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Synthesis of methyl (D-glycopyranosyl azide)uronates

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Abstract

Sodium hypochlorite oxidation catalysed by 2,2,6,6,-tetramethylpiperidine 1-oxide (TEMPO) is shown to be a mild and efficient approach to the title uronates. In the *gluco*, *galacto*, *allo*, and 2-acetamido-2-deoxy-*gluco* series, the corresponding β- or α- and β-glycosyl azides could be smoothly oxidised and alternative preparations are compared to this access.

Keywords: (D-Glycopyranosyl azide)uronates; Glycosyl azides; NaOCl–TEMPO oxidation

1. Introduction

Effective synthetic routes towards, and property studies of, biodegradable polymers from renewable resources have become a topic for synthetic efforts in recent years. In particular, access to hydrophilic polyamides has attracted special interest, and the preparation of AABB-type polyamides has been reported based on dianhydroalditol derivatives [1], glycaric acids [2,3], and diamino sugar components [4].

Very recently, both polycondensation and polyaddition routes towards the first AB-type sugar-based polyurethanes in the dianhydroalditol series have been demonstrated [5]. Along these lines, we set out to synthesise water-soluble AB-type polyamides of sugar compounds directly and this required sugar-based amino acids. A very recent

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report described the polymerisation of 2-amino-2-deoxy-3,4,5,6-tetra-*O*-methyl-D-gluconic acid via the azlactone [6].

This contribution will report the efficient and simple preparation of the required methyl (D-glycopyranosyl azide)uronates as precursors for polyamide formation. As starting materials, the unblocked 1,2-*cis*- and 1,2-*trans*-glycopyranosyl azides can be prepared by well-elaborated methods [7].

Results and discussion

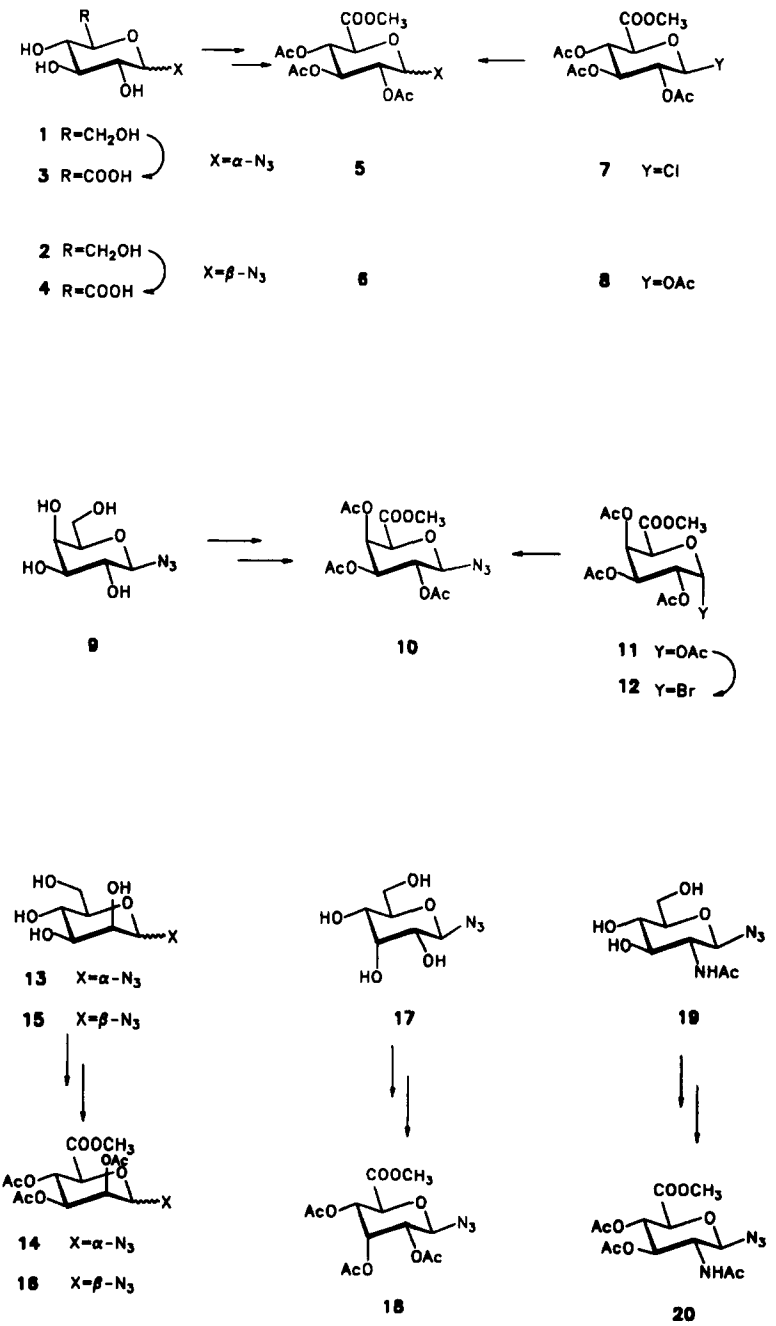
For oxidation of protected aldose derivatives to give the corresponding uronic acid, a variety of methods (CrO_3 [8–12], pyridinium dichromate [13], RuO_2 or $RuCl_3$ and HIO_4 [14–19]) are at hand and the free sugars can be converted into uronic acids employing Pt-catalysed oxidation [20] or the recent electrochemical oxidation [21]. However, we were interested in converting the unprotected glycosyl azides into the corresponding uronic acids directly, thus avoiding deprotection procedures and the use of expensive catalysts.

The oxidation of pentaerythritol with hypochlorite to give tris(hydroxymethyl)acetic acid was reported years ago [22]. Recently, a variation of this reaction by addition of the 2,2,6,6-tetramethylpiperidine 1-oxide radical (''TEMPO'') proved to be particularly effective in the NaOCl-oxidation of methyl α-D-glucopyranoside to methyl α-D-glucopyranuronate [23] (cf. also ref. [24]). In fact, by employing this oxidation procedure in aqueous sodium hydrogencarbonate with sodium hypochlorite and a catalytic amount of TEMPO on both α- and β-D-glucopyranosyl azide (**1** and **2**), the corresponding glucuronic acid derivatives **3** and **4** could be obtained in smooth reactions and in very good yields. Considerable amounts of inorganic salts are present in the mixture and therefore the water-soluble acids **3** and **4** were not isolated. Following evaporation of the crude material, esterification with methyl iodide and subsequent acetylation with acetic anhydride with catalysis by 4-dimethylaminopyridine [25,26] led to methyl (2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl azide)uronate (**5**) and the β anomer **6**. The latter compound was identical with the product obtained from methyl (2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl bromide)uronate with sodium azide [27–29].

As an alternative preparation for the 1,2-*cis*-azide **5**, a simple S_N2 reaction of the β-chloride **7** [30c,31] with sodium azide [7,32] in hexamethylphosphoric triamide (HMPT) could be realised in acceptable yield. Finally, the uronic acid ester **6** could be obtained in 80% yield by treatment of the β-acetate **8** with trimethylsilyl azide under $SnCl_4$-catalysis [7].

By similar oxidation of β-D-galactopyranosyl azide (**9**), the crystalline methyl galactopyranuronate **10** could be prepared in good yield following chromatographic purification. Alternatively, the synthesis was successful with calcium hypochlorite in aqueous suspension with catalytic amounts of TEMPO. In another approach starting with methyl (2,3,4,-tri-*O*-acetyl-α-D-galactopyranosyl bromide)uronate **12** [30], which in turn could be obtained from the α-acetate **11** [33], the β-azide **10** was prepared using sodium azide in *N,N*-dimethylformamide.

Along these lines, the mannopyranosyl azides **13** and **15** could be oxidised and


1 R=CH2OH
3 R=COOH
X=α-N3
5
7 Y=Cl
2 R=CH2OH
4 R=COOH
X=β-N3
6
8 Y=OAc
9
10
11 Y=OAc
12 Y=Br
13 X=α-N3
15 X=β-N3
14 X=α-N3
16 X=β-N3
17
18
19
20

Scheme 1.

blocked to give the corresponding anomers **14** and **16** of methyl (2,3,4-tri-*O*-acetyl-D-mannopyranosyl azide)uronate in low yields. This reaction sequence could also be employed for both β-D-allopyranosyl azide (**17**) and 2-acetamido-2-deoxy-β-D-glucopyranosyl azide (**19**) to give the crystalline uronic acid esters **18** and **20**, respectively, in good yields.

3. Experimental

General methods.—Melting points were determined with a Boëtius melting-point apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 243 polarimeter. NMR spectra were recorded with a Bruker AMX 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) instrument. TLC was performed on Merck Kieselgel 60 F_{254} (detection by charring with 5% ethanolic H_2SO_4 and flash chromatography on silica gel (Kieselgel 60, 230–400 mesh, Merck). Solvents were dried prior to use. The following abbreviations are used for solvent mixtures: 85:12:3 *i*-PrOH–AcOH–H_2O, eluent *A*; EtOAc–toluene, eluent *B*; 3:1 methyl *tert*-butyl ether–hexane, eluent *C*; 5:1 toluene–EtOAc, eluent *D*; 10:9:2 *i*-PrOH–$MeNO_2$–H_2O, eluent *E*; 3:1 toluene–EtOH, eluent *F*; 9:1 $CHCl_3$–MeOH, eluent *G*; 7:5 hexane–EtOAc, eluent *H*.

General procedures.—(*A*) The solution of the corresponding azide (10 mmol), KBr (0.11 g), and 2,2,6,6-tetramethylpiperidine 1-oxide (TEMPO, 0.10 g) in satd aq $NaHCO_3$ (53 mL) was stirred at 15–18°C while a solution of NaOCl (Merck, 67 mL) was added dropwise keeping the temperature below 23–24°C. After completion of the reaction (TLC control: eluent *A* or *E*), the solution was lyophilised, and the dry salt mixture was suspended in *N,N*-dimethylformamide (30 mL) and stirred with MeI (0.8 mL) for 20 h. Thereafter Ac_2O (3 mL) and 4-dimethylaminopyridine (0.04 g) were added and stirring was continued for 16 h at room temperature. Water (100 mL) was added and the product separated and extracted with EtOAc (3 × 120 mL). The combined extracts were washed with water (2 × 40 mL), dried ($CaCl_2$), and concentrated. The residue was applied to a silica gel column and chromatographed.

(*B*) The solution of the corresponding azide (1 mmol) and KBr (0.011 g) in satd aq $NaHCO_3$ (5.3 mL) was stirred at a temperature of 15–18°C while solid $Ca(OCl)_2$ (0.25 g) was added. After 5 min, TEMPO (0.006 g) was added in portions and the mixture was vigorously stirred at 16–20°C. To complete the reaction more $Ca(OCl)_2$ (2 × 0.25 g) and TEMPO (0.006 g) were added. The mixture was worked up as in (*A*).

*Methyl (2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl azide)uronate* (**5**).—(*a*) α-D-Glucopyranosyl azide (**1**) [34] (1.2 g, 6 mmol) was treated as described in the general procedure (*A*). The product (1.69 g, 94%) was purified by chromatography (solvent *H*) to yield **5** (0.95 g, 44%) as a syrup; $[\alpha]_D^{21}$ +151° (*c* 1.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.68 (d, 1 H, H-1), 4.96 (dd, 1 H, H-2), 5.42 (dd, 1 H, H-3), 5.16 (dd, 1 H, H-4), 4.49 (d, 1 H, H-5), 3.78 (s, 3 H, OMe), 2.06, 2.03, 1.98 (3 s, 9 H, 3 Ac); $J_{1,2}$ 6.2, $J_{2,3} = J_{3,4} = 8.3$, $J_{4,5}$ 8.5 Hz; ^{13}C NMR ($CDCl_3$): δ 20.00, 20.05, 20.17 (3 CO*Me*), 52.51 (OMe), 68.18, 68.50, 69.22, 69.47, 85.65 (C-1), 166.9, 168.9, 169.2, 169.3 (4 C=O). Anal. Calcd for $C_{13}H_{17}N_3O_9$: C, 43.46; H, 4.77; N, 11.70. Found: C, 43.56; H, 4.58; N, 11.76.

(*b*) Sodium azide (0.51 g, 7.8 mmol) was added to a stirred solution of methyl

(2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl chloride)uronate (**7**) [30c,31] (0.95 g, 2.7 mmol) in HMPT (5 mL). The suspension was stirred at room temperature (16 h), then diluted with water (60 mL) and EtOAc (80 mL). The separated organic layer was washed with water (10 mL), dried ($CaCl_2$), and concentrated to dryness. Chromatographic purification was as in (*a*). Yield: 0.54 g (56%); $[\alpha]_D^{21}$ + 144° (*c* 1.7, $CHCl_3$).

*Methyl (2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl azide)uronate* (**6**).—(*a*) β-D-Glucopyranosyl azide (**2**) [34] (4.1 g, 20 mmol) was treated as described in the general procedure (*A*). The crystalline product (5.29 g, 74%) had mp 153°C; $[\alpha]_D^{21}$ −43° (*c* 1.1, $CHCl_3$); lit. [27] mp 153°C, $[\alpha]_D^{23}$ −21.3° ($CHCl_3$); lit. [29] mp 152–153°C; ^{1}H NMR ($CDCl_3$): δ 4.12 (d, 1 H, H-1), 5.25 (m, 1 H, H-2), 4.96 (m, 1 H, H-3), 5.25 (m, 1 H, H-4), 4.71 (d, 1 H, H-5), 3.78 (s, 3 H, OMe), 2.03 (s, 6 H, 2 Ac), 2.08 (s, 3 H, Ac); $J_{1,2}$ 9.7, $J_{4,5}$ 8.6 Hz; ^{13}C NMR ($CDCl_3$): δ 20.54 (2 CO*Me*), 20.45 (CO*Me*), 53.04 (OMe), 69.04, 70.46, 71.87, 74.30, 88.11 (C-1), 166.5, 169.12, 169.27, 169.97 (4 C=O). Anal. Calcd for $C_{13}H_{17}N_3O_9$: C, 43.46; H, 4.77; N, 11.70. Found C, 43.27; H, 4.67; N, 11.65.

(*b*) Methyl 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranuronate (**8**) [35] (37.6 g, 0.1 mol) in CH_2Cl_2 (500 mL) was mixed with trimethylsilyl azide (16 mL, 0.12 mmol) and $SnCl_4$ (6 mL). Upon standing for 18–20 h, the solution was washed with aq $NaHCO_3$ to remove tin salts. The organic phase was washed with water, dried ($CaCl_2$), and concentrated to dryness. The product (33.8 g, 94%) crystallised from EtOH (240 mL) to give **6** as needles (23.75 g, 66%); mp 152–153°C; $[\alpha]_D^{22}$ −45.4° (*c* 0.68, $CHCl_3$). Anal. Found: C, 43.93; H, 4.74; N, 11.74.

*Methyl (2,3,4-tri-*O*-acetyl-β-D-galactopyranosyl azide)uronate* (**10**).—(*a*) β-D-Galactopyranosyl azide (**9**) [34] (2.05 g, 10 mmol) was treated as described in the general procedure (*B*). The waxy product (2.31 g, 64%) was purified by chromatography (solvent *B*) to yield **10** as a syrup, which crystallised; $[\alpha]_D^{21}$ +7° (*c* 3.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 4.68 (d, 1 H, H-1), 5.20 (m, 1 H, H-2), 5.10 (m, 1 H, H-3), 5.74 (d, 1 H, H-4), 4.41 (d, 1 H, H-5), 3.78 (s, 3 H, OMe), 2.10, 2.08, 2.0 (3 s, 9 H, 3 Ac); $J_{1,2}$ 8.7, $J_{2,3}$ 10.4, $J_{3,4}$ 3.6, $J_{4,5}$ 3.1 Hz; ^{13}C NMR ($CDCl_3$): δ 20.50, 20.52, 20.63 (3 CO*Me*), 52.90 (OMe), 67.78, 68.10, 70.45, 74.10, 88.44 (C-1), 165.91, 169.23, 169.73, 169.92 (4 C=O). Anal. Calcd for $C_{13}H_{17}N_3O_9$: C, 43.45; H, 4.77; N, 11.70. Found: C, 43.36; H, 4.53; N, 11.69.

(*b*) Methyl 1,2,3,4-tetra-*O*-acetyl-α-D-galactopyranuronate (**11**) (see below) (1.88 g, 5 mmol) in CH_2Cl_2 (18 mL) was mixed with trimethylsilyl azide (0.9 mL, 6.75 mmol) and $SnCl_4$ (0.3 mL). After 20 h, the solution was washed with aq $NaHCO_3$ to remove tin salts. The organic phase was washed with water, dried ($CaCl_2$), and concentrated. The syrup was purified by chromatography (solvent *D*) to yield **10** (0.96 g, 53%). The syrup solidified on standing; mp 163°C (from EtOH).

(*c*) The solution of methyl (2,3,4-tri-*O*-acetyl-α-D-galactopyranosyl bromide)uronate (**12**) [30] (2.38 g, 6 mmol) in dry HMPT (9 mL) was treated with NaN_3 (0.8 g). The mixture was stirred for 20 h and the black suspension was diluted with water (90 mL), extracted with ether (2 × 60 mL), washed with water, and concentrated. Chromatography of the syrupy material (1.4 g, solvent *D*) yielded pure **10** (0.9 g, 41%); mp 163°C (subl.) (from EtOH). Anal. Found: 43.12; H, 4.87; N, 11.68.

The products prepared under (*a*), (*b*), and (*c*) showed identical IR and ^{1}H NMR spectra.

*Methyl 1,2,3,4-tetra-*O*-acetyl-α-*D*-galactopyranuronate* (**11**) [33].—The solution of 1,2,3,4-tetra-*O*-acetyl-α-D-galactopyranuronic acid [39] (3.62 g, 10 mmol) and diazabicyclo[5.4.0]undec-7-ene (1.49 mL, 10 mmol) in dry DMF (44 mL) was stirred with MeI (0.62 mL) for 4 h. The solvent was removed in vacuo and the residue triturated with water (~ 70 mL). The precipitated product (3.25 g, 86%) crystallised from EtOH (10 mL); mp 142–143°C; $[\alpha]_D^{21}$ +142° (*c* 1.5, $CHCl_3$); lit [33a] mp 142–143°C, $[\alpha]_D$ +143°C (*c* 1, $CHCl_3$); lit. [30b] mp 142–144°C, $[\alpha]_D$ +138° (*c* 1, $CHCl_3$).

*Methyl (2,3,4-tri-*O*-acetyl-α-*D*-mannopyranosyl azide)uronate* (**14**).—α-D-Mannopyranosyl azide (**13**) [32] (0.81 g, 4 mmol) was treated as described in the general procedure (*A*). The brown syrupy product was purified by chromatography (solvent *D*) to yield **14** (0.20 g, 11%); $[\alpha]_D^{29}$ +53° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.49 (d, 1 H, H-1), 5.13 (t, 1 H, H-2), 5.40 (m, 1 H, H-3), 5.33 (dt, 1 H, H-4), 4.52 (d, 1 H, H-5), 3.80 (s, 3 H, OMe), 2.14, 2.09, 2.01 (3 s, 9 H, 3 Ac); $J_{1,2}$ 4.0, $J_{2,3}$ 3.5, $J_{3,4}$ 7.5, $J_{4,5}$ 7 Hz. Anal. Calcd for $C_{13}H_{17}N_3O_9$: C, 43.45; H, 4.77; N, 11.70. Found: C, 43.41; H, 4.64; N, 11.78.

*Methyl (2,3,4-tri-*O*-acetyl-β-*D*-mannopyranosyl azide)uronate* (**16**).—(*a*) β-D-Mannopyranosyl azide (**15**) [36a] (1.48 g, 6 mmol) was treated as described in the general procedure (*A*). The syrupy product was purified by chromatography (solvent *C*) to yield **16** (0.24 g, 11%); mp 97–100°C, $[\alpha]_D^{21}$ −171° (*c* 3.77, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 4.85 (d, 1 H, H-1), 5.47 (dd, 1 H, H-2), 5.11 (dd, 1 H, H-3), 5.43 (dd, 1 H, H-4), 4.13 (d, 1 H, H-5), 3.79 (s, 3 H, OMe); $J_{1,2}$ 1.0, $J_{2,3}$ 3.2, $J_{3,4}$ 10.0, $J_{4,5}$ 9.6 Hz; ^{13}C NMR ($CDCl_3$): δ 20.04, 20.00, 19.95 (3 CO*Me*), 52.43 (OMe), 70.89, 71.17, 72.31, 75.69, 83.06 (C-1), 165.08, 166.28, 169.11, 169.23 (4 C=O). Anal. Calcd. for $C_{13}H_{17}N_3O_9$: C, 43.46; H, 4.80; N, 11.70. Found: C, 43.45; H, 4.70; N, 11.71.

(*b*) β-D-Mannopyranosyl azide (**15**) [36a] (1.23 g, 5 mmol) was treated as described in the general procedure (*B*). The syrupy product was purified as in (*a*). Yield: 0.41 g (23%); mp 96–99°C.

*β-*D*-Allopyranosyl azide* (**17**).—2,3,4,6-Tetra-*O*-acetyl-β-D-allopyranosyl azide [37] (5.25 g, 14.06 mmol) in dry MeOH (52 mL) was treated with 1 M $NaOCH_3$ (0.7 mL). After 20 min, the solution was neutralised with Dowex 50W-X4 (H^+) ion-exchange resin and filtered. β-D-Allopyranosyl azide (**17**; 2.8 g, 97%) crystallised from EtOH (9 mL) after evaporating the solution; mp 121–123°C; $[\alpha]_D^{22}$ −42° (*c* 1.56, H_2O); ^{1}H NMR (200 MHz, D_2O): δ 5.00 (d, 1 H, H-1), 3.50 (dd, 1 H, H-2), 4.23 (dd, 1 H, H-3), 3.69 (dd, 1 H, H-4), 3.87 (ddd, 1 H, H-5), 3.77 (dd, 1 H, H-6a), 3.96 (dd, 1 H, H-6b); $J_{1,2}$ 9.0, $J_{2,3} = J_{3,4} = 3.0$, $J_{4,5}$ 10.2, $J_{5,6a}$ 5.6, $J_{5,6b}$ 2.0, $J_{6a,6b}$ 12.2 Hz; ^{13}C NMR (D_2O): δ 61.31, 66.78, 70.46, 71.18, 75.23, 88.09 (C-1). Anal. Calcd for $C_6H_{11}N_3O_5$: C, 35.12; H, 5.41; N, 20.48. Found: C, 34.80; H, 5.20; N, 19.83.

*Methyl (2,3,4-tri-*O*-acetyl-β-*D*-allopyranosyl azide)uronate* (**18**).—The freshly crystallised azide **17** (1.2 g, 6 mmol) was treated as described in the general procedure (*A*). The syrupy product was purified by chromatography (solvent *B*) to yield **18** (0.97 g, 45%); mp 64–67°C (EtOH); $[\alpha]_D^{21}$ −29.6° (*c* 2.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.04 (d, 1 H, H-1), 4.68 (dd, 1 H, H-2), 5.67 (dd, 1 H, H-3), 5.23 (dd, 1 H, H-4), 4.46 (d, 1 H, H-5), 3.79 (s, 3 H, OMe); $J_{1,2}$ 8.7, $J_{2,3}$ 3.1, $J_{3,4}$ 8.6, $J_{4,5}$ 9.7 Hz; Anal. Calcd for $C_{13}H_{17}N_3O_9$: C, 43.46; H, 4.80; N, 11.70. Found: C, 43.55; H, 4.58; N, 11.40.

*Methyl (2-acetamido-3,4-di-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl azide)uronate* (**20**).

—(*a*) 2-Acetamido-2-deoxy-β-D-glucopyranosyl azide (**19**) [38] (1.23 g, 5 mmol) was treated as described in the general procedure (*A*). The solid product (1.47 g, 82%) crystallised from EtOH; mp 175–177°C; $[\alpha]_D^{21}$ −41.8° (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 4.93 (dd, 1 H, H-1), 3.86 (dd, 1 H, H-2), 5.37 (dd, 1 H, H-3), 5.22 (dd, 1 H, H-4), 4.15 (d, 1 H, H-5), 3.77 (s, 3 H, OMe), 5.74 (d, 1 H, NH), 2.06, 2.03, 1.99 (3 s, 9 H, 3 Ac); $J_{1,2}$ 9.2, $J_{1,NH}$ 8.1, $J_{2,3}$ 10.2, $J_{3,4} = J_{4,5} = 9.7$ Hz. Anal. Calcd for $C_{13}H_{18}N_4O_8$: C, 43.57; H, 5.06; N, 15.64. Found: C, 43.79; H, 5.22; N, 15.64.

(*b*) 2-Acetamido-2-deoxy-β-D-glucopyranosyl azide (**19**) [38] (1.23 g, 5 mmol) was treated as described in the general procedure (*B*). The product (1.43 g, 79.8%) was crystallised from EtOH; mp 175–177°C.

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References

[1] J. Thiem and F. Bachmann, *Makromol. Chem.*, 192 (1991) 2163–2182.
[2] F. Bachmann and J. Thiem, *J. Polym. Sci., Part A*, 30 (1992) 2059–2062.
[3] D.E. Kiely, L. Chen, and T.-H. Lin, *J. Am. Chem. Soc.*, 116 (1994) 571–578.
[4] J. Thiem and F. Bachmann, *Makromol. Chem.* 194 (1993) 1035–1057.
[5] J. Thiem and M. Ruppenstein, unpublished results.
[6] M. de Gracia García Martín, M.V. de Paz Bánez, and J.A. Galbis Pérez, *Carbohydr. Res.*, 240 (1993) 301–306.
[7] Z. Györgydeák, L. Szilágyi, and H. Paulsen, *J. Carbohydr. Chem.*, 12 (1993) 139–163.
[8] P. Kováč, *J. Carbohydr. Nucleos. Nucleot.*, 1 (1974) 183–186.
[9] V.I. Betaneli, A. Ya. Ott, O.V. Brukhanova, and N.K. Kochetkov, *Carbohydr. Res.*, 179 (1988) 37–50.
[10] V.I. Betaneli, O.V. Brukhanova, A. Ya. Ott, and N.K. Kochetkov, *Bioorg. Khim.*, 16 (1990) 390–401.
[11] W. Steffan, C. Vogel, and H. Kristen, *Carbohydr. Res.*, 204 (1990) 109–120.
[12] H.P. Wessel, L. Lábler, and T.B. Tschopp, *Helv. Chim. Acta*, 72 (1989) 1268–1277.
[13] J.C. Jacquinet, *Carbohydr. Res.*, 199 (1990) 153–181.
[14] J. Smejkal and L. Kalvoda, *Collect. Czech. Chem. Commun.*, 38 (1973) 1981–1984.
[15] P. Garner and J.M. Park, *J. Org. Chem.*, 55 (1990) 3772–3787.
[16] S.J. Hecker and M.L. Minich, *J. Org. Chem.*, 55 (1990) 6051–6054.
[17] P.E. Morris, Jr., D.E. Kiely, and G.S. Vigee, *J. Carbohydr. Chem.*, 9 (1990) 661–673.
[18] A.G.H. Wee, *Tetrahedron*, 46 (1990) 5065–5076.
[19] G. Casiraghi, L. Colombo, G. Rassu, and P. Spanu, *J. Org. Chem.*, 56 (1991) 6523–6527.
[20] K. Heyns and H. Paulsen, *Adv. Carbohydr. Chem.*, 17 (1962) 169–221.
[21] H.J. Schäfer and R. Schneider, *Tetrahedron*, 47 (1991) 715–724.
[22] R. Bognár and L. Somogyi, *Magy. Kém. Foly.*, 71 (1965) 273–275; *Chem. Abstr.*, 63 (1965) 8187c; R. Bognár and L. Somogyi, *Acta Chim. Acad. Sci. Hung.*, 45 (1965) 57–62; *Chem. Abstr.*, 63 (1965) 16207a.
[23] N.J. Davis and S.L. Flitsch, *Tetrahedron Lett.*, 34 (1993) 1181–1184; *J. Chem. Soc., Perkin Trans. 1*, (1994) 359–367.
[24] C.E. McDonald, L.E. Nice, A.W. Shaw, and N.B. Nestor, *Tetrahedron Lett.*, 34 (1993) 2741–2744.
[25] G. Höfle, W. Steglich, and H. Vorbrüggen, *Angew. Chem.*, 90 (1978) 602–615; *Angew. Chem. Int. Ed. Engl.*, 17 (1978) 569–583.

[26] B.I. Glänzer, Z. Györgydeák, B. Bernet, and A. Vasella, *Helv. Chim. Acta*, 74 (1991) 343–369.
[27] Y. Nitta, M. Kuranari, and T. Kondo, *Yakugaku Zasshi*, 81 (1961) 1189–1194; *Chem. Abstr.*, 56 (1962) 6077i.
[28] Y. Nitta and M. Kuranari (Chugai Pharm. Co., Ltd.), Jap. Patent 2312 ('62), Aug. 13, 1959; *Chem. Abstr.*, 58 (1963) 9219e.
[29] R.T. Lee and Y.C. Lee, *Carbohydr. Res.*, 64 (1978) 303–308.
[30] (a) S. Morell, L. Baur, and K.P. Link, *J. Biol. Chem.*, 110 (1935) 719–725; (b) E.L. Pippen and R.M. McCready, *J. Org. Chem.*, 16 (1951) 262–268; (c) P. Kováč, I. Farkas, V. Mihálov, R. Palovcik, and R. Bognár, *J. Carbohydr. Nucleos. Nucleot.*, 3 (1976) 57–69.
[31] W. Korytnyk and J.A. Mills, *J. Chem. Soc.*, (1959) 636–649; K. Heyns, W.-P. Trautwein, F.G. Espinosa, and H. Paulsen, *Chem. Ber.*, 99 (1966) 1183–1191.
[32] Z. Györgydeák and H. Paulsen, *Liebigs Ann. Chem.*, (1977) 1987–1995.
[33] (a) S. Morell and K.P. Link, *J. Biol. Chem.*, 108 (1935) 763–771; (b) C. Vogel, H. Boye, and H. Kristen, *J. Prakt. Chem.*, 332 (1990) 28–36.
[34] Z. Györgydeák and L. Szilágyi, *Liebigs Ann. Chem.*, (1987) 235–241.
[35] (a) G.N. Bollenback, J.W. Long, D.G. Benjamin, and J.A. Lindquist, *J. Am. Chem. Soc.*, 77 (1950) 3310–3315; (b) P.C. Wyss, J. Kiss, and W. Arnold, *Helv. Chim. Acta*, 58 (1975) 1847–1864; (c) W.D.S. Bowering and T.E. Timell, *J. Am. Chem. Soc.*, 82 (1960) 2827–2830; (d) B. Dayal, G. Salen, J. Pardia, S. Shefer, G.S. Tint, G. Sasso, and T.H. Williams, *Carbohydr. Res.*, 240 (1993) 133–142.
[36] (a) Z. Györgydeák and H. Paulsen, *Liebigs Ann. Chem.*, (1977) 1978–1991; (b) W.A. Szarek, O. Achmatowicz, Jr., J. Plenkiewicz, and B.K. Radatus, *Tetrahedron*, 34 (1978) 1427–1437.
[37] H. Paulsen, Z. Györgydeák, and M. Friedmann, *Chem. Ber.*, 107 (1974) 1568–1578.
[38] L. Szilágyi and Z. Györgydeák, *Carbohydr. Res.*, 143 (1985) 21–41.
[39] K. Tajima, *Chem. Lett.*, (1985) 49–52; H. Wild, K. Mohrs, U. Niewöhner, and W. Steglich, *Liebigs Ann. Chem.*, (1986) 1548–1567.