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# BASE-CATALYSED REARRANGEMENT OF SOME BROMODEOXYHEPTONOLACTONES*

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ABSTRACT

The behaviour of 7-bromo-2,3,7-trideoxy-D-*arabino*-heptono-1,4-lactone (**1**), 7-bromo-2,7-dideoxy- (**13**), and 7-bromo-3,7-dideoxy-D-*gluco*-heptono-1,4-lactone (**21**) towards aqueous base has been studied. With potassium carbonate, each gives a 6,7-epoxide which undergoes subsequent slow hydrolysis. With potassium hydroxide, epoxide migration takes place, giving equilibrium mixtures of epoxides which undergo intramolecular substitution by attack of the carboxylate or an alkoxide ion. Thus, **1** is converted into 2,3-dideoxy-L-*arabino*-heptonic acid, **13** primarily forms 3,6-anhydro-2-deoxy-L-*ido*-heptonic acid, and **21** yields 2,5-anhydro-3-deoxy-L-*altro*-heptonic acid.

## INTRODUCTION

We have described the preparation of some bromodeoxyheptonolactones from D-*glycero*-D-*gulo*-heptonolactone[1]. Since treatment of bromolactones with strong base results in rearrangement *via* epoxide migration and may provide useful syntheses of deoxylactones[2–4], this type of reaction has been applied to the bromodeoxyheptonolactones.

## RESULTS AND DISCUSSION

When 7-bromo-2,3,7-trideoxy-D-*arabino*-heptono-1,4-lactone[1] (**1**) was treated with excess of potassium hydroxide in water, rapid formation of an epoxide was observed. A $^{13}C$-n.m.r. spectrum obtained after ~5 min showed that the solution contained virtually one product; the $^{13}C$ chemical shift data indicated that it was a di-secondary epoxide (epoxide carbon signals at ~ 60 p.p.m.) and, hence, either **5** or **6**. A $^{1}H$-n.m.r. spectrum obtained at the same stage of the reaction clearly showed that the product was the 5,6-epoxide **5**, because none of the epoxide protons, found at ~3 p.p.m., showed coupling to methylene protons. This epoxide must have been

*Dedicated to Professor Bengt Lindberg.

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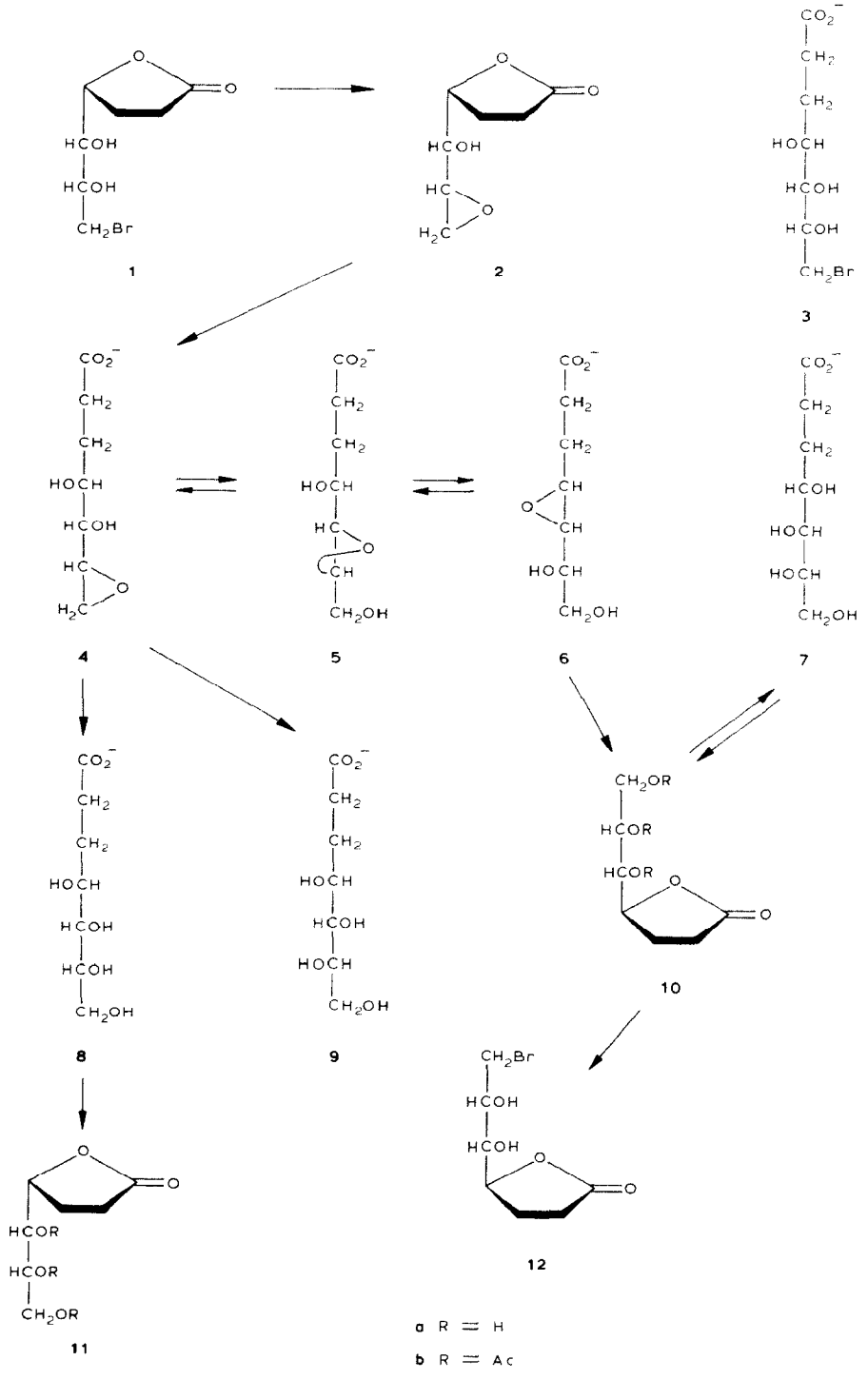
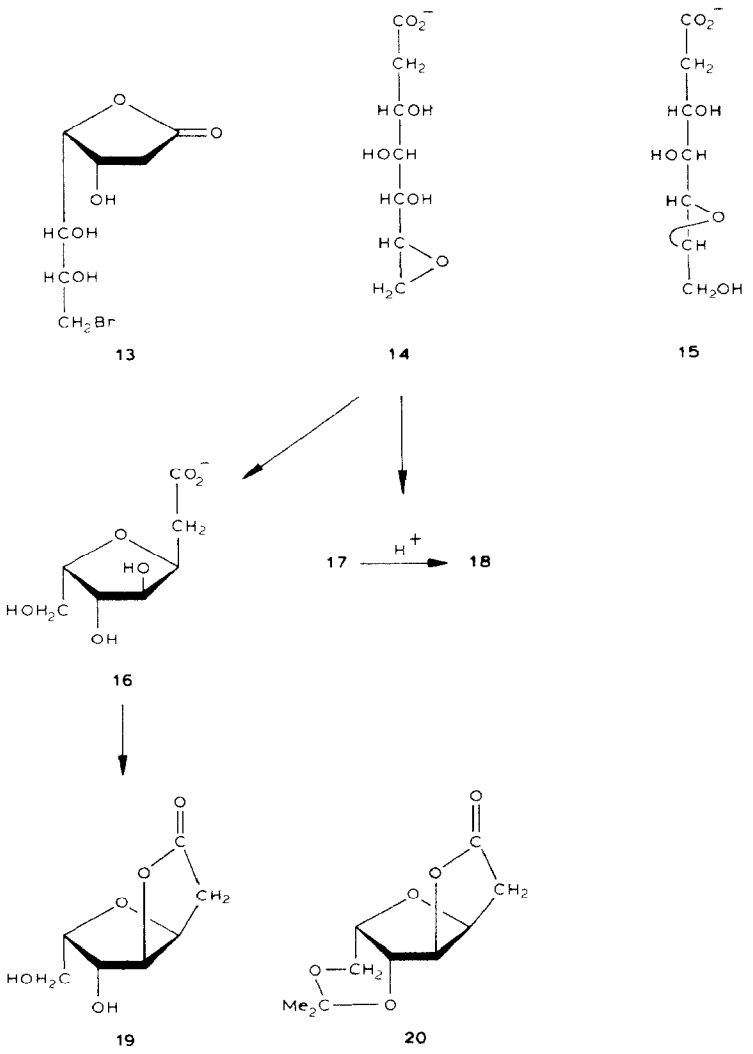

1
2
3
4
5
6
7
8
9
10
11
12
a R = H
b R = Ac

formed by rearrangement of the 6,7-epoxide **4**[2,4]. A $^{13}$C-n.m.r. spectrum obtained after 15 min showed that the aldonate **7** was present; after a few hours reaction, this was the only product observed. The epoxides **5** and **6** are probably in equilibrium and the latter may undergo intramolecular reaction by attack of the carboxylate upon C-4 *via* a five-membered transition state to give the lactone **10a**, which opens in the basic medium to give the final product **7** with inverted configurations at C-4,5,6 relative to **1**. The 4,5-epoxide **6** was not present in detectable amounts, probably because it has the less stable *cis*-configuration. The aldonate **7** was converted into the acetylated lactone **10b**, the structure of which was established by comparison with the known[5] enantiomer **11b**. Treatment of the crude lactone **10a** with hydrogen bromide in acetic acid gave the 7-bromolactone **12**, the enantiomer of **1**.

Reaction of **1** with excess of potassium carbonate in water was slower than with potassium hydroxide and gave the carboxylate **8** and another product in the ratio 2:1. The mixture was converted into the corresponding acetylated lactones and, after chromatography, 47% of the major product **11b** could be isolated, the physical constants of which agreed with those of a product previously described[5]. The minor product was not obtained pure. Hence, treatment of **1** with base may produce either of the enantiomeric products **10** and **11**, depending on the strength of the base. The reaction of **1** with potassium carbonate was monitored through $^{13}$C-n.m.r. spectra which showed that the first product formed was the 6,7-epoxylactone **2**, which was subsequently converted into the open-chain epoxide **4**. The bromoaldonate **3** was not detected. The D-*arabino*-aldonate **8** is probably formed by attack of hydroxyl ion upon C-7 of **4**. The minor product is assumed to be the L-*xylo*-aldonate **9**, formed by opening of the epoxide **4** at C-6. The rearranged epoxide **5** was not detected in the reaction with potassium carbonate.

The reaction of 7-bromo-2,7-dideoxy-D-*gluco*-heptono-1,4-lactone[1] (**13**) with aqueous base was also studied by $^{13}$C-n.m.r. spectroscopy. With excess of potassium carbonate, the 6,7-epoxide **14** was formed within ~10 min as almost the only product. After ~30 h at 20°, **14** was completely converted into a mixture of three products which were not studied further. With potassium hydroxide, the reaction was complete within 2–3 h. A spectrum obtained after 5 min showed the main, final product **16** and a di-secondary epoxide which was probably the 5,6-epoxide **15** since this is a *trans*-epoxide that would be more stable than the *cis*-4,5 epoxide. The final reaction mixture contained the 3,6-anhydrocarboxylate **16** and a minor, unidentified product **17** in the ratio 4:1. On acidification, these product formed the lactone **19** and a minor product **18**. Treatment of the mixture with acetone followed by chromatography yielded, as the main product, the isopropylidene derivative **20**, the structure of which was determined from the $^{1}$H- and $^{13}$C-n.m.r.spectra. The chemical shift (97.6 p.p.m.) of the resonance of the quaternary carbon atom shows that it is incorporated in a six-membered isopropylidene derivative[6]. Hydrolysis of **20** gave the lactone **19**, which was identified by comparison with the previously described enantiomer[7].

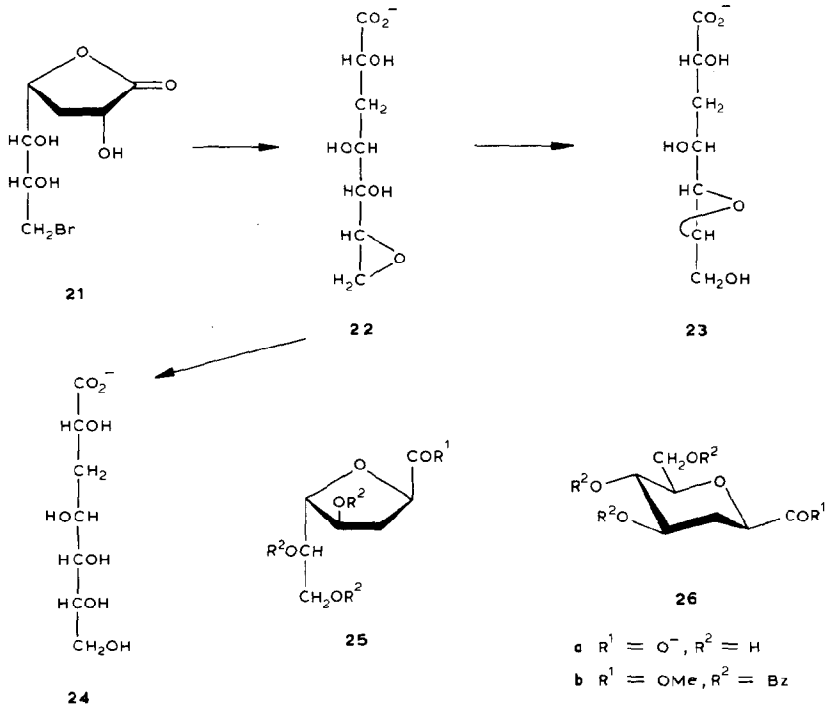
The formation of **16** form **13** must proceed by intramolecular attack of the




O-3 anion on C-6 of the 6,7-epoxide **14**. Although **14** was not detected in potassium hydroxide solution, it must be present in equilibrium with **15**. In potassium carbonate solution, **14** is present in large proportion, but it does not form **16**, probably because the base is not strong enough to form the O-3 anion.

Finally, the reaction of 7-bromo-3,7-dideoxy-D-*gluco*-heptono-1,4-lactone[1] (**21**) with base was studied. On treatment with aqueous potassium carbonate, **21** was rapidly transformed into the 6,7-epoxide **22** which subsequently yielded the 3-deoxy-D-*gluco*-heptonate **24** as almost the only product. With potassium hydroxide, **22** was not detected, but a di-secondary epoxide, probably the *trans*-epoxide **23**, was formed immediately. After ~30 min, the reaction was complete and the solution contained mainly the 2,5-anhydride **25a** and a small amount of the 2,6-anhydride

**26a**. These two products were isolated as the benzoylated methyl esters **25b** and **26b**, respectively. The reaction probably proceeds *via* the 5,6-epoxide **23**, which undergoes internal substitution by attack of the O-2 anion upon C-5 or C-6. As found for the 7-bromo-2,7-dideoxylactone **13**, the carboxylate ion does not seem to participate in the reaction.




The above reactions of the 7-bromolactones **1**, **13**, and **21** with base must proceed *via* initial formation of the respective 6,7-epoxides, **4**, **14**, or **22**. When potassium carbonate is used as the base, epoxide migration does not take place and the 6,7-epoxides react with hydroxide, preferentially at the primary carbon atoms. When potassium hydroxide is the base, rapid epoxide migration takes place[2,4,8], leading to equilibrium mixtures in which the more stable *trans*-epoxides **5**, **15**, and **23** preponderate. The course of the further reactions of these epoxide mixtures is difficult to predict. Thus, **5** is converted into **7**, probably by intramolecular attack of the carboxylate on C-4 of **6** being in equilibrium with **5**, as described above. This would be a favoured "exo mode" reaction[9] and inspection of molecular models indicates that antiperiplanar opening of the epoxide can take place[10]. Similar reactions of **15** and **23** did not proceed by participation of the carboxylate ions, but by predominant intramolecular attack of an alkoxide ion on the appropiate epoxides, **14** (being in equilibrium with **15**) and **23**, respectively. Both these reactions are

"exo mode" and allow antiperiplanar opening of the epoxides. The fact that the carboxylates do not participate in the reactions of **15** and **23** may be explained through their lower nucleophilicity compared to that of the alkoxides. The formation of tetrahydrofuran derivatives from the epoxides **4** or **6** was not observed, perhaps because this would require disfavoured "endo mode" reactions[9] and could not readily proceed *via* antiperiplanar opening of the epoxides, as seen from molecular models.

## EXPERIMENTAL

Melting points are uncorrected. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. N.m.r. spectra were recorded with Bruker WH-90 and AM-500 instruments. Microanalyses were performed by Novo Microanalytical Laboratory (Copenhagen). Column chromatography was performed on Silica Gel 60 (40–63 μm, Merck 9385), using the flash technique.

*Reaction of 7-bromo-2,3,7-trideoxy*-D-arabino-*heptono-1,4-lactone* (**1**) *with base.* — (*a*) *Potassium carbonate.* To **1**[1] (0.5 g) in a mixture of $D_2O$ and $H_2O$ (2 mL) was added potassium carbonate (0.9 g, 3 mol), and the mixture was shaken until it was almost homogeneous; potassium bromide then began to separate. A $^{13}C$-n.m.r. spectrum obtained after ~15 min showed that the epoxide-lactone **2** was the main product present: 182.5 (C-1), 83.2 (C-4), 72.0 (C-5), 53.1 (C-6), 46.3 (C-7), 29.5 (C-2), 24.2 p.p.m. (C-3). The bromocarboxylate **3** was not detected. After 2 h, the open-chain epoxide **4** was the main product. $^{13}C$-N.m.r. data: **4**, 183.6 (C-1), 73.3, 72.9 (C-4,5), 53.9 (C-6), 46.5 (C-7), 34.9 (C-2), 30.1 p.p.m. (C-3). After 24 h, only the two carboxylates **8** and **9** were observed in the ratio 2.5:1. $^{13}C$-N.m.r. data: **8**, 183.9 (C-1), 73.8, 72.4, 70.8 (C-4,5,6), 64.1 (C-7), 35.1 (C-2), 30.7 p.p.m. (C-3); **9**, 183.8 (C-1), 74.1, 73.1, 72.4 (C-4,5,6), 64.1 (C-7), 34.9 (C-2), 30.5 p.p.m. (C-3).

(*b*) *Potassium hydroxide.* To a solution of potassium hydroxide (0.4 g, 3 equiv.) in $H_2O$ + $D_2O$ (1 mL) was added **1** (0.5 g). A $^{13}C$-n.m.r. spectrum measured after 5 min showed that the 5,6-epoxide **5** was virtually the only product present. N.m.r. data: $^{13}C$, 183.2 (C-1), 72.1 (C-4), 62.4 (C-7), 61.1, 59.3 (C-5,6), 34.5 (C-2), 31.4 p.p.m. (C-3); $^1H$, δ 2.12 (H-2), 1.67 (H-3, $J_{3,4}$ 3 Hz), 3.30 (H-4, $J_{4,5}$ 6.3 Hz), 2.89 (H-5, $J_{5,6}$ 2.8 Hz), 3.05 (H-6, $J_{6,7a}$ 3.0, $J_{6,7b}$ 6.0 Hz), 3.73 (H-7a, $J_{7,7}$ 13 Hz), 3.38 (H-7b). After 15 min, the solution contained **5** and the L-*arabino*-heptonate **7** in the ratio 2:1; after 18 h at 20°, only **7** was observed. $^{13}C$-N.m.r. data: **7**, 183.8 (C-1), 73.7, 72.3, 70.7 (C-4,5,6), 63.9 (C-7), 34.9 (C-2), 30.5 p.p.m. (C-3). Acidification of the solution with hydrochloric acid gave 2,3-dideoxy-L-*arabino*-heptono-1,4-lactone (**10a**). $^{13}C$-N.m.r. data: 182.9 (C-1), 81.7 (C-4), 72.7, 72.0 (C-5,6), 63.6 (C-7), 29.5 (C-2), 24.1 p.p.m. (C-3).

*5,6,7-Tri-O-acetyl-2,3-dideoxy*-D-arabino-*heptono-1,4-lactone* (**11b**). — A solution of **1** (2.0 g) in water (20 mL) containing potassium carbonate (4 g) was kept for 24 h at 20°, then acidified with hydrochloric acid, and concentrated. The residue was extracted several times with boiling methanol, the extract was concentrated, and

toluene was evaporated from the residue which was then treated conventionally with acetic anhydride in pyridine. The product (2.4 g) crystallised from ether to give crude **11b** (800 mg). Column chromatography (ether) of the material in the mother liquor gave more (400 mg) **11b**. The combined crystals (1.2 g, 47%) were re-chromatographed and the main fraction was crystallised from ether to give **11b** (900 mg, 36%), m.p. 103–105°. Recrystallisation from ethanol gave a product with m.p. 104–106°, $[\alpha]_D^{20}$ −7.7° (*c* 2.2, methanol); lit.[5] m.p. 106°, $[\alpha]_D^{20}$ −5.2° (methanol). $^{13}$C-N.m.r. data ($CDCl_3$): 175.8 (C-1), 76.9 (C-4), 71.0, 69.7 (C-5,6), 61.2 (C-7). 27.6 (C-2), 23.5 (C-3), 20.5, 20.3 p.p.m. (OAc).

A minor fraction contained a second product which could not be obtained pure.

*5,6,7-Tri*-O-*acetyl-2,3-dideoxy*-L-arabino-*heptono-1,4-lactone* (**10b**). — A solution of **1** (2.0 g) in water (10 mL) containing potassium hydroxide (1.6 g) was kept overnight at room temperature and then worked-up, and the product was acetylated as described above. The crude acetate was crystallised from ether to give a product (1.6 g) column chromatography (ether) of which gave a main fraction that was crystallised from ether to give **10b** (1.2 g, 47%), m.p. 103–105°, unchanged by recrystallisation from ethanol; $[\alpha]_D^{20}$ +7.4° (*c* 3.8, methanol). The $^{13}$C-n.m.r. spectrum was identical with that of the enantiomer **11b**.

*Anal.* Calc. for $C_{13}H_{18}O_8$: C, 51.65; H, 6.00. Found: C, 51.79; H, 6.15.

*7-Bromo-2,3,7-trideoxy*-L-arabino-*heptono-1,4-lactone* (**12**). — The 7-bromolactone **1** (1 g) was treated with potassium hydroxide as described above. The resulting solution was acidified with hydrochloric acid and concentrated, and the residue was stirred with a 30% solution of hydrogen bromide in acetic acid (10 mL) for 15 h at room temperature. Methanol (50 mL) was then added, the mixture was kept overnight and concentrated, and a solution of the residue in water (5 mL) was extracted with ethyl acetate (5 × 10 mL). The combined extracts were dried and concentrated, and the residue was crystallised from ethyl acetate to give **12** (500 mg, 50%), m.p. 123–125°. Recrystallisation gave a sample with m.p. 126–127°, $[\alpha]_D^{20}$ +35° (*c* 2, water). The $^{13}$C-n.m.r. spectrum was identical with that of **1**.

*Anal.* Calc. for $C_7H_{11}BrO_4$: C, 35.18; H, 4.64; Br, 33.44. Found: C, 35.20; H, 4.67; Br, 33.77.

*Treatment of 7-bromo-2,7-dideoxy*-D-gluco-*heptono-1,4-lactone* (**13**) *with base.* — (*a*) *Potassium carbonate.* To a solution of **13**[1] (0.5 g) in 1:1 $H_2O$ and $D_2O$ (1 mL) was added potassium carbonate (0.81 g). $^{13}$C-N.m.r. spectra measured after 15 and 45 min showed almost only one product, the 6,7-epoxide **14**: 181.0 (C-1), 75.2, 71.8, 70.5 (C-3,4,5), 53.8 (C-6), 46.7 (C-7), 42.6 p.p.m. (C-2). After several days at 20°, the reaction was complete and the three products, none of which were identical with **16** or **17**, were not studied further.

(*b*) *Potassium hydroxide.* A solution of **13** was treated with 3 equiv. of potassium hydroxide and the reaction was monitored by $^{13}$C-n.m.r. spectroscopy. After 5 min, the solution contained equal parts of **16** and an intermediate assumed to be the 5,6-epoxide **15**. $^{13}$C-N.m.r. data: **15**, 180.7 (C-1), 75.0, 71.8 (C-3,4), 62.2 (C-7), 59.0,

58.7 (C-5,6), 42.4 p.p.m. (C-2). After a few hours, **15** had disappeared and a spectrum showed that the solution contained **16** and a minor product **17** in the ratio 4:1. $^{13}$C-N.m.r. data: **16**, 181.2 (C-1), 81.5, 79.5 (2 C), 79.2 (C-3,4,5,6), 62.3 (C-7), 38.7 p.p.m. (C-2); **17**, 181.8 (C-1), 76.6, 73.0, 71.4, 70.7 (C-3,4,5,6), 64.3 (C-7), 43.3 (C-2). When the solution was acidified, **16** was converted into the corresponding lactone **19**. $^{13}$C-N.m.r. data: 180.4 (C-1), 89.7 (C-3), 81.8, 77.0, 74.4 (C-4,5,6), 60.8 (C-7), 37.9 p.p.m. (C-2). The minor product **17** was converted into an unidentified lactone **18**. $^{13}$C-N.m.r. data: 180.4 (C-1), 88.6, 71.9, 71.0, 70.2 (C-3,4,5,6), 63.8 (C-7), 39.0 (C-2).

*3,6-Anhydro-2-deoxy-5,7-O-isopropylidene*-L-ido-*heptono-1,4-lactone* (**20**). — To a solution of **13** (2.0 g) in water (15 mL) was added potassium hydroxide (2.0 g). The solution was kept overnight at room temperature, then acidified with hydrochloric acid, and concentrated. The residue was extrated with methanol, the extract was concentrated, and the residue was kept for 24 h in acetone, then neutralised with solid sodium hydrogencarbonate, filtered, and concentrated. Column chromatography (ethyl acetate) of the product gave a main fraction (1.2 g) that crystallised from ether–pentane to give **20** (700 mg, 42%), m.p. 103–105°. Recrystallisation gave a product with m.p. 105–106°, $[\alpha]_D^{20}$ −50° (*c* 1.6, chloroform). N.m.r. data ($CDCl_3$): $^1$H, δ 2.77 (H-2a, $J_{2,2}$ 18.5, $J_{2a,3}$ 5.8 Hz), 2.69 (H-2b, $J_{2b,3}$ ~0 Hz), 5.11 (H-3, $J_{3,4}$ 4 Hz), 4.96 (H-4, $J_{4,5}$ ~0 Hz), 4.57 (H-5, $J_{5,6}$ 2.5 Hz), 3.94 (H-6, $J_{6,7a}$ 2.5, $J_{6,7b}$ ~1 Hz), 4.11 (H-7a, $J_{7,7}$ 13.5 Hz), 4.01 (H-7b), 1.40, 1.47 (-$CH_3$); $^{13}$C, 175.0 (C-1), 97.6 (*C*$Me_2$), 86.9, 77.1 (C-3,6), 72.4, 72.1 (C-4,5), 60.1 (C-7), 35.8 (C-2), 28.5, 18.8 p.p.m (C*Me*$_2$).

*Anal.* Calc. for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59. Found: C, 55.88; H, 6.57.

*3,6-Anhydro-2-deoxy*-L-ido-*heptono-1,4-lactone* (**19**). — A solution of **20** (300 mg) in trifluoroacetic acid (4 mL) and water (2 mL) was kept at 20°. After 30 min, **20** was no longer present (t.l.c., ethyl acetate). The solution was concentrated, and toluene was evaporated three times from the residue which was crystallised from ethyl acetate–pentane to give **19** (150 mg, 62%) as hygroscopic crystals, m.p. 72–74°, $[\alpha]_D^{20}$ −32° (*c* 0.6, water); lit.[7] for the D enantiomer, m.p. 72–74°, $[\alpha]_D$ +28.4° (water). $^1$H-N.m.r. data ($CDCl_3$): δ 2.77 (H-2a, $J_{2,2}$ 18.5, $J_{2a,3}$ 5.8 Hz), 2.69 (H-2b, $J_{2b,3}$ ~0 Hz), 5.05 (H-3, $J_{3,4}$ 4.2 Hz), 4.72 (H-4, $J_{4,5}$ ~0.5 Hz), 4.57 (H-5, $J_{5,6}$ 2.8 Hz), 4.06 (H-6, $J_{6,7a}$ 4.6, $J_{6,7b}$ 2.2 Hz), 4.10 (H-7a, $J_{7,7}$ 13.0 Hz), 4.05 (H-7b).

*Anal.* Calc. for $C_7H_{10}O_5$: C, 48.27; H, 5.79. Found: C, 48.30; H, 5.90.

*Treatment of 7-bromo-3,7-dideoxy*-D-gluco-*heptono-1,4-lactone* (**21**) *with base.* — (*a*) *Potassium carbonate.* To a solution of **21**[1] in $D_2O$ + $H_2O$ was added 3 mol of potassium carbonate. The $^{13}$C-n.m.r. spectrum obtained after ~10 min showed that the solution contained 90% of the epoxide **22**: 182.7 (C-1), 73.9, 70.2, 69.9 (C-2,4,5), 53.8 (C-6), 46.5 (C-7), 38.6 p.p.m (C-3). After 2 h, the 3-deoxy-D-*gluco*-heptonate **24** was detected; after 30 h at 20°, this was almost the only product: 182.9 (C-1), 74.6, 72.3, 70.5, 67.7 (C-2,4,5,6), 64.0 (C-7), 39.4 p.p.m. (C-3). When methyl 3-deoxy-D-*gluco*-heptonate[1] was heated in aqueous potassium hydroxide, the same product was obtained.

(*b*) *Potassium hydroxide.* When **21** was treated with 3 equiv. of potassium hydroxide for 5 min at 20°, the $^{13}$C-n.m.r. spectrum showed a 7:3 mixture of **25a** and the 5,6-epoxide **23**. $^{13}$C-N.m.r. data: **23**, 182.9 (C-1), 70.5, 69.6 (C-2,4), 62.7 (C-7), 61.9, 59.6 (C-5,6), 39.9 p.p.m. (C-3). After 15 min, **23** had disappeared and the solution contained mainly **25a** mixed with ~15% of **26a**. $^{13}$C-N.m.r. data: **25a**, 181.8 (C-1), 87.7 (C-5), 78.6 (C-2), 72.6, 71.9 (C-4,6), 64.0 (C-7), 40.3 p.p.m. (C-3); **26a**, 179.6 (C-1), 80.8, 77.0, 73.5, 73.1 (C-2,4,5,6), 62.5 (C-7), 38.2 p.p.m. (C-3).

*Methyl 2,5-anhydro-4,6,7-tri-*O*-benzoyl-3-deoxy-*L*-altro-heptonate* (**25b**). — The bromolactone **23** (3.0 g) was treated with potassium hydroxide (3.0 g) in water (20 mL) for 4 h. The solution was acidified with hydrochloric acid and concentrated, and the residue was kept in methanol (75 mL) for 48 h. The solution was then neutralised with solid sodium hydrogencarbonate, filtered, and concentrated, and the residue was treated conventionally with benzoyl chloride in pyridine. Column chromatography (ethyl acetate–hexane, 1:2) of the product (6.4 g) gave a main fraction (5.2 g) that crystallised from ether–pentane to give **25b** (3.4 g, 56%), m.p. 85–87°. Recrystallisation from ethanol gave a product with m.p. 88–90°, $[\alpha]_D^{20}$ −51.5° (*c* 2, chloroform). $^1$H-N.m.r data ($CDCl_3$): δ 4.80 (H-2, $J_{2,3a}$ 9.0, $J_{2,3b}$ 2.0 Hz), 2.73 (H-3a, $J_{3,3}$ 14.2, $J_{3a,4}$ 6.0 Hz), 2.56 (H-3b, $J_{3b,4}$ 2 Hz), 5.71 (H-4, $J_{4,5}$ 1.8 Hz), 4.78 (H-5, $J_{5,6}$ 6.0 Hz), 5.64 (H-6, $J_{6,7a}$ 3.5, $J_{6,7b}$ 5.2 Hz), 4.81 (H-7a, $J_{7,7}$ 12.0 Hz), 4.66 (H-7b), 3.72 (OMe).

*Anal.* Calc. for $C_{29}H_{26}O_9$: C, 67.17; H, 5.05. Found: C, 67.32; H, 5.15.

Column chromotography (ether–pentane, 1:2) of the material in the mother liquor gave three fractions. The third fraction crystallised from ether–pentane, giving methyl 2,6-anhydro-4,5,7-tri-*O*-benzoyl-D-*gluco*-heptonate (**26b**, 160 mg), m.p. 130°. Recrystallisation gave a product with m.p. 132–133°, $[\alpha]_D^{20}$ −30° (*c* 1.1, chloroform). $^1$H-N.m.r. data ($CDCl_3$): δ 4.35 (H-2, $J_{2,3a}$ 12.1, $J_{2,3e}$ 2.3 Hz), 2.06 (H-3*a*, $J_{3,3}$ 13.0, $J_{3a,4}$ 11.2 Hz), 2.77 (H-3*e*, $J_{3e,4}$ 5.2 Hz), 5.46 (H-4, $J_{4,5}$ 9.6 Hz), 5.59 (H-5, $J_{5,6}$ 10.6 Hz), 4.05 (H-6, $J_{6,7a}$ 3.0, $J_{6,7b}$ 5.2 Hz), 4.63 (H-7a, $J_{7,7}$ 12.2 Hz), 4.51 (H-7b), 3.79 (OMe).

*Anal.* Calc. for $C_{29}H_{26}O_9$: C, 67.17; H, 5.05. Found: C, 67.36; H, 5.10.

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