Amino Acids and Amino Sugars from Bromodeoxyaldonolactones*

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Treatment of 6-bromo-2,6-dideoxy-D-*arabino* hexono-1,4-lactone (**1**) with sodium azide in DMF gave the corresponding 6-azido lactone (**2**). Reduction yielded the 6-amino lactone, isolated as the 7-membered lactam (**3**) or as the 6-amino lactone hydrochloride (**4**). 2-Bromo-2,6-dideoxy-L-gluconolactone (**5**), with sodium azide in acetone, gave the 2-azido-2,6-dideoxy-L-mannonolactone (**6**), which was reduced with sodium borohydride to the azido sugar **7**; finally, hydrogenation yielded 2-amino-2,6-dideoxy-L-mannose hydrochloride (**8**). Treatment of either 2,6-dibromo-2,6-dideoxy-D-mannono- (**9**) or -D-glucono-1,4-lactone (**12**) with sodium azide in acetone gave 2-azido-6-bromo-2,6-dideoxy-D-mannono-1,4-lactone (**10**). When **9**, **10** or **12** was treated with sodium azide in DMF, 2,6-diazido-2,6-dideoxy-D-mannono-1,4-lactone (**11**) was formed. The azido lactones **10** and **11** were reduced to the corresponding sugars **13** and **14**, respectively. Catalytic hydrogenation of **13** followed by hydrolysis gave 2-amino-2,6-dideoxy-D-mannose hydrochloride (**15**), whereas **14** by the same treatment gave 2,6-diamino-2,6-dideoxy-D-mannose dihydrochloride (**17**). The bromo lactones (**9** and **12**) were equilibrated in DMF with sodium bromide.

Lately, there has been an increasing interest in synthesizing aminodeoxy sugars and non-naturally occurring amino acids, since many such compounds have been shown to exhibit antibiotic activity.[1] Previously, the behaviour of bromodeoxyaldonolactones towards oxygen nucleophiles was studied.[2,3] These investigations have now been extended to nitrogen nucleophiles. In the present paper a study of the reaction of some bromo lactones with azide ions is reported, and the subsequent conversion of the azides into aminodeoxy aldonic acids and aminodeoxy sugars is described.

Results and discussion

When 6-bromo-2,6-dideoxy-D-*arabino*-1,4-lactone (**1**)[3,4] was treated with sodium azide in *N,N*-dimethylformamide (DMF), a crystalline 6-azido-2,6-dideoxy lactone (**2**) was formed. Catalytic reduction of **2** under neutral conditions gave a compound assigned the lactam structure **3** on the basis of spectroscopic evidence. When **3** was boiled in aqueous hydrochloric acid, the 6-amino lactone hydrochloride (**4**) was formed. The latter compound was also obtained when the azide (**2**) was hydrogenated in the presence of hydrochloric acid. Sugar lactams with five-, six- and seven-membered rings have been obtained by similar procedures[5,6] whereas ε-L-gluconolactam was obtained by reduction of the oxime of D-glucofuranurono-3,6-lactone.[7]

Treatment of 2-bromo-2,6-dideoxy-L-gluconо-1,4-lactone (**5**), readily available from L-rhamnonolactone,[4] with sodium azide in acetonitrile or acetone gave 2-azido-2,6-dideoxy-L-mannono-1,4-lactone (**6**), contaminated with a small amount of the C-2 epimeric azido lactone. Crystallization gave **6** in 40–50% yield. Reduction of the lactone function with sodium borohydride yielded the azido sugar (**7**), which was shown by ^{1}H NMR spectroscopy to possess the *manno* configuration. Hydrogenation of the azido group

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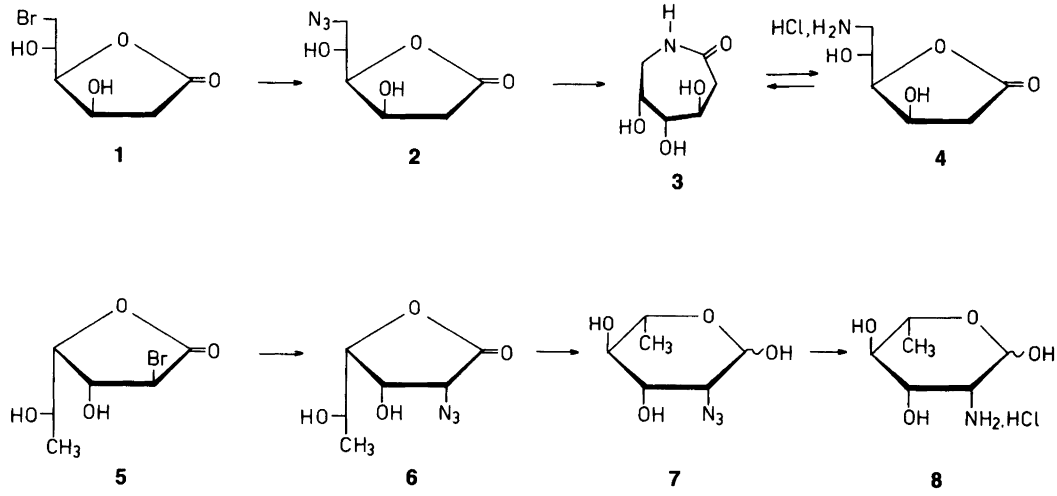
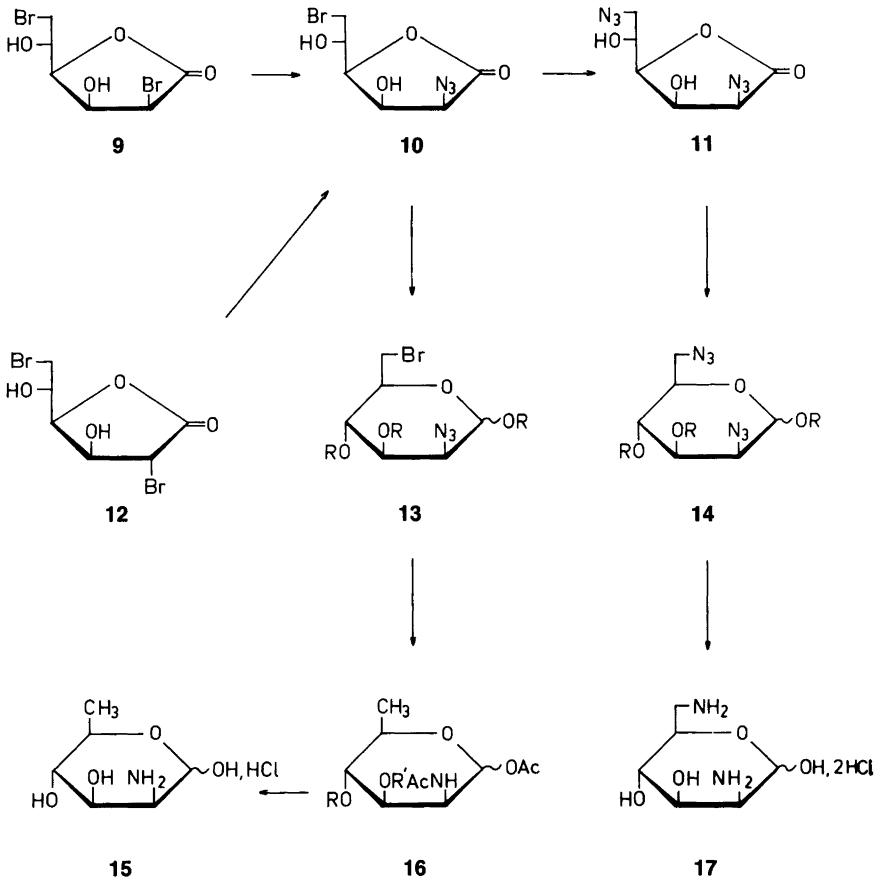


gave 2-amino-2,6-dideoxy-L-mannose, isolated as the hydrochloride.[8]

The difference in reactivity of the bromine atoms in the lactones **1** and **5** is reflected in the solvents used for the nucleophilic substitution reactions. While the C-2 bromine in **5** was substituted using acetone or acetonitrile as solvent, the C-6 bromine in **1** required DMF at the same temperature. Thus, when 2,6-dibromo-2,6-dideoxy-D-mannono-1,4-lactone (**9**) was boiled with sodium azide in acetone for 26 h, a 2-azido-6-bromo dideoxy lactone (**10**) was formed. Purification by flash chromatography gave the crystalline lactone (**10**) in 56% yield. Smaller amounts of faster-moving compounds were identified by ^{13}C NMR spectroscopy to be a 2,6-diazido lactone (~5%) and probably the C-2 epimer of **10** (~5%). Analogous treatment of 2,6-dibromo-2,6-dideoxy-D-glucono-1,4-lactone (**12**) yielded the same products. Thus, the two epimeric dibromo lactones (**9** and **12**) both gave the 2-azido lactone (**10**) as the main product. Reduction of **10** with sodium borohydride produced the corresponding hexose, which was shown by ^{1}H NMR spectroscopy to have the *manno* configuration (**13**). Reduction of the acetylated sugar **13b** gave, in one step, 2-acetamido-1,4-di-*O*-acetyl-2,6-dideoxy-D-mannose (**16b**, R′ = H). Subsequent hydrolysis in aqueous hydrochloric acid yielded crystalline 2-amino-2,6-dideoxy-D-mannose hydrochloride[9] (**15**), enantiomeric with **8**. The amino sugar (**15**) can thus be obtained from the dibromo lactone (**9**) without any intermediate purification in a yield of ca. 20%.

When the 2-azido-6-bromo lactone (**10**), or one of the two C-2 epimeric dibromo lactones (**9** and **12**), was treated with sodium azide in DMF at 80°C for 1 h, the 2,6-diazido lactone (**11**) was obtained. As seen from a ^{13}C NMR spectrum, the product was sufficiently pure to be used in further reactions. Flash chromatography gave crystalline **11**. The *manno* configuration was proved by conversion of **11** into the crystalline 2,6-diazido hexose (**14**). Catalytic hydrogenation of the latter in aqueous hydrochloric acid gave 2,6-diamino-2,6-dideoxy-D-mannose dihydrochloride (**17**),[8] thus obtained in an overall yield of about 50% from the dibromomannonolactone (**9**). The azido lactones (**10** and **11**) can be converted into the hydrochlorides of the 2-amino and 2,6-diamino lactones by catalytic hydrogenation in aqueous hydrochloric acid.[16]

The formation of **10** from both the epimers **9** and **12** was unexpected. It has recently been reported, that when lactones with a tosyl[13] or a triflate group[11,12] at O-2 were treated with azide ion, 2-azido lactones were formed with either retention[11] or inversion[12,13] of the configuration at C-2; no explanation of these results was given. We therefore looked more closely into the mechanism of the reaction, and the stability of the 2-bromo lactones was first investigated. When either **9** or **12** was heated under reflux in acetonitrile for 24 h, mixtures of **9** and **12** were ob-



tained, as seen from ^{13}C NMR spectra. Starting from **9**, the ratio between **9** and **12** was about 3:1 while it was about 1:6 when starting from **12**. This indicates that the *gluco* isomer (**12**) isomerizes slower than the *manno* isomer (**9**), and that the equilibrium is not attained within 24 h. When either of the bromo lactones was kept in DMF at room temperature, no isomerization could be detected. Addition of sodium bromide, however, caused a slow isomerization at room temperature, and on heating to 80 °C the equilibrium between **9** and **12** was attained within one hour, the ratio being 1.5:1. It has been reported that α-bromo ketones isomerize in polar media,[14] and recently it has been shown that substituted 2-bromobutyrolactones isomerize and eliminate when heated in DMF with lithium bromide.[15] The present results may be explained by isomerization of the two dibromo lactones at C-2 under the reaction conditions. When **9** was treated with sodium azide in 2-butanone at 40–50 °C, the *gluco* isomer (**12**) was observed as an intermediate in the reaction.[19] The formation of only the *manno* isomer (**10**) might then be a result of a higher reactivity of the bromo lactone having the *gluco* configuration (**12**). On the other hand, the configurational stability of 2-azido lactones in the reaction mixture should also be taken into consideration. Since we obtained predominantly one isomer in the reactions discussed in this paper, we cannot provide any clear answer to this question. This problem will be discussed in a forthcoming paper.[16]

Experimental

Melting points are uncorrected. Optical rotations were measured on a Perkin Elmer 241 polarimeter. NMR spectra were obtained on Bruker WH-90 and AM-500 NMR instruments. Dioxane (67.40 ppm) was used as internal reference for ^{13}C NMR spectra and acetone δ 2.22) for ^{1}H NMR spectra in D_2O. TMS was used as the reference for spectra in $CDCl_3$. Column chromatography was performed on silica gel 60 (40–63 μm, Merck 9385) using the flash technique. Evaporations were carried out in vacuum at 50 °C, unless otherwise indicated. Microanalyses were performed by NOVO Microanalytical Laboratory.

*6-Azido-2,6-dideoxy-D-*arabino-*hexono-1,4-lactone* (**2**). 6-Bromo-2,6-dideoxy-D-*arabino*-hexono-1,4-lactone (**1**)[3,4] (5.0 g) in DMF (25 ml) was stirred with sodium azide (5.0 g) for 1 h at 90 °C with protection from light. After cooling, the mixture was diluted with EtOAc (250 ml) and filtered. The filtrate was concentrated (1 mmHg). The red residue was redissolved in EtOAc, treated with activated carbon, filtered and concentrated to a syrup (6.0 g), which was crystallized from $CHCl_3$ to give 3.0 g (72 %) of **2**; m.p. 101–102 °C. Recrystallization from ethyl acetate–hexane gave a product with m.p. 106–108 °C; $[\alpha]_D^{20}$ +74.2° (*c* 1.7, EtOAc). Anal. $C_6H_9N_3O_4$: C, H, N. ^{13}C NMR (D_2O): 179.9 ppm (C-1), 84.1 (C-4), 62.2, 67.6 (C-3, C-5), 54.7 (C-6), 39.6 (C-2).

*6-Amino-2,6-dideoxy-D-*arabino-*hexono-1,6-lactam* (**3**). The 6-azido lactone (**2**) (1.5 g) was dissolved in CH_3OH (15 ml) and the solution stirred under H_2 for 3 h in the presence of 5 % palladium-on-carbon (100 mg). The catalyst was filtered off and washed thoroughly with aqueous CH_3OH (50 %). The combined filtrate and washings were concentrated and the residue (ca. 2 g) was crystallized from H_2O–EtOH to give 875 mg (68 %) of **3**; m.p. 202–203 °C (decomp.). Recrystallization from H_2O–EtOH gave a product with m.p. 206–207 °C (decomp.). $[\alpha]_D^{20}$ −41.0° (*c* 0.8, H_2O). Anal. $C_6H_{11}NO_4$: C, H, N. IR (KBr): 1620 (s) cm^{-1}. ^{13}C NMR (D_2O): 177.6 ppm (C-1), 76.7, 68.9, 67.3 (C-3, C-4, C-5), 42.3 (C-6), 39.2 (C-2).

*6-Amino-1,6-dideoxy-D-*arabino-*hexono-1,4-lactone hydrochloride* (**4**). The azido lactone (**2**) (1.1 g) was dissolved in water (10 ml) containing conc. HCl (1 ml) and the solution was stirred under H_2 for 20 h in the presence of 5 % palladium-on-carbon (100 mg). Filtration and concentration left a syrup (~1 g), a ^{13}C NMR spectrum of which showed the presence of **4** together with a small amount of the amino acid [74.6 ppm, 67.9, 67.1 (C-3, C-4, C-5), 43.1 (C-6), 39.0 (C-2)]. Crystallization from EtOH containing a few drops of H_2O gave **4** (526 mg, 45 %), m.p. 80–83 °C. Recrystallization from the same solvent yielded a product with m.p. 83–84 °C. ^{13}C NMR (D_2O): 179.7 ppm (C-1), 84.9 (C-4), 68.1, 65.2 (C-3, C-5), 43.2 (C-6), 39.5 (C-2). The mother liquor was absorbed on a column of acidic ion exchange resin (Amberlite IR 120, H^+). The column was washed with H_2O until neutral and then eluted with aqueous ammonia (12 %). Evaporation gave 560 mg (59%) of the lactam **3**, identical with the product described above.

2-Azido-2,6-dideoxy-L-mannono-1,4-lactone (**6**). 2-Bromo-2,6-dideoxy-L-glucono-1,4-lactone (**5**)[4] (5.0 g) was dissolved in acetonitrile (50 ml) and the solution stirred with sodium azide (10 g) at 95 °C for 7 h. After cooling, EtOAc (~100 ml) was added and the mixture filtered. Concentration left a red residue, which was dissolved in H_2O (10 ml) and extracted with EtOAc (5×50 ml). The combined organic extracts were dried (Na_2SO_4), treated with activated carbon and concentrated to a syrup (4 g, ca. 100 %). Addition of Et_2O gave crystalline **6** (1.73 g, 41.6 %); m.p. 106–110 °C. Recrystallization from ethyl acetate–hexane gave a product with m.p. 113–115 °C. $[\alpha]_D^{20}$ −15.6° (*c* 0.9, EtOAc). Anal. $C_6H_9NO_3$: C, H, N. ^{13}C NMR (D_2O): 175.4 ppm (C-1), 85.3 (C-4), 70.9, 64.7, 63.4 (C-3, C-5, C-2), 20.2 (C-6). The original crude mixture contained a 4:1 ratio, while the mother liquor from crystallization of **6** contained an equal amount of **6** and probably 2-azido-2,6-dideoxy-L-glucono-1,4-lactone, as seen from a ^{13}C NMR spectrum (D_2O): 174.3 ppm (C-1), 84.7 (C-4), 72.6, 66.4, 64.1 (C-3, C-5, C-2), 19.0 (C-6). No attempts were made to isolate this compound.

2-Azido-2,6-dideoxy-L-mannose (**7**). To a solution of the 2-azido lactone (**6**) (500 mg) in H_2O (5 ml) was added ion exchange resin (Amberlite

IR 120, H^+) (5 ml) and the mixture was cooled to 0 °C. Sodium borohydride (100 mg) was added at this temperature in the course of ca. 15 min, and the stirring was continued for another 30 min. Filtration and concentration left a residue to which CH_3OH was added and again evaporated. This was repeated twice. The residue (500 mg, ca. 100 %) was pure **7**, α:β ratio 1:1, as seen from a ^{13}C NMR spectrum (D_2O): 93.7 ppm (C-1 β), 93.0 (C-1 α), 73.2 (three carbons), 72.7, 70.8, 69.7, 67.0, 65.2 (C-2, C-3, C-4, C-5), 17.6 (C-6, α and β). ^1H NMR (90 MHz, D_2O): δ 5.00 (H-1 α, J_{12} 3.0 Hz), δ 4.80 (H-1 β, J_{12} = 1.0 Hz).

2-Amino-2,6-dideoxy-L-mannose hydrochloride (**8**). To the azido sugar **7** (500 mg) in H_2O (10 ml) was added 4 M hydrochloric acid (2 ml) and 5 % palladium-on-carbon (100 mg). The mixture was stirred under H_2 overnight. Filtration and concentration gave a product (~500 mg) which was crystallized from a small amount of water and acetone to give 350 mg (66 %) of **8** with m.p. 163–165 °C (decomp.); $[\alpha]_D^{20}$ +23.4° (*c* 1.3, H_2O, final); [reported[8] m.p. 170–5 °C (decomp.), $[\alpha]_D$ +25.5° (*c* 0.4, H_2O)]. ^{13}C NMR (D_2O): α-pyranose: 90.6 ppm (C-1), 72.2, 71.5, 69.2 (C-3, C-4, C-5), 56.1 (C-2), 16.8 (C-6); β-pyranose 90.1 (C-1), 71.7, 68.0, 66.7 (C-3, C-4, C-5), 54.9 (C-2), 16.8 (C-6).

2-Azido-6-bromo-2,6-dideoxy-D-mannono-1,4-lactone (**10**). A mixture of 2,6-dibromo-2,6-dideoxy-D-mannono-1,4-lactone (**9**) (2 g) and sodium azide (6 g) in dry acetone (50 ml) was boiled for 26 h. Cooling to room temperature, filtration and concentration left a crude product (~2 g) which was purified by flash chromatography using Et_2O as the eluent. The faster-moving minor components were identified by ^{13}C NMR spectroscopy to be the diazido lactone (**11**) (~5 %), a 2,3-unsaturated 2-azido lactone (~5 %) and probably 2-azido-6-bromo-2,6-dideoxy-D-glucono-1,4-lactone (~5 %) [^{13}C NMR (D_2O): 81.8 ppm (C-4), 72.4, 69.8 (C-3, C-5), 64.3 (C-2), 36.1 (C-6)]. None of the fractions were completely homogeneous. The compound **10** (1.1 g, 62 %) was then eluted; repeated chromatography of **10** (ethyl acetate–hexane, 1:2) gave 982 mg (56 %) with m.p. 78–81 °C. Recrystallization from ether–hexane gave a product with m.p. 80–81.5 °C; $[\alpha]_D^{20}$ +20.5° (*c* 1.1, EtOAc). Anal. $C_6H_8BrN_3O_4$: C, H, N. ^{13}C NMR (D_2O): 175.0 ppm (C-1), 81.9 (C-4), 70.6, 66.7 (C-3, C-5), 63.3 (C-2), 37.5 (C-6). ^1H NMR (500 MHz, $CDCl_3$): δ 4.25 (H-2, d, J_{23} 4.6 Hz). 4.68 (H-3, ddd, J_{34} 3.2, $J_{3,OH3}$ 1.5), 4.36 (H-4, dd, J_{45} 8.8), 4.22 (H-5, m), 3.80 (H-6, dd, J_{56} 3.0, $J_{66'}$ 11.0), 3.68 (H-6', dd, $J_{56'}$ 5.1), 2.62 (OH-3, d), 2.57 (OH-5, d, *J* 8.4).

1,3,4-Tri-O-acetyl-2-azido-6-bromo-2,6-dideoxy-D-mannopyranose (**13b**). The crude product, obtained from the reaction of **9** (5.0 g) with sodium azide (15 g) in dry acetone (125 ml) for 26 h at 80 °C as described above, was submitted to continuous extraction with ether for 30 min. This gave 3.92 g (89 %) of pale syrupy **10**, contaminated with other products (10–15 %) as described above. The product was reduced with sodium borohydride (500 mg) to the corresponding sugar **13**, as described above for the preparation of **7**. This gave a syrupy mixture (3.5 g, 80 %) of α and β **13**. ^{13}C NMR (D_2O): α-anomer: 93.6 ppm (C-1), 71.7, 70.9, 69.8 (C-3, C-4, C-5), 65.2 (C-2), 34.7 (C-6); β-anomer: 94.1 (C-1), 75.5, 73.1, 69.4 (C-3, C-4, C-5), 66.7 (C-2), 33.9 (C-6). Acetylation in pyridine (15 ml) with Ac_2O (15 ml) for 4 h gave, after work-up in the usual way, a slightly red-coloured residue (4.2 g), the ^{13}C and ^1H NMR spectra of which showed signals from two anomeric pyranoses, α:β ~ 2:1. $H_1\alpha$ (δ 6.13, J_{12} 2.0 Hz), $H_1\beta$ (δ 5.87, J_{12} 1.2 Hz).

2-Amino-2,6-dideoxy-D-mannopyranose hydrochloride (**15**). Crude **13b** (4.3 g) in EtOAc (30 ml) and Et_3N (8 ml) was stirred for 2 days under H_2 (5000 kPa) in the presence of 5 % palladium-on-carbon (800 mg). Filtration and concentration gave a residue (~3.5 g) consisting of 2-acetamido-1,4-di-*O*-acetyl-2,6-dideoxymannose together with $Et_3N \cdot HBr$. Acetylation in pyridine (10 ml) with Ac_2O (3 ml) overnight gave **16b** (2.54 g, 70 % based on **13b**). ^{13}C NMR ($CDCl_3$): 91.4 ppm (C-1), 69.9, 68.4, 67.7 (C-3, C-4, C-5), 48.8 (C-2), 22.1 (NAc), 20.0 (OAc), 16.8 (C-6). The product was boiled in 2M HCl for 2 h and the solution was then treated with activated carbon and concentrated. Addition of EtOH gave **15** (700 mg, 22 %, based on **9**); m.p. 168–170 °C; $[\alpha]_D^{20}$ −22.0° (*c* 1.0, H_2O) [reported[9] m.p. 175 °C (decomp.), $[\alpha]_D^{25}$ −23°].

2,6-Diazido-2,6-dideoxy-D-mannono-1,4-lactone (**11**). (a) From 2,6-dibromo-2,6-dideoxy-D-man-

nono-1,4-lactone (**9**). The dibromo lactone (**9**) (5.0 g) in DMF (25 ml) was stirred with sodium azide (5.0 g) at 80 °C for 1 h with protection from light. After cooling to room temperature, EtOAc (250 ml) was added. Filtration and concentration at 40 °C/1 mmHg (10–15 min) left a red syrup which contained only the diazido lactone (**11**) and traces of DMF, as seen from a ^{13}C NMR spectrum (D_2O): 174.4 ppm (C-1), 81.5 (C-4), 71.1, 67.6 (C-3, C-5), 63.2 (C-2), 54.7 (C-6); 165.5, 37.9 and 32.5 (DMF). Flash chromatography (ethyl acetate–hexane, 2:3) gave small amounts of faster-moving components followed by **11**, which crystallized to give 1.6 g (43 %); m.p. 58–60 °C. Recrystallization from ethyl acetate–hexane gave a product with m.p. 62–63 °C; $[\alpha]_D^{20}$ +30.0° (*c* 1.8, EtOAc). Anal. $C_6H_8N_6O_4$: C, H, N. ^1H NMR (500 MHz, $CDCl_3$): δ 4.26 (H-2, d, J_{23} 4.5 Hz), 4.67 (H-3, dd, J_{34} 3.0), 4.34 (H-4, dd, J_{45} 8.5), 3.54 (H-6', dd, $J_{56'}$ 5.5), 2.96 (OH-2, bs), 2.77 (OH-5, d, *J* 5.5).

(b) From 2,6-dibromo-2,6-dideoxy-D-gluconо-1,4-lactone (**12**). The dibromogluconolactone (**12**) (3.5 g) was treated with sodium azide (3.5 g) in DMF (20 ml) at 80 °C for 1 h with protection from light. Work-up as described above gave a crude product which was identical with the product obtained from the dibromomannonolactone, as seen from the ^{13}C NMR spectra. Flash chromatography (ethyl acetate–hexane, 2:3) gave 1.1 g (41 %) of crystalline material; m.p. 58–60 °C. Recrystallization from ether–pentane gave **11** with m.p. 60–62 °C, undepressed in admixture with the product above; $[\alpha]_D^{20}$ +29.3° (*c* 1.9, EtOAc). ^1H and ^{13}C NMR spectra were identical with those described above.

2,6-Diazido-2,6-dideoxy-D-mannose (**14**). The dibromo lactone (**9**) (5.0 g) was converted into the crude diazido lactone (**11**) as described above. A solution of the red product in water (25 ml) was submitted to continuous extraction with ether for 3 h. The extract was dried (Na_2SO_4), filtered and concentrated to give a colourless syrup (2.8 g). This was dissolved in water (20 ml) and treated with sodium borohydride (400 mg) in the presence of Amberlite IR 120 (H^+) as described for the preparation of **7**. This gave the diazido sugar **14** (1.94 g, 51.3 % based on **9**). Crystallization from EtOH gave a product with m.p. 128–129 °C. Recrystallization from EtOAc raised the m.p. to 130–131 °C. $[\alpha]_D^{20}$ +42.8° (*c* 1.1, H_2O, final). Anal. $C_6H_{10}N_3O_4$: C, H, N. A ^1H NMR spectrum obtained immediately after dissolving the compound in D_2O showed the major component to the β-anomer: δ 5.13 (H-1β, d, J_{12} 1.5 Hz); α-anomer: δ 5.34 (H-1α, d, J_{12} 1.5 Hz). ^{13}C NMR (125 MHz, D_2O): β-anomer: 94.0 ppm (C-1, J_{C1H1} 164 Hz), 75.7, 73.2, 68.1 (C-3, C-4, C-5), 66.7 (C-2), 51.6 (C-6). α-Anomer: 93.1 (C-1, J_{C1H1} 174 Hz), 71.7, 70.8, 68.4 (C-3, C-4, C-5), 65.2 (C-2). 51.7 (C-6).

2,6-Diamino-2,6-dideoxy-D-mannose · HCl (**17**). A solution of the syrupy 2,6-diazidomannose (**14**) (3.8 g), prepared as described above, in water (20 ml) and conc. hydrochloric acid (2 ml) was stirred under H_2 (5000 kPa) overnight in the presence of 5 % palladium-on-carbon (500 mg). Filtration and concentration gave **17** (4.1 g, 98 %). ^{13}C NMR (125 MHz, D_2O): β-anomer: 92.0 ppm (C-1), 72.8, 69.9, 68.7 (C-3, C-4, C-5), 56.2 (C-2), 41.2 (C-6); α-anomer: 91.2 (C-1), 72.6, 68.9, 67.4 (C-3, C-4, C-5), 55.2 (C-2), 41.1 (C-6). Crystallization from H_2O–EtOH gave 2.0 g (47.6 %) of β **17**; m.p. 155–156 °C (decomp.). $[\alpha]_D^{20}$ −5.2 → +2.8° (*c* 1.9, H_2O); [reported[10] m.p. 155 °C, $[\alpha]_D$ −8 → −1° (*c* 1, H_2O)].

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