α- or β-Amino Polyhydroxy Acids from the Reaction of Bromodeoxyaldonolactones with Liquid Ammonia

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Reaction of 2-bromo-2-deoxy-L-threono- (**1**) or -D-xylono-1,4-lactone (**4**) with liquid ammonia, gives 3-amino-3-deoxy-D-threonic- (**3a**) and -D-arabinonic acid (**6a**), respectively. The latter (**6a**) could be converted into the hydrochloride of 3-amino-3-deoxy-D-arabinono-1,4-lactone (**7**). The 2,5-dibromo-2,5-dideoxy-D-xylono-1,4-lactone (**13**) yielded 2,5-diamino-2,5-dideoxy-D-xylono-1,5-lactam (**21**) with liquid ammonia. This was also obtained from 2,5-dibromo-2,5-dideoxy-D-lyxono-lactone (**14**) under similar conditions. In both reactions varying amounts of the C-2 epimeric 2,5-diamino-2,5-dideoxy-D-lyxono-1,5-lactam (**20**), were formed, owing to base-catalysed epimerisation. By monitoring the reaction of 2-bromo-2-deoxy- as well as of 2,5-dibromo-2,5-dideoxyaldonolactones with aqueous ammonia by ^{13}C NMR spectroscopy, it was shown that 2,3-epoxy carboxamides were intermediates. The 2,3-epoxy function in L-erythro-(**2**) and D-lyxo-(**5**) epoxy carboxamides were stable in aqueous ammonia, while the cyclic 2,3-epoxy-D-lyxono-lactam (**17**) opened at C-2 within 20 h to give **21**.

Chemical transformation of 2-bromo-2-deoxy-aldono-1,4-lactones, readily available from aldonic acids,[1–6] provide a simple route to many sugar derivatives, avoiding tedious protection–deprotection steps which are often necessary when functionalities are introduced into the carbohydrate moiety. We have previously described the preparation of 2-amino-2-deoxy-aldonolactones from 2-bromo-2-deoxy-aldono-1,4-lactones,[7,8] and we also found that 2-bromo lactones are readily transformed into 2,3-epoxy lactones with bases as for example potassium fluoride.[9] Since it is known that 2,3-epoxy-esters and -amides react with ammonia to give 3-amino-2-hydroxy-carboxylic acid derivatives,[10,11] it was reasonable to assume that 2-bromo-2-deoxy-aldonolactones would similarly react with ammonia to give 3-amino-3-deoxy-aldonic acids, with 2,3-epoxy acid derivatives as intermediates. In continuation of our work on aminodeoxy sugars and amino-polyhydroxy acids[7,8] we decided to study the possibility of introducing an amino group at C-3 by reacting bromo-deoxyaldonolactones with ammonia. This paper describes these studies.

Results and discussion

When treated with aqueous ammonia, 2-bromo-2-deoxy-L-threono-1,4-lactone (**1**)[8] rapidly gave the 2,3-epoxy amide (**2**), which was stable towards the reagent. When liquid ammonia was used at 25 °C, only slow conversion took place, but at 90 °C the reaction was complete within 18 h, to give the 3-amino-3-deoxy-D-threonic amide (**3**), which on hydrolysis gave 3-amino-3-deoxy-D-threonic acid (**3a**). In order to verify the structure, **3a** was converted into methyl 3-acetamido-3-deoxy-2,4-di-*O*-acetyl-D-threonate (**3c**). Its ^1H NMR spectrum showed a doublet from H-2 at low field (δ 5.19) indicating that an acetoxy group was present at C-2, while H-3 (δ 4.81) showed a coupling to the NH proton.

Similarly, 2-bromo-2-deoxy-D-xylono-1,4-lactone (**4**) gave the 2,3-epoxy amide **5** when treated with liquid ammonia at room temperature. The further reaction of the epoxide was in this case even slower, requiring two days at 90 °C to run to completion, giving mainly 3-amino-3-deoxy-D-arabinonic amide (**6**) together with two minor products, presumably 2-amino-2-deoxy-D-xylonic and -D-lyxonic amides, in the ratio 8:1:1. Co-evaporation of the reaction product with hydrochloric acid caused lactonisation, and 3-amino-3-deoxy-D-arabinono-1,4-lactone, hydrochloride (**7**) crystallised in 51 % yield. The structure was confirmed by transforming **6** into the acetylated amino lactone **7b**, the ^1H NMR spectrum of which showed a doublet at low field (δ 5.72, H-2), while H-3 (δ 4.60) showed a coupling to the NH-proton. Furthermore, the coupling between H-2 and H-3 was 9.5 Hz indicating that H-2 and H-3 were *trans*-oriented in the ^3E conformation.[12] By chromatographic purification of **7b**, 2-acetamido-5-*O*-acetyl-2,3-dideoxy-D-*glycero*-pent-2-eno-1,4-lactone[8] was also isolated, confirming that the minor products formed in the reaction of **4** with NH_3 were 2-amino-2-deoxy-aldonic acid derivatives. Treatment of 2-bromo-2-deoxy-D-arabinonolactone (**8**)

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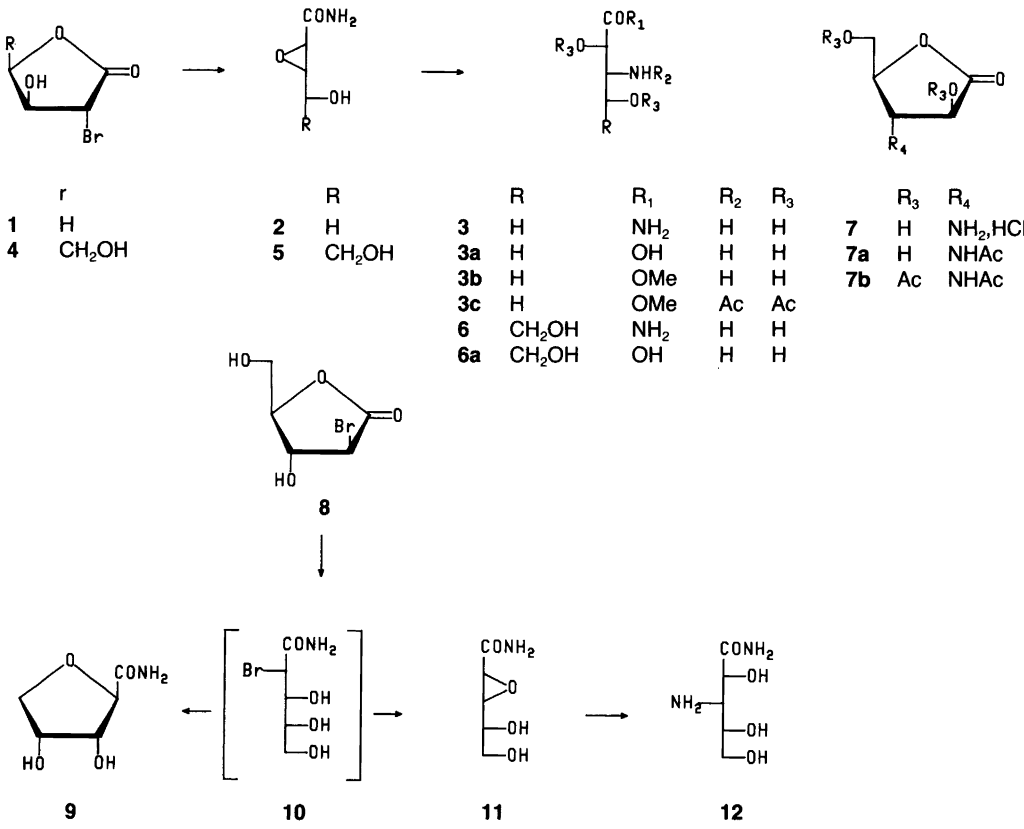


	r
1	H
4	CH_2OH

	R
2	H
5	CH_2OH

	R	R_1	R_2	R_3
3	H	NH_2	H	H
3a	H	OH	H	H
3b	H	OMe	H	H
3c	H	OMe	Ac	Ac
6	CH_2OH	NH_2	H	H
6a	CH_2OH	OH	H	H

	R_3	R_4
7	H	NH_2,HCl
7a	H	NHAc
7b	Ac	NHAc

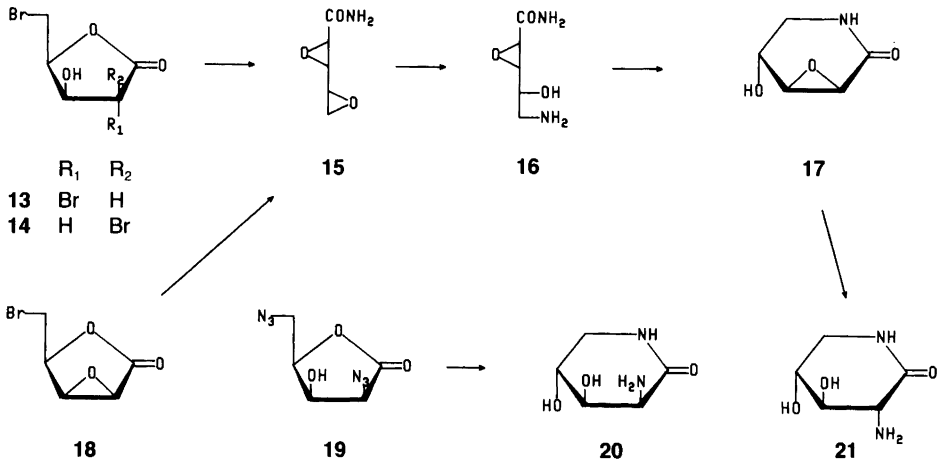
8 **9** **10** **11** **12**

with liquid ammonia at 90 °C, gave a mixture of 3-amino-3-deoxy-D-xylonic amide (**12**) and a 2,5-anhydride, presumably the 2,5-anhydro-D-ribonic amide (**9**) in the ratio **12**:**9** = 3:1. The compounds could not be separated and were only characterised by means of the ^{13}C NMR spectrum, the 5-membered anhydride showing characteristic low-field absorptions.[13] This compound (**9**) might be formed by attack of OH-5 upon the bromine of the 2-bromo-2-deoxy amide (**10**) as a competing reaction to the formation of the epoxide **11**.

When 2,5-dibromo-2,5-dideoxy-pentonolactones were treated with liquid ammonia, 2,5-diamino-2,5-dideoxy-aldonic acid derivatives were obtained. Thus, the dibromoxylonolactone (**13**) gave, by reaction at room temperature for 6 days, the 2,5-diamino-2,5-dideoxy-D-xylono-1,5-lactam (**21**) as the only product as seen from the ^{13}C NMR spectrum. After de-ionisation, the compound could be crystallised in 45–50 % yield. When the work-up was performed after 1 day the reaction mixture consisted of a 2,3-epoxy lactam (**17**) together with the amino lactam (**21**) in the ratio **17**:**21** = 3:1. When the reaction time was extended to 10 days or performed at a higher temperature (80 °C, 18 h) the reaction product consisted of **21** together with 30–50 % of another lactam, presumably the C-2 epimer **20**. The structure of **20** was confirmed by independent synthesis by catalytic hydrogenation of 2,5-diazido-2,5-dideoxy-D-lyxonolactone.[14] The formation of **20** was also observed during various work-up procedures. Thus, when a pure reaction product of **21** was de-ionised with an anion-exchange resin (OH^-), the eluate contained considerable amounts of **20**. An even greater degree of epimerisation was observed, when **21** was absorbed on a cation-exchange resin (H^+) and eluted with ammonia. In addition it was found that in the reaction of **11** with ammonia the amount of **20** was increased by increasing the concentration of the bromo lactone **13** relative to the ammonia (from 6 % of **20** at 0.2 M to 12 % at 1.0 M).

These observations might be explained by assuming that the ammonium bromide formed during the reaction effected the rate of epimerisation. To investigate this, a 0.1 M solution of the 2,5-diamino-D-xylono-1,5-lactam (**21**) was treated with liquid ammonia for three days at 25 °C. No formation of **20** was observed. When a similar experiment was performed with addition of NH_4Br (1 M), ca. 10 % of **20** was formed. This isomerisation is not really understood, but it may be favoured in the more ionic medium, since a proton abstraction at C-2 is responsible for the reaction.

Treatment of 2,5-dibromo-2,5-dideoxy-D-lyxono-1,4-lactone (**14**) with liquid NH_3 under similar reaction conditions as for the dibromoxylonolactone (**13**) also gave the 2,5-diamino-2,5-dideoxy-D-xylono-1,5-lactam (**21**) in addition to a small amount of **20**. When the reaction was interrupted after 1 day the main product was the 2,3-epoxy lactam **17**. This must be formed through a rapid, base-



	R_1	R_2
13	Br	H
14	H	Br

15 **16** **17**

18 **19** **20** **21**

catalysed equilibration between the dibromo lactones with lyxo- (**14**) and xylo- (**13**) configuration, favouring the latter, which then is converted into the epoxy lactone **18**.

The reactions of the dibromo lactones with aqueous NH_3 were monitored by ^{13}C NMR spectroscopy. Thus, a spectrum of the dibromoxylonolactone **13** immediately showed the presence of the 2,3;5,6-bis(epoxy)-D-lyxonamide (**15**). After ca. 10 min the 5-amino-2,3-epoxy-carboxamide **16** was present, being formed by opening of the primary epoxy group. After ca. 1 h the main product was the 2,3-epoxy lactam **17**, formed from **16**. Opening of the epoxy function in **17** proceeded within 20 h to give the 2-aminoxylonolactam **21**. Smaller amounts of unidentified products were observed in the ^{13}C NMR spectra, presumably arising from hydrolysis reactions. The reaction of the known crystalline 5-bromo-5-deoxy-2,3-epoxy-D-lyxonolactone (**18**)[8] with aqueous NH_3, gave the same epoxy intermediates leading to the diamino lactam **21**. When the reaction of the 2,5-dibromolyxonolactone (**14**) with aqueous NH_3 was monitored by ^{13}C NMR spectroscopy, more complex mixtures were observed, since under aqueous conditions opening of the lactone is faster, allowing formation of both *cis*- and *trans*-2,3-epoxides. Under non-aqueous conditions the oxirane **18** is apparently formed prior to opening of the lactone function. Thus, more homogeneous products are obtained by reacting the dibromo lactones **13** or **14** with liquid NH_3. The reactions time is, however, longer (6 days) in liquid NH_3, probably due to less electrophilic assistance by NH_4^+ in opening of the epoxide.[15]

As discussed above, in the reactions of 2-bromo-2-deoxy- or of 2,5-dibromo-2,5-dideoxy-aldonolactones with NH_3, 2,3-epoxy carboxamides were established as intermediates. The acyclic 2,3-epoxy carboxamides **2** and **5** were opened by the nucleophile mainly at C-3, the regioselectivity of opening the 2,3-epoxy function being ca. 9:1. This is in accordance with the findings by Sharpless for simple 2,3-epoxy carboxamides.[10] In contrast with this, the cyclic 2,3-epoxy carboxamide **17** opens exclusively at C-2. It should also be noted, that the acyclic epoxy amides **2** and **5** were stable towards aqueous NH_3, in contrast with the cyclic epoxy amide **17**. Recently we found that fluoride ions reacted with 2,3-epoxy lactones exclusively at C-2.[9] This is in accordance with the observations by Halvorsen and Songstad[16] who found that with charged nucleophiles the reaction occurred alpha to the carbonyl function. With neutral nucleophiles, in contrast, the attack occurred at the β-carbon. In the reactions discussed above the neutral nucleophile NH_3 opens the acyclic epoxides at the β-carbon, while in substitution at the α-carbon of the cyclic epoxy lactam **17**, steric effects should probably also be taken into consideration.

Experimental

Melting points are uncorrected. Optical rotations were measured using a Perkin Elmer 241 polarimeter. NMR Spectra were recorded on Bruker WH-90, AC-250 and AM-500 NMR instruments. Dioxane (δ 67.40) was used as an internal reference for ^{13}C NMR spectra, and acetone (δ 2.22) for ^1H NMR spectra in D_2O. Tetramethylsilane 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. Spots were visualised on TLC by charring with H_2SO_4. Evaporations were carried out in vacuum at 50 °C, unless otherwise indicated. Microanalyses were performed by NOVO Microanalytical Laboratory, Bagsværd, Denmark.

3-Amino-3-deoxy-D-threonic acid (**3a**). To 2-bromo-2-deoxy-L-threono-1,4-lactone (**1**)[8] (0.5 g) in CH_3OH (0.5 ml) was carefully added liquid NH_3 (20 ml). The solution was kept in a sealed vessel at 90 °C for 18 h, after which time the container was cooled to −70 °C and opened and the solution was concentrated to a residue containing 3-amino-3-deoxy-D-threonamide **3**. ^{13}C NMR (D_2O): δ 176.7 (C-1), 68.9 (C-2), 60.6 (C-4) and 55.3 (C-3). The crude product was placed on a column of ion-exchange resin (IR 120, H^+) and eluted with 5 % aqueous NH_3. Concentration gave a residue (0.27 g, 72 %), containing 3-amino-3-deoxy-D-threonic acid (**3a**) as the main product.

^{13}C NMR (D_2O): δ 179.1 (C-1), 71.4 (C-2), 63.5 (C-4) and 54.9 ppm (C-3). ^1H NMR (D_2O): δ 4.1 (d, H-2, $J_{2,3}$ 5 Hz), 3.86 (dd, H-4, $J_{3,4}$ 5 Hz, $J_{4,4'}$ 12 Hz), 3.70 (dd, H-4', $J_{3,4}$ 8 Hz) and 3.52 (dt, H-3). The product was contaminated with two minor amino compounds (ratio 5:1:1), probably the two isomeric 2-amino-2-deoxy-D-tetronic acids [^{13}C NMR (D_2O): 71.9, 63.1, 53.8 and 70.5, 61.6, 55.6].

Methyl 3-acetamido-3-deoxy-2,4-di-O-acetyl-D-threonate (**3c**). Treatment of **1** (1.0 g) with NH_3 as described above gave the amide **3** (1.1 g) which was dissolved in CH_3OH (20 ml), and the solution was saturated with HCl. After 20 h at 25 °C the reaction mixture was neutralised with $NaHCO_3$, filtered and concentrated to a residue containing the hydrochloride of methyl 3-amino-3-deoxy-D-threonate (**3b**). ^{13}C NMR in D_2O: δ 173.6 (C-1), 68.3 (C-2), 59.8 (C-4), 55.3 (C-3) and 54.7 (OMe). Acetylation in Et_3N (10 ml) and Ac_2O (20 ml) at room temperature for 18 h followed by addition of CH_3OH (20 ml) and concentration, gave a product which was purified by flash chromatography using EtOAc as the eluant to give methyl 3-acetamido-3-deoxy-2,4-di-*O*-acetyl-D-threonate (**3c**) as a syrup (0.32 g, 21 %). ^{13}C NMR ($CDCl_3$): δ 170.2, 170.0, 169.4, 168.0 (C-1, OAc, NAc), 70.3 (C-2), 61.6 (C-4), 48.0 (C-3), 52.4 (OMe), 22.5 (NAc), 20.3 and 20.0 (OAc). ^1H NMR ($CDCl_3$): δ 6.08 (d, NH, $J_{3,NH}$ 9 Hz), 5.19 (d, H-2, $J_{2,3}$ 2.5 Hz), 4.81 (dddd, H-3, $J_{3,4'}$ 6 Hz, $J_{3,4}$ 7 Hz), 4.17 (dd, H-4, $J_{4,4'}$ 11 Hz), 4.09 (dd, H-4'), 3.76 (s, OMe), 2.20 (s, NAc), 2.08 and 2.02 (s, OAc).

3-Amino-3-deoxy-D-arabino-1,4-lactone hydrochloride (**7**). 2-Bromo-2-deoxy-D-xylono-1,4-lactone (**4**)[3] (3.8 g) was dissolved in liquid NH_3 (100 ml), and the solution kept in a pressure vessel at 90 °C for 2 days, after which time it was cooled to −70 °C, opened, and kept at room temperature allowing the NH_3 to evaporate. The residue contained two compounds in the ratio 4:1, as seen from its ^{13}C NMR spectrum. The major compound was the hydrobromide of 3-amino-3-deoxy-D-arabinonic acid (**6a**). ^{13}C NMR (D_2O): δ 179.8 (C-1), 73.0 and 71.6 (C-2, C-4), 64.3 (C-5), 55.2 ppm (C-3). The minor compound had the following ^{13}C NMR data (D_2O): δ 71.9, 70.3, 63.9 and 53.5 ppm. The product was eluted from a strongly basic ion-exchange column (Amberlite IRA-400, OH^-, 100 ml) using 1 M HCl and concentrated to a pale yellow syrup. Addition of 4 M HCl, followed by evaporation (repeated three times) caused the 3-amino-3-deoxy-D-arabinono-1,4-lactone, hydrochloride (**7**) to crystallise by addition of CH_3OH (1.68 g, 51 %); m.p. 189–194 °C. Recrystallisation from EtOAc/CH_3OH furnished a product with m.p. 202–204 °C, $[\alpha]_D^{20}$ + 4.8° (*c* 0.5, H_2O). ^{13}C NMR (D_2O): δ 175.2 (C-1), 78.7 (C-4), 71.3 (C-2), 60.2 (C-5) and 54.1 (C-3). Anal. $C_5H_{10}ClNO_4$: C, H, N, Cl. The mother liquor contained **7** and two other amino lactones in the ratio 3:1:1. The by-products were presumably two epimeric 2-amino-2-deoxy lactones.

3-Acetamido-3-deoxy-2,5-di-O-acetyl-D-arabinono-1,4-lactone (**7b**). (a) Treatment of 2-bromo-2-deoxy-D-xylono-1,4-lactone (**4**)[3] (1.5 g) with liquid NH_3 (50 ml) as described above gave, after elution from an acidic ion-exchange column (Amberlite IR120, H^+, 100 ml) with 2.5 % aqueous NH_3 and concentration, a residue containing **6a** (1.19 g). CH_3OH (40 ml) and Ac_2O (5 ml) were added, and the mixture was stirred for 18 h and concentrated. The resulting residue was treated with pyridine (10 ml) and Ac_2O (5 ml) for 4 h at room temperature, quenched with water (50 ml) and extracted with EtOAc (3×50 ml). The combined extracts were washed with aqueous HCl (1 M, 10 ml) and aqueous $NaHCO_3$ (10 ml), dried ($MgSO_4$), filtered and concentrated (0.91 g). A ^{13}C NMR spectrum showed several by-products, formed during the acetylation. Flash chromatography (EtOAc–hexane 2:1) gave 3-acetamido-3-deoxy-2,5-di-*O*-acetyl-D-arabinono-1,4-lactone (**7b**) (0.17 g, 9 %). ^{13}C NMR ($CDCl_3$): δ 171.2, 170.5, 169.9 and 169.5 (C-1, OAc, NAc), 77.6 (C-4), 71.1 (C-2), 62,2 (C-5), 51.9 (C-3), 22.7 (NAc), 20.4 and 20.2 ppm (OAc). ^1H NMR ($CDCl_3$): δ 6.65 (d, NH), 5.72 (d, H-2, $J_{2,3}$ 9.5 Hz), 4.60 (ddd, H-3, $J_{3,4}$ 9.0 Hz, $J_{3,NH}$ 8.0 Hz), 4.54 (ddd, H-4, $J_{4,5}$ 2.5 Hz, $J_{4,5'}$ 5.5 Hz), 4.49 (dd, H-5, $J_{5,5}$ 1.3 Hz), 4.25 (dd, H-5'), 2.20 (s, NAc), 2.12 (s, OAc) and 2.03 (s, OAc). A faster-moving fraction of 2-acetamido-2,3-dideoxy-5-*O*-acetyl-D-*glycero*-pent-2-eno-1,4-lactone[8] (0.08 g) was also isolated.

(b) The 3-amino lactone hydrochloride **7** (300 mg) was stirred in CH_3OH (5 ml) with K_2CO_3 (500 mg) and Ac_2O (1 ml) for 15 min. Filtration and concentration gave a residue of **7a** [^{13}C NMR (D_2O): δ 80.5 (C-4), 72.1 (C-2), 60.2 (C-5), 53.6 (C-3), 22.8 (NAc)] together with some Ac_2O. Ac_2O (2 ml) and aq. $HClO_4$ (2 drops) were added. After 30 min $CHCl_3$ (20 ml) was added and the mixture was neutralised with pyridine and concentrated. Flash chromatography (EtOAc–hexane 2:1) gave some elimination products and **7b** (300 mg, 67 %). $[\alpha]_D^{20}$ + 41.9° (*c* 1.8, $CHCl_3$). Anal: $C_{11}H_{15}NO_7$: C, H, N.

Reaction of 2-bromo-2-deoxy-D-arabinono-1,4-lactone (**8**) *with ammonia.* Treatment of 2-bromo-2-deoxy-D-arabinono-1,4-lactone (**8**)[3] (1.0 g) with NH_3 (25 ml) in a sealed pressure vessel at 90 °C for 2 days as described above, gave, after allowing the NH_3 to evaporate at room temperature, a residue (1.2 g) consisting of 3-amino-3-deoxy-D-xylonamide (**12**) and 2,5-anhydro-D-ribonamide (**9**) in the ratio 3:1. ^{13}C NMR (D_2O): **9** δ 178.8 (C-1), 73.6 and 72.4 (C-2, C-4), 63.8 (C-5) and 55.0 (C-3); **10** δ 81.1 (C-2), 76.3, 73.9, 72.0 (C-3, C-4, C-5).

2,5-Diamino-2,5-dideoxy-D-xylono-1,5-lactam (**21**). (a) *From 2,5-dibromo-2,5-dideoxy-D-xylono-1,4-lactone* (**13**). Treatment of **13**[3] (5.41 g) with liquid NH_3 (100 ml) (0.24 M) in a sealed pressure vessel at room temperature for 6 days, followed by evaporation at room temperature, gave a residue which was dissolved in water (25 ml), placed on a

column of basic ion-exchange resin (Amberlite IRA-400, OH^-, 150 ml), which was eluted with water (250 ml). The combined eluates were evaporated to leave a crystalline residue (3.0 g). Crystallisation from MeOH–EtOAc 1:1 gave 1.33 g (46 %) of 2,5-diamino-2,5-dideoxy-D-xylono-1,4-lactam (**21**) with m.p. 162–166 °C. Recrystallisation from the same solvent furnished a product with m.p. 169–171 °C, $[\alpha]_D^{20} + 15.0°$ (*c* 0.4, H_2O). Anal. $C_5H_{10}N_2O_3$: C, H, N. ^{13}C NMR (D_2O): δ 174.7 (s, C-1), 75.4 and 68.9 (2×d, 147 Hz and 140 Hz, C-3 and C-4), 56.7 (d, 135 Hz, C-2) and 45.3 ppm (t, 142 Hz, C-5). ^1H NMR (D_2O): δ 3.96 (dt, H-4, $J_{3,4} = J_{4,5'}$ 9 Hz, $J_{4,5}$ 6 Hz), 3.63 (t, H-3, $J_{2,3}$ 9 Hz), 3,53 (dd, H-5, $J_{5,5'}$ 12 Hz), 3.38 (d, H-2) and 3.14 (dd, H-5′).

The mother liquor contained a mixture (2:1:1) of **21**, the C-2 epimeric lactam **20** [^{13}C NMR (D_2O): δ 172.9 (s, C-1), 70.0 and 67.0 (2×d, 151 and 149 Hz, C-3 and C-4), 51.0 (d, 135 Hz, C-2) and 45.2 (t, 142 Hz, C-5)], and a third compound [^{13}C NMR (D_2O): δ 70.6, 67.6, 55.1 and 47.2 ppm].

(b) *From 2,5-dibromo-2,5-dideoxy-D-lyxono-1,4-lactone* (**14**). Treatment of **14**[4] (0.50 g) with liquid NH_3 (25 ml) (0.07 M) for 6 days at 25 °C as described above, gave **21** (0.10 g, 38 %); m.p. 162–166 °C; $[\alpha]_D^{25} + 16.0°$ (*c* 0.7, H_2O). The NMR spectra were identical with those described above.

2,5-Diamino-2,5-dideoxy-D-lyxono-1,5-lactam (**20**). The 2,5-diazido-2,5-dideoxy-D-lyxono-1,4-lactone (**19**)[14] (140 mg) was dissolved in CH_3OH (20 ml) and Pd/C (5 %, 50 mg) was added. The mixture was hydrogenolysed at 101 kPa H_2-pressure for 18 h. Filtration and evaporation gave a residue (110 mg), which by crystallisation from MeOH gave 2,5-diamino-2,5-dideoxy-D-lyxono-1,5-lactam (**20**) (70 mg, 68 %); m.p. 195–200 °C; ^{13}C NMR (D_2O): δ 172.9 (C-1), 70.0 (C-4), 67.0 (C-3), 51.0 (C-2) and 45.2 ppm (C-5).

Reaction of the bromodeoxy lactones with aqueous NH_3. ^{13}C NMR experiments. The lactone [**13**, **14** or **18** (100 mg)] was dissolved in 0.8 ml 25 % aqueous NH_3 + 0.2 ml D_2O. ^{13}C NMR spectra were measured at intervals. The following intermediates were observed: **15** δ 172.4 (C-1), 58.7, 54.3, 50.6 (C-2, C-3, C-4) and 45.8 (C-5); **16** δ 171.8 (C-1), 71.7 (C-4), 60.6 and 55.2 (C-2 and C-3), 44.8 (C-5); **17** δ 171.3 (C-1), 63.6 (dt, *J* 149.2 and 5 Hz, C-4), 56.1 (dd, *J* 187.3 and 4 Hz) and 51.2 (dd, *J* 190 and 4 Hz) (C-2 and C-3), 44.4 (t, *J* 143 Hz, C-5); **21** δ 174.7 (C-1), 75.5 (d, *J* 143.4 Hz, C-4), 68.6 (d, 143.0 Hz, C-3), 56.6 (d, *J* 134.0 Hz, C-2), 45.2 (t, *J* 142.3 Hz, C-5); **20** δ 176.5 (C-1), 71.2 (C-4), 67.4 (C-3), 51.3 (C-2), 45.6 (C-5).

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References

1. Bock, K., Lundt, I. and Pedersen, C. *Carbohydr. Res. 68* (1979) 313.
2. Bock, K., Lundt, I. and Pedersen, C. *Carbohydr. Res. 90* (1981) 7.
3. Bock, K., Lundt, I. and Pedersen, C. *Carbohydr. Res. 90* (1981) 17.
4. Bock, K., Lundt, I. and Pedersen, C. *Carbohydr. Res. 104* (1982) 79.
5. Bock, K., Lundt, I. and Pedersen, C. *Acta Chem. Scand., Ser. B 38* (1984) 555.
6. Bock, K., Lundt, I., Pedersen, C. and Refn, S. *Acta Chem. Scand., Ser. B 40* (1986) 740.
7. Bock, K., Lundt, I. and Pedersen, C. *Acta Chem. Scand., Ser. B 41* (1987) 435.
8. Bols, M. and Lundt, I. *Acta Chem. Scand., Ser. B 42* (1988) 67.
9. Bols, M. and Lundt, I. *Acta Chem. Scand. 44* (1990) 252.
10. Behrens, C. H. and Sharpless, K. B. *J. Org. Chem. 50* (1985) 5697.
11. Kato, K., Saino, T., Nishizawa, R., Takita, T., Umezawa, H. *J. Chem. Soc., Perkin Trans. 1* (1980) 1618.
13. Bock, K. and Pedersen, C. *Adv. Carbohydr. Biochem. 41* (1983) 27.
14. Bols, M. and Lundt, I. *Unpublished results.*
15. McManus, S. P., Larson, C. A. and Hearn, R. A. *Synth. Commun. 3* (1973) 177.
16. Halvarsen, A. and Songstadt, J. *J. Chem. Soc., Chem. Commun.* (1973) 177.

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