding 1-propenyl β-glycoside, which was converted into oxazoline **2** by the action of mercuric chloride–mercuric oxide in acetonitrile. Glycosylation of benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside with **2**, and subsequent *O*-deacetylation at O-4′ gave a glycosyl acceptor, benzyl 2-acetamido-4-*O*-[2-acetamido-6-*O*-benzyl-3-*O*-(2-butenyl)-2-deoxy-β-D-glucopyranosyl]-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside.

INTRODUCTION

As part of our studies of bacterial cell-wall constituents as immunologic adjuvants devoid of the deleterious side-effects of Freund's Complete Adjuvant, synthetic *O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-*O*-(*N*-acetyl-β-muramoyl-L-alanyl-D-isoglutamine)-(1→4)-2-acetamido-2-deoxy-D-glucopyranose (**1**), the repeating trisaccharide dipeptide unit of the bacterial cell-wall peptidoglycan, was needed, in order to assist in the identification of the minimal, structural components for the

*Bacterial Cell-Wall Constituents, Part IV. For Part III, see ref. 1.
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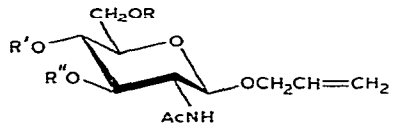
examined. Attempts at partial benzylation of the 6-hydroxyl group with α-bromotoluene in *N*,*N*-dimethylformamide in the presence of barium oxide and barium hydroxide led to the formation not only of the desired 6-benzyl ether 4-ol (**6**), but also, in similar amount (as estimated by t.l.c. on silica gel), the positionally isomeric 4-benzyl ether 6-ol (**7**), as well as some 4,6-dibenzyl ether (**8**). The lack of regioselectivity in this particular reaction was surprising, in view of results obtained with several related substrates, namely, benzyl 2-acetamido-3-*O*-allyl-2-deoxy-α-D-glucopyranoside[1,19], benzyl 2-acetamido-3-*O*-benzyl-2-deoxy-α-D-glucopyranoside[20], 6-(benzyloxycarbonylamino)hexyl 2-acetamido-3-*O*-benzyl-2-deoxy-β-D-glucopyranoside[21], and allyl 2-acetamido-3-*O*-benzyl-2-deoxy-α- and -β-D-glucopyranoside[7,8], with which only minimal proportions of their respective 4-benzyl ether 6-ol were obtained.



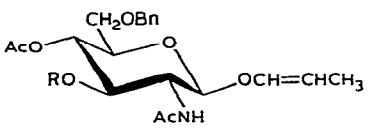
5 R = R' = H, R" = $CH_2CH{=}CHCH_3$
6 R = Bn, R' = H, R" = $CH_2CH{=}CHCH_3$
7 R = H, R' = Bn, R" = $CH_2CH{=}CHCH_3$
8 R = R' = Bn, R" = $CH_2CH{=}CHCH_3$
9 R = CPh_3, R' = Bn, R" = $CH_2CH{=}CHCH_3$
10 R = Bn, R' = Ac, R" = $CH_2CH{=}CHCH_3$

Isolation of the two monobenzyl ethers, **6** and **7**, was efficiently effected by treatment of the crude mixture of benzylation products with chlorotriphenylmethane in pyridine, which resulted in selective tritylation of the primary hydroxyl group in **7**, to give a mixture (in order of decreasing mobility in t.l.c.) of the 4-benzyl-6-trityl ether **9**, the 4,6-dibenzyl ether **8**, and the desired 6-benzyl ether 4-ol **6**, that was resolved by column chromatography on silica gel. Treatment of **9** with hydrogen bromide in acetic acid afforded allyl 2-acetamido-4-*O*-benzyl-3-*O*-(2-butenyl)-2-deoxy-β-D-glucopyranoside (**7**). Assignment of structure to the two monobenzyl ethers, **6** and **7**, was made on the basis of their reactivity toward chlorotriphenylmethane (as just discussed) and their 300-MHz, ^{1}H-n.m.r. spectra (in particular, the extent to which the n.m.r. signals for the benzylic methylene, diastereotopic protons are different is significantly greater for isomer **7**, which has the benzyl ether group more proximate to a chiral center). The observed reactivity of the 6-hydroxyl group in **7** toward chlorotriphenylmethane in pyridine may be contrasted with the reported inertness of two related substrates, allyl 2-acetamido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside[6] and 6-(benzyloxycarbonylamino)hexyl 2-acetamido-3,4-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside[21].

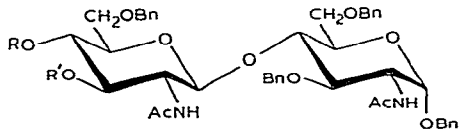
Allyl 2-acetamido-6-*O*-benzyl-3-*O*-(2-butenyl)-2-deoxy-β-D-glucopyranoside (**6**) was obtained in 33% yield, and was converted with acetic anhydride in pyridine into

the fully protected allyl 2-acetamido-4-*O*-acetyl-6-*O*-benzyl-3-*O*-(2-butenyl)-2-deoxy-β-D-glucopyranoside (**10**). Treatment of **10** with chlorotris(triphenylphosphine)-rhodium(I) gave mainly the corresponding 1-propenyl β-glycoside **11**, as a mixture of the *cis*- and *trans*-isomers (as indicated by the 300-MHz, ^{1}H-n.m.r. spectrum). The yield of the isomerization was found to improve when the reaction was performed with <10mM substrate **10**. The 1-propenyl glycoside **11** was converted into 2-methyl-[2-acetamido-4-*O*-acetyl-6-*O*-benzyl-3-*O*-(2-butenyl)-1,2-dideoxy-α-D-glucopyrano]-[2,1-*d*]-2-oxazoline (**2**) by the mercuric ion-catalyzed procedure developed by Anderson and co-workers (mercuric chloride and mercuric oxide in acetonitrile)[10,11]. The oxazoline structure of **2** was supported by its 300-MHz, ^{1}H-n.m.r. spectrum (δ 6.02 for the anomeric proton, with $J_{1,2}$ 7.5 Hz, and 2.06 for the 2-methyl protons, with $^5J_{2,CH_3}$ 1.7 Hz).

The glycosylating potential of oxazoline **2** was indicated by its reaction with benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside[20] in 1,2-dichloroethane in the presence of *p*-toluenesulfonic acid, to afford, in 31% yield, the completely substituted disaccharide, namely benzyl 2-acetamido-4-*O*-[2-acetamido-4-*O*-acetyl-6-*O*-benzyl-3-*O*-(2-butenyl)-2-deoxy-β-D-glucopyranosyl]-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside (**12**). The 4-hydroxyl group at the nonreducing end of **12** was selectively deprotected with sodium methoxide in methanol, to give the potential glycosyl acceptor, benzyl 2-acetamido-4-*O*-[2-acetamido-6-*O*-benzyl-3-*O*-(2-butenyl)-2-deoxy-β-D-glucopyranosyl]-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside (**13**).



11 R = $CH_2CH{=}CHCH_3$



12 R = Ac, R' = $CH_2CH{=}CHCH_3$
13 R = H, R' = $CH_2CH{=}CHCH_3$

EXPERIMENTAL

General methods. — Solutions were evaporated below 50° under diminished pressure. Melting points were determined with a Thomas–Hoover "Unimelt" apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer Model 241 polarimeter. ^{1}H-N.m.r. spectra were recorded at 300 MHz with a Varian SC-300 n.m.r. spectrometer. Chemical shifts are given on the δ scale. Spectra were measured at ambient temperature for solutions in chloroform-*d*, with tetramethylsilane (δ = 0.00) as the internal standard. Spectra were analyzed on a first-order basis. T.l.c. was performed on plates (250 μm) of Silica Gel GF_{254} (Analtech), and indication was effected with ultraviolet light, a ceric sulfate (1%)–sulfuric acid (10%) spray, or a 1:1:18 (v/v) anisaldehyde–sulfuric acid–ethanol spray[6,7,22]. Gravity column-chromatography was conducted with silica gel No. 7734 (E. Merck: 70–230 mesh). Preparative h.p.l.c. was performed on dual Prep-PAK™ 500 silica

columns using a Waters Associates Prep LC/System 500. Acetonitrile and 1,2-dichloromethane were dried by distillation over phosphorus pentaoxide, and stored over activated[23] 3A molecular sieves. *N,N*-Dimethylformamide was dried by sequential treatment with 3A molecular sieves[24]. Petroleum ether refers to a fraction having b.p. 35–60°.

Allyl 2-acetamido-4,6-O-benzylidene-3-O-(2-butenyl)-2-deoxy-β-D-glucopyranoside (**4**). — To a solution of allyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside[8,14] (**3**; 64.8 g, 185 mmol) in dry *N,N*-dimethylformamide (500 mL) were successively added barium oxide (124 g), barium hydroxide octahydrate (37 g), and crotyl bromide (38.5 mL, 374 mmol). The mixture was mechanically stirred for 30 min at room temperature (formation of a thick gel occurred!), diluted with chloroform (3.5 L), washed successively with 60% acetic acid (600 mL), water, saturated aqueous sodium hydrogencarbonate, and water, dried (potassium carbonate), and evaporated, to afford the 3-(2-butenyl) ether **4** as a chromatographically homogeneous solid; yield 67.3 g (90%). An analytical sample was obtained by recrystallization from methanol: m.p. 234–237° (dec.), $[\alpha]_D^{27}$ −19° (*c* 1.4, chloroform), {lit.[11] m.p. 230–245° (dec.), $[\alpha]_D^{25}$ −16.6° (*c* 1.1, chloroform)}: ^{1}H-n.m.r. data: δ 5.53 (s, benzylic H), 5.29 [d, =CH(*t*), $J_{2,3(allyl)}$ 17 Hz], 5.21 [d, =CH(*c*), $J_{2,3(allyl)}$ 11 Hz], 5.16 (d, $J_{1,2}$ 8.3 Hz, H-1), 1.99 (s, 3 H, NHAc), and 1.68 (broadened d, $OCH_2CH=CHCH_3$).

Anal. Calc. for $C_{22}H_{29}NO_6 \cdot 0.25\ H_2O$ (407.99): C, 64.77; H, 7.29; N, 3.43. Found: C, 65.01; H, 7.28; N, 3.71.

Allyl 2-acetamido-3-O-(2-butenyl)-2-deoxy-β-D-glucopyranoside (**5**). — A mixture of **4** (67.2 g, 167 mmol) and 60% acetic acid (1.2 L) was stirred for 2 h at 80°, and the resulting solution was cooled, evaporated, and coevaporated several times with toluene, to afford pure diol **5** as a crystalline solid; yield 48.7 g (93%). An analytical sample was obtained by recrystallization from acetone–hexane; m.p. 178–179°, $[\alpha]_D^{27}$ −39.5° (*c* 1, methanol), {lit.[11] m.p. 168–169.5°, $[\alpha]_D^{25}$ −33.3° (*c* 0.88, ethanol)}: ^{1}H-n.m.r. data: δ 5.28 [d, =CH(*t*), $J_{2,3(allyl)}$ 17 Hz], 5.20 [d, =CH(*c*), $J_{2,3(allyl)}$ 10.5 Hz], 4.99 (d, $J_{1,2}$ 8.4 Hz, H-1), 2.54 (d, OH-4), 2.11 (t, OH-6), 1.99 (s, 3 H, NHAc), and 1.72 (broadened d, $OCH_2CH=CHCH_3$).

Anal. Calc. for $C_{15}H_{25}NO_6 \cdot 0.25\ H_2O$ (319.89): C, 56.32; H, 8.04; N, 4.38. Found: C, 56.66; H, 8.19; N, 4.13.

Partial benzylation of **5**. — To a solution of diol **5** (48.7 g, 154 mmol) in dry *N,N*-dimethylformamide (300 mL) were successively added barium oxide (108 g), barium hydroxide octahydrate (25.6 g), and α-bromotoluene (27.5 mL, 231 mmol), and the mixture was stirred overnight at room temperature, diluted with chloroform (2.5 L), washed successively with 60% acetic acid (600 mL), water, saturated aqueous sodium hydrogencarbonate, and water, dried (sodium sulfate), and evaporated, to give a crude product mixture (51.5 g) that was dissolved in pyridine (85 mL) and treated with chlorotriphenylmethane (21.2 g, 76 mmol) for 62 h at room temperature. The solution was evaporated to a syrup that was extracted with diethyl ether (2 × 350 mL), and taken up in dichloromethane; undissolved solids were removed by

filtration, and the filtrate was concentrated to a small volume that was applied to a column of silica gel (1 kg). Elution with dichloromethane, followed by 10:1 and 5:1 dichloromethane–diethyl ether, and, finally, 30:20:1 dichloromethane–diethyl ether–methanol, afforded the following fractions (in order of decreasing mobility in t.l.c., with 1:1 dichloromethane–diethyl ether as the eluant): (*1*) allyl 2-acetamido-4-*O*-benzyl-3-*O*-(2-butenyl)-2-deoxy-6-*O*-trityl-β-D-glucopyranoside (**9**) (13.9 g); (*2*) a mixture (4.5 g) of **9** and allyl 2-acetamido-4,6-di-*O*-benzyl-3-*O*-(2-butenyl)-2-deoxy-β-D-glucopyranoside (**8**); (*3*) compound **8** (2.3 g); and (*4*) allyl 2-acetamido-6-*O*-benzyl-3-*O*-(2-butenyl)-2-deoxy-β-D-glucopyranoside (**6**) as a crystalline solid: yield 20.5 g (33%). An analytical sample was obtained by recrystallization from ethyl acetate–hexane: m.p. 137.5–139°, $[\alpha]_D^{27}$ −23° (*c* 1.2, chloroform); ^{1}H-n.m.r. data: δ 5.26 [d, =CH(*t*), $J_{2,3(allyl)}$ 17 Hz], 5.20 [d, =CH(*c*), $J_{2,3(allyl)}$ 11 Hz], 4.98 (d, H-1), 4.59 (AB q, 2 H, OC*H*$_2$Ph), 2.78 (d, OH-4), 1.98 (s, 3 H, NHAc), and 1.70 (broadened d, $OCH_2CH{=}CHCH_3$).

Anal. Calc. for $C_{22}H_{31}NO_6$ (405.5): C, 65.16; H, 7.71; N, 3.45. Found: C, 64.83; H, 7.76; N, 3.71.

*Allyl 2-acetamido-4-*O*-benzyl-3-*O*-(2-butenyl)-2-deoxy-β-*D*-glucopyranoside* (**7**). — This compound was obtained by treatment of a solution of the 6-trityl ether **9** in glacial acetic acid with 31% hydrogen bromide in acetic acid. After the usual detritylation processing[25], chromatography of the residue on a column of silica gel, with 1:1 dichloromethane–diethyl ether as the eluant, afforded **7** as a crystalline solid; m.p. 185–186.5°, $[\alpha]_D^{27}$ +1.6° (*c* 1.2, chloroform); ^{1}H-n.m.r. data: δ 5.28 [d, =CH(*t*)], 5.19 [d, =CH(*c*)], 4.96 (d, H-1), 4.85 (d, 1 H, OC*H*Ph), 4.65 (d, 1 H, OC*H*Ph), 1.98 (s, 3 H, NHAc), and 1.69 (d, $OCH_2CH{=}CHCH_3$).

Anal. Calc. for $C_{22}H_{31}NO_6$ (405.5): C, 65.16; H, 7.71; N, 3.45. Found: C, 65.18; H, 7.95; N, 3.17.

*Allyl 2-acetamido-4-*O*-acetyl-6-*O*-benzyl-3-*O*-(2-butenyl)-2-deoxy-β-*D*-glucopyranoside* (**10**). — To a solution of **6** (13.9 g, 34.3 mmol) in pyridine (30 mL) at 0° was added acetic anhydride (15 mL). After 3.5 h at 0°, the mixture was evaporated, and the residue coevaporated several times with toluene. The resulting solid was dried *in vacuo*, to afford a quantitative yield (15.3 g) of the 4-acetate **10**. A sample was recrystallized from methanol–diethyl ether–petroleum ether: m.p. 137.5–140°, $[\alpha]_D^{27}$ +15.4° (*c* 1.2, chloroform); ^{1}H-n.m.r. data: δ 5.29 [d, =CH(*t*)], 5.20 [d, =CH(*c*)], 5.10 (d, $J_{1,2}$ 8.2 Hz, H-1), 4.91 (t, $J_{3,4} = J_{4,5}$ = 9.2 Hz, H-4), 4.53 (s, 2 H, OC*H*$_2$Ph), 1.98 (s, 6 H, OAc and NHAc), and 1.69 (d, $OCH_2CH{=}CHCH_3$).

Anal. Calc. for $C_{24}H_{33}NO_7$ (447.53): C, 64.41; H, 7.43; N, 3.13. Found: C, 64.05; H, 7.70; N, 3.31.

*1-Propenyl 2-acetamido-4-*O*-acetyl-6-*O*-benzyl-3-*O*-(2-butenyl)-2-deoxy-β-*D*-glucopyranoside* (**11**). — To a solution of **10** (2.9 g, 6.5 mmol) in 7:3:1 ethanol–toluene–water (100 mL) were added, under nitrogen, 1,4-diazabicyclo[2.2.2]octane (725 mg, 6.5 mmol) and chlorotris(triphenylphosphine)rhodium(I) (100 mg). The mixture was boiled under reflux for 1 h under a nitrogen atmosphere, at which time a second addition of the Wilkinson catalyst (50 mg) was made; refluxing was continued

for 1 h, and the mixture was allowed to cool. This process was repeated four more times on the same scale (4 × 2.9 g of **10**), so that a total of 14.5 g of allyl β-glycoside **10** was treated. The reaction mixtures were combined, and evaporated, the residue was taken up in chloroform (300 mL), and the solution was washed successively with saturated aqueous potassium chloride, 0.1M hydrochloric acid (500 mL), and saturated aqueous potassium chloride, dried (sodium sulfate), and evaporated to a syrup that was dissolved in the minimal volume of 5:1 dichloromethane–diethyl ether, and subjected to purification by h.p.l.c. on silica gel, with 5:1 dichloromethane–diethyl ether as the eluant; yield 8.8 g (61%). A sample crystallized from toluene–hexane; m.p. 130–133°, $[\alpha]_D^{27}$ +26.5° (*c* 1.2, chloroform).

Anal. Calc. for $C_{24}H_{33}NO_7$ (447.53): C, 64.41; H, 7.43; N, 3.13. Found: C, 64.51; H, 7.39; N, 2.96.

2-Methyl-[2-acetamido-4-O-acetyl-6-O-benzyl-3-O-(2-butenyl)-1,2-dideoxy-α-D-glucopyrano]-[2,1-d]-2-oxazoline (**2**). — To a solution of **11** (7.3 g, 16.3 mmol) in acetonitrile (125 mL) were added, under a nitrogen atmosphere, mercuric chloride (6.38 g, 23.5 mmol) and yellow mercuric oxide (6.45 g, 29.8 mmol); the mixture was stirred under nitrogen for 5 h at room temperature, filtered through Celite, and the filtrate evaporated. The residue was taken up in dichloromethane, the suspension filtered through Celite, and the filtrate washed twice with saturated aqueous potassium iodide and twice with water, dried (sodium sulfate), and evaporated; the residue was subjected to purification by h.p.l.c. on a column of silica gel (pretreated with 9:1 diethyl ether–triethylamine and then equilibrated with 5:1 diethyl ether–dichloromethane containing 0.2% of triethylamine). Elution with the latter solvent-system gave chromatographically homogeneous (t.l.c. on silica gel with diethyl ether as the eluant) oxazoline **2** as a syrup; yield 3.2 g (50%); $[\alpha]_D^{27}$ +11.9° (*c* 2, chloroform); ^{1}H-n.m.r. data: δ 6.02 (d, $J_{1,2}$ 7.5 Hz), 4.58 (s, 2 H, OCH_2Ph), 2.06 (d, J_{2,CH_3} 1.7 Hz, C-CH_3), 2.00 (s, 3 H, NHAc), and 1.70 (d, $OCH_2CH{=}CHCH_3$).

Anal. Calc. for $C_{21}H_{27}NO_6$ (389.46): C, 64.76; H, 6.99; N, 3.60. Found: C, 64.58; H, 7.09; N, 3.49.

Benzyl 2-acetamido-4-O-[2-acetamido-4-O-acetyl-6-O-benzyl-3-O-(2-butenyl)-2-deoxy-β-D-glucopyranosyl]-3,6-di-O-benzyl-2-deoxy-α-D-glucopyranoside (**12**). — To a solution of oxazoline **2** (1.32 g, 3.39 mmol) in 1,2-dichloroethane (15 mL) was added benzyl 2-acetamido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside[20] (1.63 g, 3.32 mmol). A nitrogen atmosphere was then introduced, *p*-toluenesulfonic acid (27.6 mg) was added, and the mixture was heated under nitrogen for 3 h at 75°, at which time a second addition of **2** (1.34 g, 3.44 mmol) was made, and heating at 75° was continued for 9 h. The mixture was cooled, and evaporated, and the residue was treated overnight with acetic anhydride and pyridine, the solution evaporated, and the residue co-evaporated several times with toluene, dissolved in a small volume of chloroform, and the solution applied to a column of silica gel (320 g, packed as a slurry in 5:1 chloroform–diethyl ether) that was eluted with 3:1 chloroform–diethyl ether. Combination and evaporation of the appropriate fractions afforded pure, protected disaccharide **12** as a white solid; yield 910 mg (31.2%). A sample was

recrystallized from ethanol; m.p. 217–218°, $[\alpha]_D^{27}$ +64° (*c* 0.9, chloroform): ^{1}H-n.m.r. data: δ 4.94 (d, $J_{1,2}$ 3.8 Hz, H-1), 1.95, 1.84, and 1.76 (3 s, 9 H, 2 NHAc and 1 OAc), and 1.70 (d, $OCH_2CH{=}CHCH_3$).

Anal. Calc. for $C_{50}H_{60}N_2O_{12}$ (881.04): C, 68.16; H, 6.86; N, 3.18. Found: C, 68.09; H, 6.84; N, 2.90.

*Benzyl 2-acetamido-4-*O*-[2-acetamido-6-*O*-benzyl-3-*O*-(2-butenyl)-2-deoxy-β-*D*-glucopyranosyl]-3,6-di-*O*-benzyl-2-deoxy-α-*D*-glucopyranoside* (**13**). — To a mixture of **12** (850 mg, 0.96 mmol) in methanol (200 mL) was added a catalytic amount of sodium methoxide. After being kept overnight at room temperature, the mixture was made neutral with Bio-Rad AG 50W X4 (H^+) ion-exchange resin, the suspension filtered, and the filtrate evaporated to a solid; yield 757 mg (93%); m.p. 195–206° (dec.), $[\alpha]_D^{27}$ +53° (*c* 0.8, chloroform); ^{1}H-n.m.r. data: δ 4.93 (d, $J_{1,2}$ 3.8 Hz, H-1), 1.83 and 1.75 (2 s, each 3 H, 2 NHAc), and 1.72 (d, $OCH_2CH{=}CHCH_3$).

Anal. Calc. for $C_{48}H_{58}N_2O_{11} \cdot 0.5\ H_2O$ (848.01): C, 67.99; H, 7.01; N, 3.30. Found: C, 68.04; H, 7.00; N, 3.50.

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