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Synthesis of 6-amino-1,6-anhydro-6-deoxysugar derivatives

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Abstract

Staudinger reaction of triphenylphosphine with 2,3,4-tri-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-β-D-glycopyranosyl azides led to an anomeric iminophosphorane which rearranged in situ by elimination of the sulfonate at C-6. The 1,6-anhydro-6-deoxy-6-triphenylphosphonioamino-β-D-glycopyranose salts thus obtained were transformed into the corresponding 2,3,4-tri-*O*-acetyl-6-amino-1,6-anhydro-6-deoxy-β-D-glycopyranoses which were further *N*-acylated or *N*-alkoxycarbonylated. ^{1}H and ^{13}C NMR of these products show the occurrence of two rotamers in solution, due to restricted rotations around the amide bond.

Keywords: 6-*O*-*p*-tolylsulfonyl-β-D-glycosyl azide ; Staudinger reaction ; 6-Amino-1,6-anhydro-6-deoxy-β-D-glycopyranose derivatives

1. Introduction

Only a few examples of 6-amino-1,6-anhydro-6-deoxy sugars have been described in the literature. Thus, treatment of 6-amino-6-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose in acidic conditions led to an acyclic derivative, which was transformed under basic conditions into 6-amino-6-deoxy-L-idopyranose. The latter underwent a spontaneous and practically quantitative dehydratation into 6-amino-1,6-anhydro-6-deoxy-β-L-idopyranose [1–4]. The anhydro ring closure was evidently favored by the stereochemistry of the hydroxyl groups in equatorial position. Under the same conditions, a similar transformation was not observed in the D-*gluco* and D-*galacto* series since, in this case, a conformational inversion would be necessary to obtain the anhydro derivative [4]. Recently, Pradera et al. showed that a 6-amino-1,6-anhydro-6-deoxy-2,3,4-tri-*O*-mesyl-β-D-glucopyranose derivative could be prepared by treatment of *N*-diethoxycarbonylvinyl-2,3,4,6-tetra-*O*-mesyl-β-D-glucopyranosylamine under basic conditions [5]. The attack of the nitrogen atom was regiospecific at the 6-position. With 2,3,6-tri-*O*-acyl-*N*-diethoxycarbonylvinyl-4-*O*-mesyl-glycopyranosylamines, syntheses of *O*-protected 4-deoxy-4-diethoxycarbonylvinylaminoaldoses were also possible, through nucleophilic substitution of the mesyloxy group at *C*-4 with inversion of configuration [6].

In our previous papers on β-glycosylation in the 2-amino-2-deoxy-D-glucose and lactosamine series, starting from 1,2-*trans*-2-deoxy-2-iodo-α-D-glyco-

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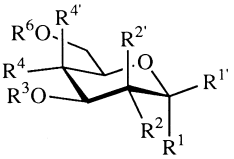
pyranosyl azides [7,8], β-glycosides were obtained by the Staudinger reaction of the azido function with triphenylphosphine [9]. Nucleophilic attack of the nitrogen at C-2 led to an unstable aziridine intermediate, which was opened by the alcohol at the anomeric position. A further application of the Staudinger reaction towards the synthesis of 6-amino-1,6-anhydro-6-deoxysugar derivatives (D-*gluco*, D-*galacto* and D-*manno* series) is reported in the present paper.

2. Results and discussion

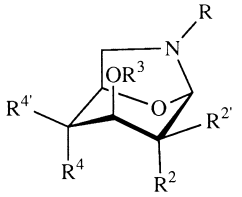
Reaction of azido sugars or glycosyl azides and their corresponding imino-phosphoranes has already been reported in the literature [8,10–15]. Due to their ylide structure, in which the nitrogen atom is negatively charged, sugar iminophosphoranes are strong nucleophiles which could intramolecularly substitute a 6-*O*-*p*-tolylsulfonyl group in the same way as an anomeric hydroxyl group [16] or mercapto group [17], leading to 1,6-anhydro derivatives.

Therefore, 2,3,4-tri-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-β-D-gluco- and galactopyranosyl azides **3** and **4** were prepared in two steps from 1,2,3,4-tetra-*O*-acetyl-6-*O*-*p*-tolyl-sulfonyl-D-gluco- and D-galactopyranose **1** [18] and **2** [19], by treatment with 33% hydrogen bromide in acetic acid and transformation of the glycosyl bromides into glycosyl azides by phase transfer catalysis in the presence of sodium azide according to Roy et al. [20]. 2,3,4-Tri-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-β-D-mannopyranosyl azide **6** was synthesized in three steps from 2,3,4,6-tetra-*O*-benzoyl-β-D-mannopyranosyl azide **5** [21], (i.e. debenzoylation according to Zemplén, regioselective tosylation of the 6-OH and acetylation) in a 56% overall yield. Treatment of the azides **3**, **4** or **6** with a slight excess of triphenylphosphine (1.05 equiv) in dichloromethane afforded quantitatively the expected 2,3,4-tri-*O*-acetyl-1,6-anhydro-6-deoxy-6-triphenylphosphonioamino-β-D-glycopyranose *p*-tolylsulfonates **7**, **8** and **9**. The structure of these salts was evidenced from ^{1}H-, ^{13}C- and ^{31}P NMR spectra; thus, ^{1}H NMR couplings values were characteristic of a $^{1}C_4$ (D) conformation as in 1,6-anhydrosugar derivatives [22,23], and the presence of the C-6–N–C-1 bridge was ascertained by ^{1}H NMR couplings $J_{H,P}$ ($J_{1,P}$ 8.3–8.7 Hz, $J_{6b,P}$ 10–13 Hz) and ^{13}C chemical shift for C-6 (δ 48.34–49.67 ppm). The formation of phosphonioamino salts was also supported by the ^{31}P chemical shifts (δ 43.26–45.69) and by the coupling constants $J_{C,P}$ for C_{ipso}, C_{ortho}, C_{meta} and C_{para} of the triphenyl-phosphonio moiety [8,24,25]. The salts **7–9** were transformed into the crude 3,4,6-tri-*O*-acetyl-6-amino-1,6-anhydro-6-deoxy-β-D-glycopyranoses **10–12** by anionic exchange of the anion [Dowex 2X8 (OH^-) column in dichloromethane] via the phosphonioamino hydroxide derivative, which rearranged immediately, affording triphenylphosphine oxide as by-product. These derivatives were not isolable by column chromatography and were used directly for *N*-protection reactions. Futhermore, ^{1}H NMR of **12** displayed a second *N*-acetylated product **13**, resulting from the O– > N migration of the O-2 acetyl group. This was confirmed by peracetylation of the mixture, which afforded **16** only. ^{1}H and ^{13}C NMR signals of derivatives **10** and **11** were fully assigned at 500 MHz in hexadeuteroacetone, using NOESY and ^{1}H–^{13}C 2D experiments. ROESY [26] was also necessary for **10** in which most of the vicinal and long-range coupling constants were of the same order of magnitude [22,23].



1 $R^1, R^{1'}$ = OAc ,H, $R^2 = R^4$ = OAc, R^3 = Ac, R^6 = Ts, $R^{2'} = R^{4'}$ = H
2 $R^1, R^{1'}$ = OAc, H, $R^2 = R^{4'}$ = OAc, R^3 = Ac, R^6 = Ts, $R^{2'} = R^4$ = H
3 $R^{1'} = N_3$, $R^2 = R^4$ = OAc, R^3 = Ac, R^6 = Ts, $R^1 = R^{2'} = R^{4'}$ = H
4 $R^{1'} = N_3$, $R^2 = R^{4'}$ = OAc, R^3 = Ac, R^6 = Ts, $R^1 = R^{2'} = R^4$ = H
5 $R^{1'} = N_3$, $R^{2'} = R^4$ = OBz, $R^3 = R^6$ = Bz, $R^1 = R^2 = R^{4'}$ = H,
6 $R^{1'} = N_3$, $R^{2'} = R^4$ = OAc, R^3 = Ac, R^6 = Ts, $R^1 = R^2 = R^{4'}$ = H

N-Acylation of the crude derivatives **10,11** and the mixture **12,13** (pyridine/acetic anhydride) gave the pure 6-acetamido-2,3,4-tri-*O*-acetyl-1,6-anhydro-6-deoxy-β-D-glycopyranoses **14–16** in high yields. ^{1}H NMR spectra of **14,15** and **16** in deuterochloroform revealed the presence of two conformers, the proportions of which were dependent of their structures (**14**: 52/48, **15**: 55/45, **16**: 43/57). This could be due to restricted rotations around the amide bond [1,27–30]. On increasing the temperature, in hexadeuterodimethyl-sulfoxide, the signals coalescence was observed above 115 °C for compound **14**. The presence of two rotamers was also confirmed by the ^{13}C NMR spectra of derivatives **14–16**.



7 $R^2 = R^4 = OAc$, $R^{2'} = R^{4'} = H$, $R^3 = Ac$, $R = PPh_3^+, TsO^-$
8 $R^2 = R^{4'} = OAc$, $R^{2'} = R^4 = H$, $R^3 = Ac$, $R = PPh_3^+, TsO^-$
9 $R^{2'} = R^4 = OAc$, $R^2 = R^{4'} = H$, $R^3 = Ac$, $R = PPh_3^+, TsO^-$
10 $R^2 = R^4 = OAc$, $R^{2'} = R^{4'} = R = H$, $R^3 = Ac$
11 $R^2 = R^{4'} = OAc$, $R^{2'} = R^4 = R = H$, $R^3 = Ac$
12 $R^{2'} = R^4 = OAc$, $R^2 = R^{4'} = R = H$, $R^3 = Ac$
13 $R^{2'} = OH$, $R^4 = OAc$, $R^2 = R^{4'} = H$, $R = Ac$
14 $R^2 = R^4 = OAc$, $R^{2'} = R^{4'} = H$, $R = R^3 = Ac$
15 $R^2 = R^{4'} = OAc$, $R^{2'} = R^4 = H$, $R = R^3 = Ac$
16 $R^{2'} = R^4 = OAc$, $R^2 = R^{4'} = H$, $R = R^3 = Ac$
17 $R^2 = R^4 = OAc$, $R^{2'} = R^{4'} = H$, $R^3 = Ac$, $R = COOMe$
18 $R^2 = R^4 = OAc$, $R^{2'} = R^{4'} = H$, $R^3 = Ac$, $R = COOAll$
19 $R^2 = R^4 = OAc$, $R^{2'} = R^{4'} = H$, $R^3 = Ac$, $R = COC_{13}H_{27}$
20 $R^2 = R^4 = OAc$, $R^{2'} = R^{4'} = H$, $R^3 = Ac$, $R = COC_7H_{15}$
21 $R^2 = R^4 = OH$, $R^{2'} = R^{4'} = R^3 = H$, $R = COC_{13}H_{27}$
22 $R^2 = R^4 = OH$, $R^{2'} = R^{4'} = H$, $R^3 = H$, $R = COC_7H_{15}$

Since 6-*N*-acyl-6-amino-1,6-anhydro-6-deoxy-β-D-glycopyranoses could find applications in the field of detergents, liquid crystals or surface-active complexing agents, crude compound **10** was alkoxycarbonylated or acylated. Thus, reaction of **10** in pyridine with an excess of alkyl chloroformate (methyl or allyl chloroformate) or acyl chloride (octanoyl or tetradecanoyl chloride) afforded the expected carbamates **17,18** and amides **19** and **20** in good to high yields. As for acetamide derivatives, ^1H and ^{13}C NMR spectra of the carbamates also dispalyed the presence of two rotamers at room temperature. Product **19** and **20** were deacetylated by the Zemplén procedure, and solubility in water of the deprotected sugars **21** and **22** was determined. 1,6-Anhydro-6-deoxy-6-tetradecanoyl-amino-β-D-glucopyranose (**21**) was insoluble in water, contrary to 1,6-anhydro-6-deoxy-6-octanoylamino-β-D-glucopyranose (**22**). Krafft temperature of **22** was shown to be below 20 °C and the surface tension (γ) measurements were carried out by the ring method of Lecomte du Nouÿ [31] and corrected according to Harkins and Jordan [32]. Measurements were performed at room temperature (20 °C) and the cmc was determined at the break of the slope in the γ versus log[C] plots, as usual. The interfacial area per molecule (*ao*) was calculated for concentrations just below the cmc according to the Gibbs law. The experimental values thus determined were, respectively, 0.019 mM for the cmc, 30.5 $mN \cdot m^{-1}$ for γ at the interface and 39 $Å^2$ for a_o. The cmc value was very close to that found for octyl β-D-glucopyranoside [33], but a_o was smaller (49 $Å^2$ for octyl β-D-glucopyranoside [34]), which could indicate a lower hydratation of the carbohydrate head.

In conclusion, application of the Staudinger reaction to 6-*O*-*p*-tolylsulfonyl-2,3,4-tri-*O*-acetyl-β-D-glycopyranosyl azides allowed the formation of 6-amino-1,6-anhydro-6-deoxy-β-D-glycopyranose derivatives, which could be *N*-alkoxycarbonylated or *N*-acylated. This methodology is short and efficient, and well suited for the preparation of new surfactants.

2. Experimental

General methods.—Pyridine was dried by boiling with CaH_2 prior to distillation. Dichloromethane was washed twice with water, dried with $CaCl_2$ and distilled from CaH_2. Methanol was refluxed with NaOMe before distillation. Pyridine and CH_2Cl_2 were stored over 4 Å molecular sieves and MeOH over 3 Å molecular sieves. Melting points were determined on a Büchi apparatus and were uncorrected. Thin layer chromatography was performed on aluminium sheets coated with Silica Gel 60 F_{254} (E. Merck). Compounds were visualized by spraying the TLC plates with dilute 15% aq H_2SO_4, followed by charring at 150 °C for a few min. Column chromatography was performed on Silica-gel Geduran Si 60 (E. Merck). Optical rotations were recorded on a Perkin–Elmer 241 polarimeter in a 1 dm cell at 21 °C. ^1H and ^{13}C NMR spectra were recorded with Bruker AC-200, AM-300 or DRX-500 spectrometers working at 200, 300 or 500 MHz and 50, 75.5 or 125 MHz, respectively, with Me_4Si as internal standard. Elemental analyses were performed by the "Laboratoire Central d'Analyses du CNRS" (Vernaison, France).

2,3,4-Tri-O-*acetyl-6*-O-p-*tolylsulfonyl*-β-D-*glucopyranosyl azide* (**3**).—1,2,3,4-Tetra-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-α,β-D-glucopyranose (**1**) [18] (4.50 g, 8.95 mmol) in CH_2Cl_2 (5 mL) was treated with 33% HBr in AcOH (12 mL). After 1.5 h, the mixture was concentrated, the residue was dissolved in $CHCl_3$ (100 mL), the organic phase was washed with cooled aq $NaHCO_3$, then with water, dried and concentrated again. To a soln of this glucosyl bromide (8.95 mmol), Bu_4NHSO_4 (3.04 g, 8.95 mmol, 1 equiv.) and NaN_3 (2.33 g, 4 equiv) in

CH_2Cl_2 (50 mL), was added satd aq $NaHCO_3$ (50 mL); the two phase mixture was vigorously stirred for 2 h; addition of EtOAc (450 mL), washing of the organic phase with aq $NaHCO_3$ (2×100 mL), then with brine (100 mL), drying and concentration afforded the crude product **2** which was recrystallized twice from absolute EtOH: 3.13 g, yield 72%; mp 129–130 °C (lit [35]. mp 128–130 °C); $[\alpha]_D$ +19.0° (*c* 1.0, $CHCl_3$); R_f 0.70 (1:1 EtOAc–petroleum ether).

2,3,4-Tri-O-*acetyl-6*-O-*tosyl*-β-D-*galactopyranosyl azide* (**4**).—Prepared in 75% yield, as described previously from 1,2,3,4-tetra-*O*-acetyl-6-*O*-tosyl-α,β-D-galactopyranose (**2**) [19]; mp 94 °C (EtOH) [lit [35] mp 92–94 °C (diethyl ether)]; $[\alpha]_D$ −16.3° (*c* 1.0, $CHCl_3$); R_f 0.70 (1:1 EtOAc–petroleum ether).

2,3,4-Tri-O-*acetyl-6*-O-p-*tolysulfonyl*-β-D-*manno-pyranosyl azide* (**6**).—2,3,4,6-Tetra-*O*-benzoyl-β-D-mannopyranosyl azide (**5**) [21] (4.10 g, 6.60 mmol) was treated overnight in MeOH (50 mL) containing a catalytic amount of sodium; after concentration, the residue was washed with petroleum ether (3×30 mL), dissolved in C_5H_5N (12 mL) and cooled to −12 °C; a soln of TsCl (1.67 g, 8.76 mmol, 1.32 equiv) in C_5H_5N (6 mL) was added dropwise for 1 h and the mixture was allowed to reach room temperature. Stirring was maintained overnight, then the soln was concentrated and the residue was purified by column chromatography (EtOAc) affording the 6-*O*-monosulfonate as a syrup (1.66 g, 70% yield). The latter was immediatly acetylated in a 2:1 mixture of C_5H_5N and Ac_2O (15 mL). After 16 h, concentration of the soln and column chromatography of the residue (1:1 EtOAc–petroleum ether) afforded the pure product **6** (1.79 g, 56% overall yield) as a cristalline solid: mp 128–129 °C; $[\alpha]_D$ +43.0° (*c* 1.0, $CHCl_3$); R_f 0.67 (1:1 EtOAc–petroleum ether); ^{1}H NMR ($CDCl_3$): δ 7.80 and 7.34 (2d, 4 H, *J* 8.2 Hz, CH_3-*Ph*), 5.41 (dd, 1 H, $J_{1,2}$ 1.2 Hz, $J_{2,3}$ 3.1 Hz, H-2), 5.15 (dd, 1 H, $J_{3,4}$ 10.1 Hz, $J_{4,5}$ 9.7 Hz, H-4), 5.01 (dd, 1 H, H-3), 4.64 (d, 1 H, H-1), 4.15 (d, 2 H, $J_{5,6a}$ 4.5 Hz, $J_{5,6b}$ 4.5 Hz, H-6a,6b), 3.80 (dt, 1 H, H-5), 2.45 (s, 3 H, C*H*$_3$Ph), 2.17, 2.05, 1.98 (3s, 9 H, C*H*$_3$COO); ^{13}C NMR ($CDCl_3$): δ 169.87, 169.83, 169.63 (3 C, CH_3*C*OO), 145.22 (*C*SO_2), 132.42 (*C*CH_3), 129.96 and 128.06 (4 C, *Ph*SO_2), 84.85 (C-1), 74.46, 70.72, 69.21, 65.44 (C-2,3,4,5), 67.91 (C-6), 21.66 (*C*H_3Ph), 20.67, 20.59, 20.48 (3 C, *C*H_3COO). Anal. Calcd for $C_{19}H_{23}N_3O_{10}S$ (485.46): C, 47.00; H, 4.78; N, 8.66. Found: C, 46.97; H, 4.91, N, 8.78.

General procedure for the preparation of the cyclic 1,6-anhydro-6-deoxy-6-triphenylphosphonio-amino p-*tolylsulfonates* (**7–9**).—A soln of PPh_3 (0.57–1.14 g, 2.17–4.34 mmol) in CH_2Cl_2 (2–4 mL) was added dropwise under an argon atmosphere, to a soln of the peracetylated 6-*O*-*p*-tolylsulfonyl glycosylazides **3, 4** or **6** (1.00–2.00 g, 2.06–4.12 mmol) in dry CH_2Cl_2 (6–12 mL). Evolution of nitrogen started after a few minutes and the soln was stirred overnight. After concentration, the ^{1}H NMR spectrum of the residue showed the presence of the expected product besides some traces of PPh_3 and PPh_3O, which could be removed by three successive washings with CH_2Cl_2 (1 mL) and petroleum ether (10 mL).

2,3,4-Tri-O-*acetyl-1,6-anhydro-6-deoxy-6-triphenyl-phosphonioamino*-β-D-*gluco-pyranose* p-*tolylsulfonate* (**7**).—Obtained quantitatively as described above from 2,3,4-tri-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-β-D-glucopyranosyl azide (**3**) (2.00 g, 4.12 mmol). Amorphous hygroscopic solid; $[\alpha]_D$ −12.9° (*c* 1.0, $CHCl_3$); ^{1}H NMR (CD_3COCD_3): δ 8.08–7.85 (m, 15 H, 3 *Ph*), 7.64 and 7.02 (2d, 4 H, *J* 8.2 Hz, CH_3-*Ph*), 5.67 (ddd, 1 H, $J_{1,2}$, $J_{1,3}$ 1.4 Hz, $J_{1,P}$ 8.3 Hz, H-1), 5.04 (dddd, 1 H, $J_{3,5}$, $J_{4,5}$ 1.4 Hz, $J_{5,6a}$ 1.7 Hz, $J_{5,6b}$ 6.8 Hz, H-5), 4.88 (dddd, 1 H, $J_{3,4}$, $J_{2,3}$ 1.4 Hz, H-3), 4.83 (dd, 1 H, H-4), 4.50 (dd, 1 H, H-2), 3.92 (dd, 1 H, $J_{6a,6b}$ 9.7 Hz, H-6a), 3.84 (ddd, 1 H, $J_{6b,P}$ 10.5 Hz, H-6b), 2.27 (s, 3 H, C*H*$_3$Ph), 2.20, 2.10, 1.97 (3s, 9 H, C*H*$_3$COO); ^{31}P NMR ($CDCl_3$): δ 43.69; ^{13}C NMR ($CDCl_3$): δ 169.11, 169.09, 168.46 (3 C, CH_3*C*OO), 144.55 (*C*SO_2), 137.92 (*C*CH_3), 136.06 (d, 3 C, $J_{C,P}$ 2.7 Hz, C_{para}), 133.47 (d, 6 C, $J_{C,P}$ 11.1 Hz, C_{ortho}), 130.70 (d, 6 C, $J_{C,P}$ 14.3 Hz, C_{meta}), 127.92 and 125.92 (4 C, *Ph*SO_2), 117.88 (d, 3 C, $J_{C,P}$ 101.9 Hz, C_{ipso}), 86.45 (d, $J_{C1,P}$ 3.2 Hz, C-1), 76.19 (d, $J_{C5,P}$ 6.1 Hz, C-5), 68.71 (C-4), 68.57 (d, $J_{C2,P}$ 6.5 Hz, C-2), 68.25 (C-3), 49.05 (C-6), 21.01 (Ph*C*H_3), 20.68, 20.61, 20.37 (3 C, *C*H_3COO). Anal. Calcd for $C_{37}H_{38}NO_{10}PS$, $2H_2O$ (755.76): C, 58.80; H, 5.60; N, 1.85. Found: C, 58.87; H, 5.44, N, 1.92.

2,3,4-Tri-O-*acetyl-1,6-anhydro-6-deoxy-6-triphenyl-phosphonioamino*-β-D-*galactopyranose* p-*tolylsulfonate* (**8**).—Obtained quantitatively as described above from 2,3,4-tri-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-β-D-galactopyranosyl azide (**4**) (2.00 g, 4.12 mmol). Amorphous solid; $[\alpha]_D$ +14.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR (CD_3COCD_3): δ 8.08–7.85 (m, 15 H, 3 *Ph*), 7.64 and 7.02 (2d, 4 H, *J* 8.2 Hz, CH_3-*Ph*), 5.62 (ddd, 1 H, $J_{1,2}$, $J_{1,3}$ 1.4 Hz, $J_{1,P}$ 8.4 Hz, H-1), 5.34 (dddd, 1 H, $J_{2,3}$, $J_{3,5}$ 1.4 Hz, $J_{3,4}$ 5.1 Hz, H-3), 5.24

(dd, 1 H, $J_{4,5}$ 4.4 Hz H-4), 5.02 (m, 1 H, H-5), 4.72 (dd, 1 H, H-2), 3.87 (dd, 1 H, $J_{5,6a}$ 1.5 Hz, $J_{6a,6b}$ 7.8 Hz, H-6a), 3.82 (ddd, 1 H, $J_{5,6b}$ 5.8 Hz, $J_{6b,P}$ 9.0 Hz, H-6b), 2.27 (s, 3 H, CH_3Ph), 2.18, 1.99, 1.95 (3s, 9 H, CH_3COO); ^{31}P NMR ($CDCl_3$): δ 43.26; ^{13}C NMR ($CDCl_3$): δ 169.08, 169.01, 168.96 (3 C, CH_3COO), 144.72 (CSO_2), 137.95 (CCH_3), 136.13 (d, 3 C, $J_{C,P}$ 2.9 Hz, C_{para}), 133.58 (d, 6 C, $J_{C,P}$ 11.1 Hz, C_{ortho}), 130.38 (d, 6 C, $J_{C,P}$ 13.2 Hz, C_{meta}), 127.93 and 125.98 (4 C, $PhSO_2$), 117.92 (d, 3 C, $J_{C,P}$ 102.0 Hz, C_{ipso}), 86.40 (d, $J_{C1,P}$ 3.3 Hz, C-1), 74.55 (d, $J_{C5,P}$ 6.3 Hz, C-5), 71.00 (d, $J_{C2,P}$ 7.0 Hz, C-2), 67.03 (C-3), 63.94 (C-4), 48.34 (C-6), 21.05 (PhCH_3), 20.54, 20.35, 20.33 (3 C, CH_3COO). Anal. Calcd for $C_{37}H_{38}NO_{10}PS$, $2H_2O$ (755.76): C, 58.80; H, 5.60; N, 1.85. Found: C, 58.53; H, 5.38, N, 1.66.

2,3,4-Tri-O-*acetyl-1,6-anhydro-6-deoxy-6-triphenylphosphonioamino*-β-D-*mannopyranose* p-*tolylsulfonate* (**9**).—Obtained quantitatively as described above from 2,3,4-tri-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-*β*-D-mannopyranosyl azide (**6**) (1.00 g, 2.06 mmol). Amorphous solid; $[\alpha]_D$ −28.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR (CD_3COCD_3): δ 8.12–7.85 (m, 15 H, 3 *Ph*), 7.63 and 7.02 (2d, 4 H, *J* 8.0 Hz, CH_3-*Ph*), 5.78 (ddd, 1 H, $J_{1,2}$ 2.7 Hz, $J_{1,3}$ 0.7 Hz, $J_{1,P}$ 8.7 Hz, H-1), 5.35 (dddd, 1 H, $J_{2,3}$ 5.2 Hz, $J_{3,4}$, $J_{3,5}$ 1.4 Hz, H-3), 5.09 (dddd, 1 H, $J_{4,5}$ 1.4 Hz, $J_{5,6a}$ 2.7 Hz, $J_{5,6b}$ 7.2 Hz, H-5), 5.03 (dd, 1 H, H-2), 5.01 (m, 1 H, H-4), 4.05 (ddd, 1 H, $J_{4,6a}$ 1.4 Hz, $J_{6a,6b}$ 9.9 Hz, H-6a), 3.84 (ddd, 1 H, $J_{6b,P}$ 13.2 Hz, H-6b), 2.37 (s, 3 H, CH_3Ph), 2.27, 2.13, 1.70 (3s, 9 H, CH_3COO); ^{31}P NMR ($CDCl_3$): δ 45.69; ^{13}C NMR ($CDCl_3$): δ 169.19, 169.10, 168.88 (3 C, CH_3COO), 144.70 (CSO_2), 137.83 (CCH_3), 135.94 (d, 3 C, $J_{C,P}$ 2.7 Hz, C_{para}), 133.63 (d, 6 C, $J_{C,P}$ 8.9 Hz, C_{ortho}), 130.51 (d, 6 C, $J_{C,P}$ 13.2 Hz, C_{meta}), 127.86 and 125.86 (4 C, $PhSO_2$), 118.22 (d, 3 C, $J_{C,P}$ 101.9 Hz, C_{ipso}), 86.64 (C-1), 75.66 (d, $J_{C5,P}$ 5.4 Hz, C-5), 71.09 (C-4), 66.45 (C-3), 66.14 (d, $J_{C2,P}$ 6.4 Hz, C-2), 49.67 (C-6), 21.92 (PhCH_3), 20.68, 20.59, 20.19 (3 C, CH_3COO). Anal. Calcd for $C_{37}H_{38}NO_{10}PS$, $2H_2O$ (755.76): C, 58.80; H, 5.60; N, 1.85. Found: C, 58.89; H, 5.36, N, 1.79.

General procedure for the preparation of the 6-acetamido-2,3,4-tri-O-*acetyl-1,6-anhydro-6-deoxy*-β-D-*hexopyranoses* (**14–16**).—A soln of the crude salts **7**, **8** or **9**, prepared from **3**, **4** or **6** (0.337 g, 0.695 mmol) and PPh_3 (0.191 g, 1.05 equiv in CH_2Cl_2 (1 mL), was applied at the top of a column of Dowex 2X8 (OH^-) in CH_2Cl_2 and eluted with the same solvent. Concentration of the eluate afforded a mixture of the expected product **10** or **11** (from **7** or **8**) or **12/13** (from **9**) with PPh_3O. These compounds were too instable to be purified by column chromatography on silica-gel.

NMR spectroscopy of crude 2,3,4-tri-O-*acetyl-6-amino-1,6-anhydro-6-deoxy*-β-D-*glucopyranose* (**10**). ^{1}H (CD_3-$COCD_3$): δ 4.98 (ddd, 1 H, $J_{1,2}$, $J_{1,3}$ 1.4 Hz, $J_{1,5}$ 0.6 Hz, H-1), 4.78 (dddd, 1 H, $J_{2,3}$, $J_{3,4}$, $J_{3,5}$ 1.4 Hz, H-3), 4.54 (dddd, 1 H, $J_{2,4}$, $J_{4,5}$ 1.4 Hz, $J_{4,6b}$ 0.6 Hz, H-4), 4.50 (dddd, 1 H, $J_{5,6a}$ 7.0 Hz, $J_{5,6b}$ 1.5 Hz, H-5), 3.15 (dd, 1 H, $J_{6a,6b}$ 10.2 Hz, H-6a), 3.09 (ddd, 1 H, H-6b), 2.08, 2.06, 2.06 (3s, 9 H, CH_3COO); ^{13}C (CD_3COCD_3): δ 169.19, 169.10, 168.88 (3 C, CH_3COO), 88.05 (C-1), 74.03 (C-5), 72.95 (C-4), 72.90 (C-2), 71.07 (C-3), 46.07 (C-6), 20.68, 20.59, 20.19 (3 C, CH_3COO).

NMR spectroscopy of crude 2,3,4-tri-O-*acetyl-6-amino-1,6-anhydro-6-deoxy*-β-D-*galactopyranose* (**11**). ^{1}H (CD_3-$COCD_3$): δ 5.16 (ddd, 1 H, $J_{1,3}$, $J_{2,3}$ 1.4 Hz, $J_{3,4}$ 5.5 Hz, H-3), 5.08 (ddd, 1 H, $J_{4,5}$ 4.3 Hz, $J_{4,6b}$ 0.9 Hz, H-4), 4.98 (dd, 1 H, $J_{1,2}$ 1.4 Hz, H-1), 4.62 (dd, 1 H, H-2), 4.37 (ddd, 1 H, $J_{5,6a}$ 1.0 Hz, $J_{5,6b}$ 6.4 Hz, H-5), 3.39 (dd, 1 H, $J_{6a,6b}$ 9.8 Hz, H-6a), 3.03 (ddd, 1 H, H-6b), 2.15, 2.13, 2.03 (3s, 9 H, CH_3COO); ^{13}C (CD_3COCD_3): δ 170.23, 169.94, 169.79 (3 C, CH3*C*OO), 88.03 (C-1), 73.86 (C-2), 72.77 (C-5), 68.52 (C-3), 66.96 (C-4), 44.78 (C-6), 20.87, 20.78, 20.60 (3 C, CH_3COO).

Acetylation of the crude coumpounds **10**, **11** or **12/13** with a 2:1 pyridine–Ac_2O mixture (15 h) followed by concentration afforded products **14**, **15** or **16** which were purified by column chromatography (7:1 EtOAc–EtOH).

6-Acetamido-2,3,4-tri-O-*acetyl-1,6-anhydro-6-deoxy*-β-D-*glucopyranose* (**14**).—Obtained as described above from **7** (0.695 mmol); 0.192 g (84%): mp 124 °C; $[\alpha]_D$ −45.8° (*c* 1.0, $CHCl_3$); R_f 0.31 (EtOAc); major rotamer (52%): ^{1}H NMR ($CDCl_3$): δ 5.74 (bs, 1 H, H-1), 4.93 (bs, 1 H, H-3), 4.88 (bs, 1 H, H-2), 4.72 (m, 1 H, H-5), 4.63 (bs, 1 H, H-4), 3.65 (m, 2 H, H-6a,6b), 2.20, 2.19, 2.17, 2.08 (4s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 169.70, 169.15, 168.31, 167.82 (4 C, CH_3CO), 84.00 (C-1), 75.65 (C-5), 69.66 (C-4), 68.87 (C-3), 66.36 (C-2), 44.76 (C-6), 22.19, 20.78, 20.68, 20.56 (4 C, CH_3CO); minor rotamer (48%): ^{1}H NMR ($CDCl_3$): δ 5.51 (bs, 1 H, H-1), 4.91 (bs, 1 H, H-3), 4.69 (m, 1 H, H-5), 4.67 (bs, 1 H, H-4), 4.61 (bs, 1 H, H-2), 3.72 (dd, 1 H, $J_{5,6a}$ 6.6 Hz, $J_{6a,6b}$ 9.2 Hz, H-6a), 3.59 (d, 1 H, H-6b), 2.17, 2.16, 2.10, 2.08 (4s, 12 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 169.94, 169.63, 168.76, 166.90 (4 C, CH_3CO), 83.88 (C-1),

74.88 (C-5), 69.26 (C-4), 68.78 (C-3), 68.31 (C-2), 46.32 (C-6), 22.09, 20.78, 20.68, 20.50 (4 C, *C*H$_3$CO). Anal. Calcd for $C_{14}H_{19}NO_8$ (329.30): C, 51.06; H, 5.82; N, 4.25. Found: C, 51.04; H, 5.94; N, 4.18.

6-Acetamido-2,3,4-tri-O-*acetyl-1,6-anhydro-6-deoxy*-β-D-*galactopyranose* (**15**).—Obtained as described above from **8** (0.695 mmol); 0.187 g (82%): mp 124 °C; $[\alpha]_D$ +22.1° (*c* 1.0, $CHCl_3$); R_f 0.30 (EtOAc); major rotamer (55%): ^{1}H NMR ($CDCl_3$): δ 5.66 (dd, 1 H, $J_{1,2}$, $J_{1,3}$ 1.5 Hz, H-1), 5.33–5.30 (m, 1 H, H-3), 5.27 (dd, 1 H, $J_{3,4}$ 5.4 Hz, $J_{4,5}$ 4.3 Hz, H-4), 5.04 (dd, 1 H, $J_{2,3}$ 1.9 Hz, H-2), 4.58–4.54 (m, 1 H, H-5), 3.77 (d, 1 H, $J_{6a,6b}$ 8.8 Hz, H-6a), 3.61 (dd, 1 H, $J_{5,6b}$ 5.9 Hz, H-6b), 2.18, 2.14, 2.09, 2.03 (4s, 12 H, C*H*$_3$CO); ^{13}C NMR ($CDCl_3$): δ 169.83, 169.64, 169.46, 169.21 (4 C, CH$_3$*C*O), 84.09 (C-1), 73.72 (C-5), 70.94 (C-2), 67.34 (C-3), 64.70 (C-4), 44.31 (C-6), 22.57, 21.00, 20.76, 20.76 (4 C, CH$_3$CO); minor rotamer (45%): ^{1}H NMR ($CDCl_3$): δ 5.46 (dd, 1 H, $J_{1,2}$, $J_{1,3}$ 1.7 Hz, H-1), 5.33–5.30 (m, 1 H, H-3), 5.27 (dd, 1 H, $J_{3,4}$ 5.4 Hz, $J_{4,5}$ 4.3 Hz, H-4), 4.77 (dd, 1 H, $J_{2,3}$ 1.7 Hz, H-2), 4.54–4.52 (m, 1 H, H-5), 3.76 (d, 1 H, $J_{6a,6b}$ 10.9 Hz, H-6a), 3.52 (dd, 1 H, $J_{5,6b}$ 6.1 Hz, H-6b), 2.16, 2.11, 2.08, 2.04 (4s, 12 H, C*H*$_3$CO); ^{13}C NMR ($CDCl_3$): δ 170.05, 169.21, 168.49, 167.15 (4 C, CH$_3$*C*O), 84.24 (C-1), 74.46 (C-5), 69.00 (C-2), 67.42 (C-3), 64.82 (C-4), 45.58 (C-6), 22.59, 20.99, 20.77, 20.77 (4 C, *C*H$_3$CO). Anal. Calcd for $C_{14}H_{19}NO_8$ (329.30): C, 51.06; H, 5.82; N, 4.25. Found: C, 51.20; H, 5.82; N, 3.98.

6-Acetamido-2,3,4-tri-O-*acetyl-1,6-anhydro-6-deoxy*-β-D-*mannopyranose* (**16**).—Obtained as described above from **9** (0.695 mmol); 0.189 g (82%): oily material; $[\alpha]_D$ −94.1° (*c* 1.0, $CHCl_3$); R_f 0.31 (EtOAc); major rotamer (57%): ^{1}H NMR ($CDCl_3$): δ 5.48 (dd, 1 H, $J_{1,2}$ 2.5 Hz, $J_{1,3}$ 1.4 Hz, H-1), 5.32 (ddd, 1 H, $J_{2,3}$ 5.1 Hz, $J_{3,4}$ 1.9 Hz, H-3), 5.24 (dd, 1 H, H-2), 4.84 (dd, 1 H, $J_{4,5}$ 1.7 Hz, H-4), 4.68 (ddd, 1 H, $J_{5,6a}$ 1.7 Hz, $J_{5,6b}$ 6.8 Hz, H-5), 3.78–3.66 (m, 2 H, H-6a,6b), 2.18, 2.10, 2.08, 2.06 (4s, 12 H, C*H*$_3$CO); ^{13}C NMR ($CDCl_3$): δ 169.84, 169.64, 168.41, 167.82 (4 C, CH$_3$*C*O), 84.62 (C-1), 75.45 (C-5), 72.06 (C-4), 67.85 (C-3), 67.75 (C-2), 45.64 (C-6), 22.78, 20.99, 20.69, 20.69 (4 C, *C*H$_3$CO); minor rotamer (43%): ^{1}H NMR ($CDCl_3$): δ 5.94 (dd, 1 H, $J_{1,2}$, 2.7 Hz, $J_{1,3}$ 1.2 Hz, H-1), 5.35 (dd, 1 H, $J_{2,3}$ 5.3 Hz, $J_{3,4}$ 1.8 Hz, H-3), 5.16 (dd, 1 H, H-2), 4.83 (dd, 1 H, $J_{4,5}$ 1.7 Hz, H-4), 4.71 (m, 1 H, H-5), 3.77–3.66 (m, 2 H, H-6a,6b), 2.18, 2.10, 2.08, 2.06 (4s, 12 H, C*H*$_3$CO); ^{13}C NMR ($CDCl_3$): δ 170.05, 169.25, 169.20, 167.05 (4 C, CH$_3$*C*O), 82.55 (C-1), 76.00 (C-5), 72.31 (C-4), 67.98 (C-3), 67.39 (C-2), 46.98 (C-6), 22.68, 21.30, 21.03, 20.95 (4 C, *C*H$_3$CO). Anal. Calcd for $C_{14}H_{19}NO_8$, H_2O (347.316): C, 48.41; H, 6.09; N, 4.03. Found: C, 48.12; H, 5.74, N, 3.91.

General procedure for the preparation of N-*alkoxycarbonyl and* N-*acyl derivatives of the 2,3,4-tri*-O-*acetyl-6-amino-1,6-anhydro-6-deoxy*-β-D-*glucopyranose* (**17–20**).—Alkyl chloroformate or acyl chloride (1.3 equiv.) was added at 0 °C to a soln of crude compound **10** [obtained from the salts **7** (0.695 mmol) as previously described] in C_5H_5N (5 mL). Stirring was maintained overnight; the soln was then concentrated and the residue was purified by column chromatography.

2,3,4-Tri-O-*acetyl-1,6-anhydro-6-deoxy-6-methoxycarbonylamino*-β-D-*glucopyranose* (**17**).—Obtained as described above from **10** and methyl chloroformate; the crude product was purified by column chromatography (2:1 EtOAc–petroleum ether); 0.212 g (88%): oily material; $[\alpha]_D$ −36.0° (*c* 1.0, $CHCl_3$); R_f 0.50 (2:1 EtOAc–petroleum ether); major rotamer (62%): ^{1}H NMR ($CDCl_3$): δ 5.48 (bs, 1 H, H-1), 4.87–4.65 (m, 4 H, H-2,3,4,5), 3.77 (s, 3 H, COOC*H*$_3$), 3.60 (m, 2 H, H-6a,6b), 2.17, 2.07, 2.07 (3s, 9 H, C*H*$_3$COO); ^{13}C NMR ($CDCl_3$): δ 169.51, 169.20, 168.44 (3 C, CH$_3$*C*OO), 153.12 (N*C*OO), 83.59 (C-1), 74.67 (C-5), 69.45 (C-4), 68.67 (C-3), 67.06 (C-2), 52.74 (COO*C*H$_3$), 45.25 (C-6), 20.67, 20.60, 20.37 (3 C, *C*H$_3$COO); minor rotamer (38%): ^{1}H NMR ($CDCl_3$): δ 5.57 (bs, 1 H, H-1), 4.87–4.65 (m, 4 H, H-2,3,4,5), 3.77 (s, 3 H, COO*Me*), 3.60 (m, 2 H, H-6a,6b), 2.17, 2.07, 2.07 (3s, 9 H, C*H*$_3$COO); ^{13}C NMR ($CDCl_3$): δ 169.51, 169.20, 168.44 (3 C, CH$_3$*C*O), 153.12 (N*C*OO), 84.12 (C-1), 75.36 (C-5), 69.45 (C-4), 68.67 (C-3), 66.77 (C-2), 52.74 (COO*C*H$_3$), 45.25 (C-6), 20.67, 20.60, 20.37 (3 C, *C*H$_3$COO). Anal. Calcd for $C_{14}H_{19}NO_9$ (345.30): C, 48.69; H, 5.55; N, 4.06. Found: C, 48.36; H, 5.62, N, 3.94.

2,3,4-Tri-O-*acetyl-6-allyloxycarbonylamino-1,6-anhydro-6-deoxy*-β-D-*glucopyranose* (**18**).—Obtained as described above from **10** and allyl chloroformate; the crude product was purified by column chromatography (5:2 EtOAc–petroleum ether); 0.237 g (92%): oily material; $[\alpha]_D$ −38.6° (*c* 1.0, $CHCl_3$); R_f 0.70 (2:1 EtOAc–petroleum ether); major rotamer (63%): ^{1}H NMR ($CDCl_3$): δ 5.93 (m, 1 H, allyl C*H*=), 5.52 (bs, 1 H, H-1), 5.35 and 5.25 (m, 2 H, allyl CH_2=), 4.88–4.65 (m, 6 H, H-2,3,4,5, allyl CH_2), 3.60 (m, 2 H, H-6a,6b), 2.17,

2.07, 2.07 (3s, 9 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 169.65, 169.34, 168.60 (3 C, CH_3COO), 152.39 (NCOO), 132.20 (CH=), 117.94 (CH_2=), 83.65 (C-1), 74.85 (C-5), 69.53 (C-4), 68.86 (C-3), 67.19 (C-2), 66.18 (CH_2O), 45.36 (C-6), 20.83, 20.74, 20.53 (3 C, CH_3COO); minor rotamer (37%): ^{1}H NMR ($CDCl_3$): δ 5.93 (m, 1 H, allyl CH=), 5.57 (bs, 1 H, H-1), 5.35 and 5.25 (m, 2 H, allyl CH_2=), 4.88–4.65 (m, 6 H, H-2,3,4,5, allyl CH_2), 3.60 (m, 2 H, H-6a,6b), 2.17, 2.07, 2.07 (3s, 9 H, CH_3COO); ^{13}C NMR ($CDCl_3$): δ 169.65, 169.34, 168.60 (3 C, CH_3COO), 152.39 (NCOO), 132.42 (CH=), 117.94 (CH_2=), 84.31 (C-1), 75.54 (C-5), 69.71 (C-4), 68.86 (C-3), 66.90 (C-2), 66.18 (CH_2O), 45.36 (C-6), 20.83, 20.74, 20.53 (3 C, CH_3COO). Anal. Calcd for $C_{16}H_{21}NO_9$ (371.335): C, 51.75; H, 5.70; N, 3.77. Found: C, 51.69; H, 5.79, N, 3.67.

2,3,4-Tri-O-*acetyl-1,6-anhydro-6-deoxy-6-tetradecanoylamino*-β-D-*glucopyranose* (**19**).—Obtained as described above from **10** and tetradecanoyl chloride; the crude product was purified by column chromatography (4:3 EtOAc–petroleum ether); 0.280 g (81%): mp 58–59 °C; $[\alpha]_D$ −26.0° (*c* 1.0, $CHCl_3$); R_f 0.44 (1:1 EtOAc–petroleum ether); major rotamer (52%): ^{1}H NMR ($CDCl_3$): δ 5.76 (bs, 1 H, H-1), 4.94 (bs, 1 H, H-3), 4.88 (bs, 1 H, H-2), 4.73 (m, 1 H, H-5), 4.63 (bs, 1 H, H-4), 3.65 (m, 2 H, H-6a,6b), 2.34 (m, 2 H, CH_2CO), 2.20, 2.18, 2.07 (3s, 9 H, CH_3COO), 1.67 (m, 2 H, CH_2CH$_2$CO), 1.26 (m, 20 H, 10 CH_2), 0.88 (t, 3 H, *J* 6.4 Hz, CH_3CH$_2$); ^{13}C NMR ($CDCl_3$): δ 170.61, 170.15, 169.84, 168.28 (4 C, 3 CH_3CO, CH_2CO), 84.22 (C-1), 75.66 (C-5), 69.99 (C-4), 69.05 (C-3), 66.66 (C-2), 45.77 (C-6), 34.67, 31.81, 29.53–29.01, 25.19–24.29, 22.57 (12 CH_2), 20.81, 20.70, 20.63 (3 C, CH_3COO), 14.00 (CH_3CH$_2$); minor rotamer (48%): ^{1}H NMR ($CDCl_3$): δ 5.55 (bs, 1 H, H-1), 4.92 (bs, 1 H, H-3), 4.69 (m, 1 H, H-5), 4.68 (bs, 1 H, H-4), 4.61 (bs, 1 H, H-2), 3.70 (dd, 1 H, $J_{5,6a}$ 6.6 Hz, $J_{6a,6b}$ 9.2 Hz, H-6a), 3.58 (d, 1 H, H-6b), 2.34 (m, 2 H, CH_2CO), 2.21, 2.16, 2.07 (3s, 9 H, CH_3CO), 1.67 (m, 2 H, CH_2CH$_2$CO), 1.26 (m, 20 H, 10 CH_2), 0.88 (t, 3 H, *J* 6.4 Hz, CH_3CH$_2$); ^{13}C NMR ($CDCl_3$): δ 169.99, 169.69, 169.14, 168.75 (4 C, 3 CH_3CO, CH_2CO), 83.39 (C-1), 74.72 (C-5), 69.30 (C-4), 68.91 (C-3), 68.47 (C-2), 44.79 (C-6), 34.61, 31.81, 29.53–29.01, 25.19–24.29, 22.57 (12 CH_2), 20.81, 20.71, 20.52 (3 C, CH_3CO), 14.00 (CH_3CH$_2$). Anal. Calcd for $C_{26}H_{43}NO_8$ (497.61): C, 62.75; H, 8.71; N, 2.81. Found: C, 62.94; H, 8.87; N, 2.63.

2,3,4-Tri-O-*acetyl-1,6-anhydro-6-deoxy-6-octanoylamino*-β-D-*glucopyranose* (**20**).—Obtained as described above from **10** and octanoyl chloride; the crude product was purified by column chromatography (5:2 EtOAc–petroleum ether); 0.241 g (84%): mp 78–80 °C; $[\alpha]_D$ −28.3° (*c* 1.0, $CHCl_3$); R_f 0.62 (5:2 EtOAc–petroleum ether); major rotamer (54%): ^{1}H NMR ($CDCl_3$): δ 5.76 (bs, 1 H, H-1), 4.93 (bs, 1 H, H-3), 4.88 (bs, 1 H, H-2), 4.72 (m, 1 H, H-5), 4.61 (bs, 1 H, H-4), 3.66 (m, 2 H, H-6a,6b), 2.33 (m, 2 H, CH_2CO), 2.19, 2.18, 2.06 (3s, 9 H, CH_3COO), 1.67 (m, 2 H, CH_2CH$_2$CO), 1.26 (m, 8 H, 4 CH_2), 0.88 (t, 3 H, *J* 6.4 Hz, CH_3CH$_2$); ^{13}C NMR ($CDCl_3$): δ 170.55, 170.06, 169.87, 168.36 (4 C, 3 CH_3CO, CH_2CO), 84.30 (C-1), 75.79 (C-5), 70.07 (C-4), 69.13 (C-3), 66.74 (C-2), 45.84 (C-6), 34.75, 31.65, 29.37, 29.05, 24.36, 22.59 (6 CH_2), 20.93, 20.83, 20.73 (3 C, CH_3CO), 14.05 (CH_3CH$_2$); minor rotamer (46%): ^{1}H NMR ($CDCl_3$): δ 5.55 (bs, 1 H, H-1), 4.90 (bs, 1 H, H-3), 4.72 (m, 1 H, H-5), 4.68 (bs, 1 H, H-4), 4.61 (bs, 1 H, H-2), 3.70 (dd, 1 H, $J_{5,6a}$ 6.6 Hz, $J_{6a,6b}$ 9.2 Hz, H-6a), 3.58 (d, 1 H, H-6b), 2.28 (m, 2 H, CH_2CO), 2.20, 2.16, 2.07 (3s, 9 H, CH_3CO), 1.67 (m, 2 H, CH_2CH$_2$CO), 1.26 (m, 8 H, 4 CH_2), 0.88 (t, 3 H, *J* 6.4 Hz, CH_3CH$_2$); ^{13}C NMR ($CDCl_3$): δ 170.06, 169.76, 169.20, 168.82 (4 C, 3 CH_3CO, CH_2CO), 83.50 (C-1), 74.83 (C-5), 69.42 (C-4), 69.04 (C-3), 68.60 (C-2), 44.87 (C-6), 34.69, 31.65, 29.22, 29.02, 25.27, 22.59 (6 CH_2), 20.93, 20.82, 20.64 (3 C, CH_3CO), 14.05 (CH_3CH$_2$). Anal. Calcd for $C_{20}H_{31}NO_8$ (413.455): C, 58.10; H, 7.56; N, 3.39. Found: C, 58.05; H, 7.72; N, 3.33.

1,6-Anhydro-6-deoxy-6-tetradecanoylamino-β-D-*glucopyranose* (**21**).—The product **19** (0.249 g, 0.50 mmol) was dissolved in dry MeOH (15 mL) and treated with a catalytic amount of NaOMe. After 16 h at room temperature, the mixture was concentrated and the residue was purified on a short column of silica-gel (6:1 EtOAc–EtOH); 0.154 g (83%): mp 97–98 °C; $[\alpha]_D$ −3.0° (*c* 1.0, 1:1 $CHCl_3$–EtOH); R_f 0.55 (6:1 EtOAc–EtOH); major rotamer (75%): ^{1}H NMR (C_5D_5N): δ 6.27 (bs, 1 H, H-1), 4.94 (bd, 1 H, $J_{5,6b}$ 6.5 Hz, H-5), 4.59 (m, 2 H, H-3,4), 4.18 (bs, 1 H, H-2), 4.05 (d, 1 H, $J_{6a,6b}$ 8.5 Hz, H-6a), 3.72 (dd, 1 H, H-6b), 2.35 (t, 2 H, CH_2CO), 1.77 (m, 2 H, CH_2CH$_2$CO), 1.19 (m, 20 H, 10 CH_2), 0.84 (t, 3 H, *J* 6.4 Hz, CH_3CH$_2$); minor rotamer (25%): ^{1}H NMR (C_5D_5N): δ 5.99 (bs, H-1), 4.92 (bd, 1 H, $J_{5,6b}$ 7.8 Hz, H-5), 4.59 (m, 2 H, H-3,4), 4.33 (bs, 1 H, H-2), 4.25 (d, 1 H, $J_{6a,6b}$ 10.4 Hz, H-6a), 3.90 (dd, 1 H, H-6b), 2.43 (t, 2 H,

CH_2CO), 1.77 (m, 2 H, CH_2CH_2CO), 1.19 (m, 20 H, 10 CH_2), 0.84 (t, 3 H, *J* 6.4 Hz, CH_3CH_2). Anal. Calcd for $C_{20}H_{37}NO_5$ (371.50): C, 64.66; H, 10.04; N, 3.77. Found: C, 64.81; H, 10.02; N, 3.72.

1,6-Anhydro-6-deoxy-6-octanoylamino-β-D-*gluco-pyranose* (**22**).—Prepared as described above from **21** (0.206 g, 0.50 mmol). The crude product was purified on a short column of silica-gel (4:1 EtOAc–EtOH); 0.121 g (84%): mp 69–70 °C; $[\alpha]_D$ −5.8° (*c* 1.0, H_2O); R_f 0.35 (4:1 EtOAc–EtOH); major rotamer (75%): ^{1}H NMR (C_5D_5N): δ 6.31 (bs, 1 H, H-1), 4.99 (bd, 1 H, $J_{5,6b}$ 6.9 Hz, H-5), 4.62 (m, 2 H, H-3,4), 4.17 (bs, 1 H, H-2), 4.05 (d, 1 H, $J_{6a,6b}$ 8.4 Hz, H-6a), 3.71 (dd, 1 H, H-6b), 2.36 (t, 2 H, CH_2CO), 1.77 (m, 2 H, CH_2CH_2CO), 1.16 (m, 8 H, 4 CH_2), 0.79 (t, 3 H, *J* 6.4 Hz, CH_3CH_2); ^{13}C NMR (C_5D_5N): δ 170.74 (CH_2CO), 88.09 (C-1), 79.92 (C-5), 74.18, 72.71, 69.80 (3 C, C-2,3,4), 46.69 (C-6), 35.06, 32.08, 29.75, 29.59, 24.99, 23.00 (6 CH_2), 14.38 (CH_3CH_2); minor rotamer (25%): ^{1}H NMR (C_5D_5N): δ 6.00 (bs, 1 H, H-1), 4.96 (bd, 1 H, $J_{5,6b}$ 8.4 Hz, H-5), 4.59 (m, 2 H, H-3,4), 4.35 (bs, 1 H, H-2), 4.25 (d, 1 H, $J_{6a,6b}$ 10.3 Hz, H-6a), 3.89 (dd, 1 H, H-6b), 2.45 (t, 2 H, CH_2CO), 1.77 (m, 2 H, CH_2CH_2CO), 1.19 (m, 8 H, 4 CH_2), 0.84 (t, 3 H, *J* 6.4 Hz, CH_3CH_2); ^{13}C NMR (C_5D_5N): δ 169.42 (CH_2CO), 88.35 (C-1), 79.07 (C-5), 74.18, 72.87, 72.22 (3 C, C-2,3,4), 46.46 (C-6), 35.06, 32.08, 29.75, 29.59, 25.65, 23.00 (6 CH_2), 14.38 (CH_3CH_2). Anal. Calcd for $C_{14}H_{25}NO_5$ (287.35): C, 58.51; H, 8.77; N, 4.87. Found: C, 58.74; H, 8.82; N, 4.83.

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