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Note

Synthesis of N^4-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-L-asparagine analogues. *n*-Butyramide, 3-chloropropionamide, 3-aminopropionamide, and isovaleramide analogues

Jerry J. Kaylor, John M. Risley*

Department of Chemistry, The University of North Carolina at Charlotte, 9201 University City Boulevard, Charlotte, NC 28223-0001, USA

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Abstract

The syntheses of four analogues of N^4-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-L-asparagine are described. Activated carboxylic acids were reacted with 2-acetamido-2-deoxy-β-D-glucopyranosylamine. *n*-Butyric anhydride gave *N*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-*n*-butyramide. 3-Chloropropionic anhydride was synthesized from 3-chloropropionic acid and gave *N*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-3-chloropropionamide. Equilibration of the latter with ammonium bicarbonate gave N^1-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-3-aminopropionamide. Succinimidyl isovalerate was synthesized and gave *N*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-isovaleramide.

Keywords: β-*N*-Acetylglucosaminyl-L-asparagine analogues; *n*-Butyric acid analogue; 3-Chloropropionic acid analogue; 3-Aminopropionic acid analogue; Isovaleric acid analogue

Glycosylasparaginase ((GA), aspartylglucosaminidase (AGA), N^4-(β-*N*-acetyl-D-glucosaminyl)-L-asparaginase; EC 3.5.1.26) catalyzes the hydrolysis of the amide bond between *N*-acetylglucosamine and asparagine in the principle linkage of N-linked glycoproteins and is a key enzyme in the catabolism of N-linked glycoproteins.[1] For a study of the active site fingerprint of GA, we have synthesized analogues of the natural substrate, N^4-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-L-asparagine ((GlcNAc-)Asn).[2–4] To further this study, we required the GlcNAc(β1-N)-*n*-butyramide **1**, 3-chloropropionamide **2**, 3-aminopropionamide **3**, and isovaleramide **4** analogues of the amino acid of (GlcNAc-)Asn, which possess no free carboxyl groups. The syntheses of these four analogues are described in this paper. The 3-aminopropionamide **3** analogue is of particular interest as

* Corresponding author. Tel.: +1-704-6874844; fax: +1-704-6873151.

E-mail address: jmrisley@email.uncc.edu (J.M. Risley).

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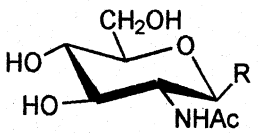
the analogue of (GlcNAc-)Asn where the α-carboxyl group has been substituted with a hydrogen; it may also have application for incorporation into C-terminal glycopeptides containing no C-terminal carboxyl group.



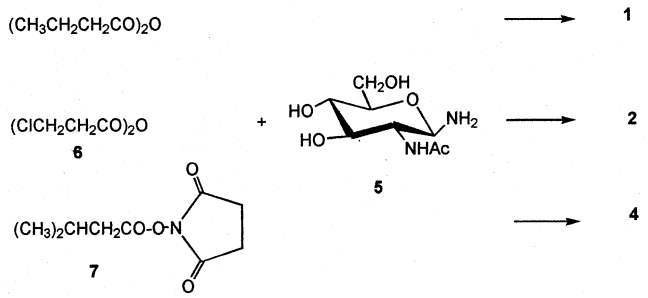
1 R = $NHCOCH_2CH_2CH_3$

2 R = $NHCOCH_2CH_2Cl$

3 R = $NHCOCH_2CH_2NH_2$

4 R = $NHCOCH_2CH(CH_3)_2$

The syntheses of the four analogues, **1**, **2**, **3**, and **4**, of (GlcNAc-)Asn utilizing 2-acetamido-2-deoxy-β-D-glucopyranosylamine (**5**) required activated carboxylic acids. While there are many methods to activate a carboxylic acid, we chose the anhydride because we have had previous success in the synthesis of other analogues.[2,4] *n*-Butyric acid was commercially available as *n*-butyric anhydride, while 3-chloropropionic acid and isovaleric acid required activation. Attempted synthesis of 3-chloropropionic anhydride (**6**) using (1) 1:1 thionyl chloride–acetyl chloride[5] was not successful; (2) thionyl chloride gave very low yields; and (3) 1:1 *N*-hydroxysuccinimide–*N*,*N*′-dicyclohexylcarbodiimide[6] gave low yields; finally, using *N*,*N*′-dicyclohexylcarbodiimide alone, the synthesis of **6** was successful. Attempted synthesis of isovaleric anhydride using (1) 1:1 thionyl chloride–acetyl chloride[5] gave the acetic isovaleric mixed anhydride and (2) thionyl chloride gave no anhydride. Because activation of isovaleric acid as the anhydride proved difficult, we attempted to prepare the succinimidyl derivative, and succinimidyl isovalerate **7** was synthesized successfully from *N*-hydroxysuccinimide and *N*,*N*′-dicyclohexylcarbodiimide.[6]



Scheme 1.

Compounds **6** and **7** were used without further purification.

Repeated attempts to synthesize **1**, **2**, and **4** in single, large reactions of **5** with *n*-butyric anhydride, **6**, and **7**, respectively, were not successful (Scheme 1). While this may be understood in terms of possible miscibility problems of the *n*-butyric anhydride and water, which were not encountered with anhydrides we used in the synthesis of other analogues,[2,4] it is not clear why the reactions were not successful for **6** and **7** performed in dimethyl sulfoxide, which has been shown to be a good solvent for formation of the *N*-glycosylic bond.[7,8] It was found that a set of smaller reactions could be prepared that were successful. The reactions of *n*-butyric anhydride, **6**, and **7** with the β amino group of **5** occurred exclusively at the amino group to form the *N*-glycosylic bond, which followed the well-established preference of activated carboxylic acids to react with the amino group to form the *N*-glycosylic (amide) bond rather than with the sugar hydroxyl groups on carbohydrate molecules (Refs. 2–4 and references cited therein). Thus, although **5**, used in the reaction, contained approximately 30% GlcNAc, the reaction of **5** with *n*-butyric anhydride, **6**, and **7**, did not occur with a sugar hydroxyl group to form a carboxylate ester between GlcNAc and the acids. The synthesis of **3** from **2** was based on the amination reaction of *N*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)chloroacetamide with ammonium carbonate to give N^1-(2-acetamido-2-deoxy-β-D-glucopyranosyl)glycinamide.[9] When we attempted to use ammonium carbonate or ammonium chloride with **2**, only the elimination, vinyl, product was obtained, as shown by ^{1}H NMR signals at δ 5.5–6.5. We found that ammonium bicarbonate gave **3** as the hydrochloride salt. The four analogues, **1**, **2**, **3**, and **4**, were purified by reversed-phase HPLC. The properties of each analogue indicated their successful synthesis. However, the purified yields were lower than expected based on our previous experience. The low yield of **1** may be understood, again, in terms of the possible miscibility problem of the *n*-butyric anhydride and water. A homogeneous solution was obtained at the end of the reaction, and therefore

the competing hydrolysis reaction of the anhydride was significant. The low yields of **2** and **4** would indicate that, under the conditions of the reactions used here, the formation of the amide bond was very slow. To remove the dimethyl sulfoxide solvent used in these two reactions, the combined samples were extracted with diethyl ether; any unreacted **6** or **7** was removed at this step in the procedure, but analysis of these extracts was not carried out. Unreacted **5** or GlcNAc and the analogues were well separated on reversed-phase HPLC, and therefore no further analysis of the reaction was done. As we observed, **2** is prone to undergo elimination in the amination reaction to **3**, and therefore the low yield of **3** from **2** by amination with ammonium bicarbonate is a consequence of the side-elimination reaction to give the vinyl analogue, which eluted well separated from **3** on reversed-phase HPLC. While these procedures provided sufficient quantities of the four analogues for our studies, an increased yield may be possible utilizing other procedures, as for example in Refs. 7, 8 and 10. The nomenclature used to assign the NMR signals follows that used for (GlcNAc-)Asn.[11] The NMR spectra agree with data reported for (GlcNAc-)-Asn[11] and other analogues.[2–4] The characteristic doublet for the anomeric proton in the ^{1}H NMR spectrum appears at $\delta \sim 5.05$ with $J_{1,2} \sim 9.77$ Hz.[11,12] The ^{1}H NMR signals for the 1,2-disubstituted ethane groups in **2** and **3** might be expected to have AA′BB′ spectra, but they are first order, as are all of the signals for each analogue. However, of note is the non-equivalence of the two γ-methyl groups in **4** that appear as two doublets. The ^{13}C NMR signals for each analogue could be assigned without difficulty.

1. Experimental

Materials.—Chemicals purchased from the following suppliers were: deuterium oxide (99.9 atom% ^{2}H), $CHCl_3$-*d* (99.8 atom% ^{2}H), and acetone-d_6 (99.9 atom% ^{2}H) from Cambridge Isotopes Laboratories; isovaleric acid from Eastman Organic Chemicals; 2-acetamido-2-deoxy-D-glucopyranose and 3-chloropropionic acid from Janssen Chemica; *n*-butyric anhydride, *N*,*N*′-dicyclohexylcarbodiimide, and *N*-hydroxysuccinimide from Sigma; NH_4HCO_3 from Spectrum. All other chemicals were at least analytical grade.

General methods.—A GE 300 spectrometer was used to record NMR spectra. ^{1}H NMR spectra were recorded at 300.2 MHz in a 5-mm probe at ambient temperature with a 2000 Hz sweep width, 30° pulse angle, and an 8k data block; no line-broadening factor was applied to the accumulated FID. Natural abundance ^{13}C NMR spectra were recorded at 75.5 MHz in a 5-mm probe at ambient temperature with a 10,000 Hz sweep width, 30° pulse angle, and an 8k data block; protons were broad-band decoupled and a line-broadening factor of 2.0 Hz was applied to the accumulated FID. The error in the measured chemical shifts is ± 0.002 ppm for ^{1}H NMR and ± 0.032 ppm for ^{13}C NMR; the error in the measured coupling constants is ± 0.50 Hz. Reversed-phase HPLC was carried out on a BioRad model 2800 liquid chromatograph equipped with a BioRad UV 1806 UV–Vis detector and a Whatman Partisil 10 ODS-3 M/9-50 preparative column. Water was used as the mobile phase at a flow rate of 3.0 or 5.0 mL/min, and the column was monitored at 195 nm. Evaporation of solvents was conducted on a rotary evaporator at ~ 60–70 °C at water aspirator vacuum. Elemental analyses were done at Atlantic Microlabs, Inc. (Norcross, GA).

*Preparation of 2-acetamido-2-deoxy-β-*D*-glucopyranosylamine*[2–4] (**5**).—2-Acetamido-2-deoxy-D-glucopyranose (GlcNAc) was dissolved in satd aq NH_4HCO_3 (~ 1.5 M) to give a molar ratio of 5:1 ammonia–sugar. The reaction was allowed to proceed to equilibrium at 40 °C with intermittent addition of solid NH_4HCO_3 to maintain saturation. Following removal of excess NH_4HCO_3 by evaporation at 40 °C and rotary evaporation, the white solid contained 70% **5** and 30% of the α and β anomers of GlcNAc as determined by integration of the ^{1}H NMR signals in D_2O for anomeric protons of δ 4.142 ($J_{1,2}$ 8.79 Hz), δ 5.180 ($J_{1,2}$ 3.42 Hz), and δ 4.324 ($J_{1,2}$ 9.76 Hz), respectively, and was used without further purification.

N-*(2-Acetamido-2-deoxy-β-D-glucopyranosyl)*-n-*butyramide hydrate* (**1**).—Compound **5** (50 mg, 0.227 mmol) was dissolved in water (four drops) and *n*-butyric anhydride (37.2 μL, 0.227 mmol) was added.[2,13] A total of 15 sample vials were prepared. The samples were vortexed at rt for 1 h; any solid that formed was dissolved by addition of a minimal amount of water. The samples were combined and purified by HPLC in fractions. Eluent with a retention time between 29.0 and 40.0 min (depending on fraction size) was collected. The eluents were combined and lyophilized to give 257 mg (26%) of **1** as fluffy, white crystals: mp 233.5–235.0 °C; ^{1}H NMR (D_2O, reference acetone (2.225 ppm)): δ 0.855 (t, 3 H, $J_{\beta,\gamma}$ 7.33 Hz, H-γ (CH_3)), 1.585 (m, 2 H, $J_{\alpha,\beta}$ 7.33 Hz, H-β (CH_2)), 1.979 (s, 3 H, $COCH_3$), 2.221 (t, 2 H, H-α (CH_2)), 3.457 (dd, 1 H, $J_{3,4}$ 9.92, $J_{4,5}$ 8.81 Hz, H-4 (C*H*OH)), 3.520 (m, 1 H, $J_{5,6a}$ 2.46, $J_{5,6b}$ 3.42 Hz, H-5 (CHO–)), 3.586 (dd, 1 H, $J_{2,3}$ 10.26 Hz, H-3 (C*H*OH)), 3.729 (dd, 1 H, $J_{6a,6b}$ −12.04 Hz, H-6b (CH_2OH)), 3.797 (dd, 1 H, $J_{1,2}$ 9.76 Hz, H-2 (C*H*NHAc)), 3.864 (dd, 1 H, H-6a (CH_2OH)), 5.025 (d, 1 H, H-1 (C*H*NH)); ^{13}C NMR (D_2O, reference *p*-dioxane (66.667 ppm)): δ 13.552 (C-γ), 19.827 (C-β), 22.964 ($COCH_3$), 38.715 (C-α), 55.340 (C-2), 61.517 (C-6), 70.541 (C-4), 75.199 (C-3), 78.627 (C-5), 79.306 (C-1), 175.625 (*C*OCH_3), 178.827 (NHCO). Anal. Calcd for $C_{12}H_{22}N_2O_6\cdot 0.5H_2O$: C, 48.18; H, 7.75; N, 9.37. Found: C, 48.30; H, 7.39; N, 9.31.

Preparation of 3-chloropropionic anhydride (**6**).—Using the basic procedure of Ouihia et al.,[6] 3-chloropropionic acid (2.0 g, 18.4 mmol) was dissolved in CH_2Cl_2 (40 mL). *N*,*N*′-Dicyclohexylcarbodiimide (3.8 g, 18.4 mmol) was added slowly with stirring. After the addition was completed, the solution was stirred for 5 min and filtered to remove dicyclohexylurea. The precipitate was washed with CH_2Cl_2 and the filtrates were combined. Solvent was removed by rotary evaporation to give a viscous, yellowish, opaque liquid (1.275 g). ^{1}H NMR ($CDCl_3$) showed the sample contained 65% **6** by integration of the two methylene groups at δ 2.85 and 3.75 for the acid and δ 2.95 and 3.85 for the anhydride, and was used without further purification.

N-*(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-3-chloropropionamide hydrate* (**2**).—Compound **5** (50 mg, 0.227 mmol) was dissolved in dimethyl sulfoxide (ten drops), and compound **6** (47.6 mg, 0.239 mmol) was added.[2,13] A total of 18 sample vials were prepared. The samples were vortexed at rt overnight. The samples were combined, and the solvent was extracted with Et_2O (six aliquots of 50 mL each). Evaporation of residual Et_2O left an oily residue that was dissolved in water and purified by HPLC in fractions. Eluent with a retention time between 20.2 and 24.5 min (depending on fraction size) was collected. The eluents were combined and lyophilized to give 350 mg (28%) of **2** as a fluffy, white crystalline solid: mp 201.3–202.0 °C; ^{1}H NMR (D_2O, reference acetone (2.225 ppm)): δ 1.934 (s, 3 H, $COCH_3$), 2.680 (t, 2 H, $J_{\alpha,\beta}$ 7.08 Hz, H-α (CH_2)), 3.424 (dd, 1 H, $J_{3,4}$ 9.28, $J_{4,5}$ 10.72 Hz, H-4 (C*H*OH)), 3.483 (m, 1 H, $J_{5,6a}$ 1.95, $J_{5,6b}$ 4.89 Hz, H-5 (CHO–)), 3.554 (dd, 1 H, $J_{2,3}$ 10.74 Hz, H-3 (C*H*OH)), 3.694 (dd, 1 H, $J_{6a,6b}$ −11.74 Hz, H-6b (CH_2OH)), 3.728 (t, 2 H, H-β (CH_2Cl)), 3.764 (dd, 1 H, $J_{1,2}$ 9.77 Hz, H-2 (C*H*NHAc)), 3.820 (dd, 1 H, H-6a (CH_2OH)), 5.054 (d, 1 H, H-1 (C*H*NH)); ^{13}C NMR (D_2O, reference *p*-dioxane (66.667 ppm)): δ 23.158 ($COCH_3$), 39.621 (C-α), 41.109 (C-β), 55.372 (C-2), 61.485 (C-6), 70.477 (C-4), 75.166 (C-3), 78.692 (C-5), 79.306 (C-1), 174.719 (*C*OCH_3), 175.689 (NHCO). Anal. Calcd for $C_{11}H_{19}ClN_2O_6\cdot 0.25H_2O$: C, 41.91; H, 6.23; Cl, 11.25; N, 8.89. Found: C, 41.87; H, 6.01; Cl, 10.99; N, 8.55.

N^1-*(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-3-aminopropionamide hydrochloride dihydrate* (**3**).—Using a modification of Manger et al.,[9] compound **2** (50 mg, 0.227 mmol) was dissolved in water (0.5 mL) in a glass ampule containing a stir bar. NH_4HCO_3 (0.5 g, 6.41 mmol) was added. Two ampules were prepared. Each ampule was sealed, placed in an oil bath at 40–50 °C, and stirred for 2 days. The ampules were broken, and the solutions combined and filtered through glass wool. Water (3 mL) was added to the filtrate, and the solution was placed in a water bath at 40 °C for 2 h to evaporate residual NH_4HCO_3. The product was purified by HPLC in frac-

tions. Eluent with a retention time between 6.0 and 10.5 min (depending on fraction size) was collected. The eluents were combined and lyophilized to give 17 mg (18%) of **3** as very hygroscopic, sticky, white crystals: mp 189.1–191.0 °C; ^{1}H NMR (D_2O, reference acetone (2.225 ppm)): δ 2.006 (s, 3 H, $COCH_3$), 2.689 (t, 2 H, $J_{\alpha,\beta}$ 6.59 Hz, H-α (CH_2)), 3.245 (t, 2 H, H-β (CH_2)), 3.473 (dd, 1 H, $J_{3,4}$ 10.25, $J_{4,5}$ 8.30 Hz, H-4 (C*H*OH)), 3.540 (m, 1 H, $J_{5,6a}$ 2.00, $J_{5,6b}$ 5.13 Hz, H-5 (CHO–)), 3.613 (dd, 1 H, $J_{2,3}$ 9.76 Hz, H-3 (C*H*OH)), 3.744 (dd, 1 H, $J_{6a,6b}$ −12.45 Hz, H-6b (CH_2OH)), 3.829 (dd, 1 H, $J_{1,2}$ 9.77 Hz, H-2 (C*H*NHAc)), 3.879 (dd, 1 H, H-6a (CH_2OH)), 5.071 (d, 1 H, H-1 (C*H*NH)); ^{13}C NMR (D_2O, reference *p*-dioxane (66.667 ppm)): δ 23.029 ($COCH_3$), 33.185 (C-α), 36.387 (C-β), 55.210 (C-2), 61.517 (C-6), 70.509 (C-4), 75.166 (C-3), 78.595 (C-5), 79.339 (C-1), 173.975 ($COCH_3$), 175.819 (NHCO). Anal. Calcd for $C_{11}H_{21}N_3O_6 \cdot HCl \cdot 2H_2O \cdot 2.5NH_4Cl$: C, 26.56; H, 7.29; N, 15.48. Found: C, 26.64; H, 6.56; N, 15.44.

Preparation of succinimidyl isovalerate (**7**).—Using the basic procedure of Ouihia et al.,[6] isovaleric acid (2.15 mL, 19.58 mmol) was placed in CH_2Cl_2 (40 mL), and *N*-hydroxysuccinimide (2.25 g, 19.55 mmol) was added and dissolved. The solution was stirred at rt, and *N*,*N*′-dicyclohexylcarbodiimide (3.8 g, 18.4 mmol) was added slowly. After 1 week dicyclohexylurea was removed by filtration and washed with CH_2Cl_2. The filtrates were combined, and the solvent was removed on a rotary evaporator to give a viscous, cloudy, white liquid (2.637 g). ^{1}H NMR (acetone-d_6) showed the sample contained a minimum 90% of **7** by integration of the isovaleric C-2 methylene group at δ 2.33 for the acid and δ 2.45 for the anhydride. The product was used without further purification.

N-*(2-Acetamido-2-deoxy-β-*D*-glucopyranosyl)isovaleramide hydrate* (**4**).—Compound **5** (50 mg, 0.227 mmol) was dissolved in dimethyl sulfoxide (ten drops), and compound **7** (47.8 mg, 0.240 mmol) was added.[2,13] A total of 15 sample vials were prepared. The samples were vortexed at rt for 1 week. The samples were combined, and the solvent was extracted with Et_2O (six aliquots of 50 mL each). Evaporation of residual Et_2O left a viscous, oily residue with suspended white lumps that was dissolved in water and purified by HPLC in fractions. Eluents with a retention time between 44.4 and 54.3 min (depending on fraction size) was collected. The eluents were combined and lyophilized to give 206 mg (20%) of **4** as a fluffy, white crystalline solid: mp 245.8–247.5 °C; ^{1}H NMR (D_2O, reference acetone (2.225 ppm)): δ 0.880 (d, 3 H, $J_{\beta,\gamma}$ 6.35 Hz, H-γ (CH_3)), 0.910 (d, 3 H, $J_{\beta,\gamma'}$ 6.83 Hz, H-γ′ (CH_3)), 1.980 (m, 1 H, $J_{\alpha,\beta}$ 7.32 Hz, H-β (CH)), 1.986 (s, 3 H, $COCH_3$), 2.133 (d, 2 H, H-α (CH_2)), 3.469 (dd, 1 H, $J_{3,4}$ 9.28, $J_{4,5}$ 8.55 Hz, H-4 (C*H*OH)), 3.536 (m, 1 H, $J_{5,6a}$ 2.35, $J_{5,6b}$ 5.37 Hz, H-5 (CHO–)), 3.594 (dd, 1 H, $J_{2,3}$ 10.01 Hz, H-3 (C*H*OH)), 3.741 (dd, 1 H, $J_{6a,6b}$ −12.45 Hz, H-6b (CH_2OH)), 3.812 (dd, 1 H, $J_{1,2}$ 9.77 Hz, H-2 (C*H*NHAc)), 3.875 (dd, 1 H, H-6a (CH_2OH)), 5.054 (d, 1 H, H-1 (C*H*NH)); ^{13}C NMR (D_2O, reference *p*-dioxane (66.667 ppm)): δ 22.220 (C-γ), 22.479 (C-γ′), 23.029 ($COCH_3$), 27.169 (C-α), 46.057 (C-β), 55.243 (C-2), 61.517 (C-6), 70.509 (C-4), 75.263 (C-3), 78.627 (C-5), 79.209 (C-1), 175.592 ($COCH_3$), 178.309 (NHCO). Anal. Calcd for $C_{13}H_{24}N_2O_6 \cdot 0.5H_2O$: C, 49.86; H, 8.05; N, 8.95. Found: C, 49.59; H, 7.80; N, 8.89.

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References

[1] Aronson, Jr., N. N. *Biochim. Biophys. Acta* **1999**, *1455*, 139–154.
[2] Xia, Y. -Q.; Risley, J. M. *J. Carbohydr. Chem.* **2001**, *20*, 45–55.
[3] Huang, D. H.; Risley, J. M. *Carbohydr. Res.* **2000**, *329*, 487–493.
[4] Malik, J. J.; Risley, J. M. *Magn. Reson. Chem.* **2001**, *39*, 98–100.

[5] Naps, M.; Johns, I. B. *J. Am. Chem. Soc.* **1940**, *62*, 2450–2457.
[6] Ouihia, A.; Rene, L.; Guilhem, J.; Pascard, C.; Badet, B. *J. Org. Chem.* **1993**, *58*, 1641–1642.
[7] Cohen-Anisfeld, S. T.; Lansbury, Jr., P. T. *J. Am. Chem. Soc.* **1993**, *115*, 10531–10537.
[8] Meinjohanns, E.; Meldal, M.; Paulsen, H.; Dwek, R. A.; Bock, K. *J. Chem. Soc., Perkin Trans. 1* **1998**, 549–560.
[9] Manger, I. D.; Rademacher, T. W.; Dwek, R. A. *Biochemistry* **1992**, *31*, 10724–10732.
[10] Lubineau, A.; Auge, J.; Drouillat, B. *Carbohydr. Res.* **1995**, *266*, 211–219.
[11] Vliegenthart, J. F. G.; Dorland, L.; van Halbeek, H. *Adv. Carbohydr. Chem. Biochem.* **1983**, *41*, 209–373.
[12] Monsigny, M.; Quétard, C.; Bourgerie, S.; Delay, D.; Pichon, C.; Midoux, P.; Mayer, R.; Roche, A. C. *Biochimie* **1998**, *80*, 99–108.
[13] Urge, L.; Jackson, D. C.; Gorbics, L.; Wroblewski, K.; Graczyk, G.; Otvos, Jr., L. *Tetrahedron* **1994**, *50*, 2373–2390.